Charge Carrier Selective Contacts for Silicon Heterojunction and Metal Halide Perovskite Solar Cells:

Probing Energy Level Alignment and Defect States at the Electronic Interface with Photoelectron Spectroscopies

vorgelegt von

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ZUSAMMENFASSUNG

Tandem-Solarzellen bestehen aus zwei übereinander gestapelten Einzelsolarzellen und erlauben durch unterschiedliche Bandlückenenergien der beiden Absorber in den Sub-Zellen, sowohl Transmissions- als auch Thermalisationsverluste zu reduzieren. Insbesondere Silizium/Perowskit Tandem-Solarzellen mit Energiewandlungswirkungsgraden von aktuell nahe der 30%-Marke, und somit weit über jenen der Einzelsolarzellen, stehen im Fokus der jüngeren Forschung. Der Wirkungsgrad hängt dabei maßgeblich vom Ladungsträgertransport über die Grenzflächen im Zellstapel ab, wobei insbesondere die Anordnung der Energiebänder der einzelnen Materialien an deren Grenzflächen relevant ist und mittels Photoelektronenspektroskopie (PES) analysiert werden kann. In dieser Arbeit wird hierzu eine spezielle Variante der PES verwendet: Die zur Anregung verwendete Energie der Photonen wird variiert $(3-7 \,\mathrm{eV})$ und die Photoelektronenausbeute eines konstanten Endzustands, also bei einer festen kinetischen Energie der Photoelektronen, vermessen (constant final state yield spectroscopy, CFSYS). Diese Methode vereint zwei wesentliche Vorteile miteinander: Einen großen Dynamikbereich von bis zu sieben Größenordnungen, der die Messung von geringen Zustandsdichten im Bereich der Valenzbandkante und Defektdichten in der Bandlücke bis hinunter zu etwa $10^{15} \,\mathrm{eV^{-1} cm^{-3}}$ ermöglicht; sowie eine große Ausdringtiefe der Photoelektronen von 5-10 nm, was die Charakterisierung von vergrabenen Grenzflächen und die direkte Bestimmung des Valenzbandoffsets an einem Heteroübergang erlaubt. In der vorliegenden Arbeit werden zwei Grenzflächen, jeweils zwischen einem photovoltaisch aktiven Absorber und einem ladungsträgerselektiven Kontakt betrachtet. Zunächst werden, aufbauend auf der Untersuchung des lochselektiven Heterokontakts zwischen Indium-Wolfram-Oxid (IWO_x) und n-dotiertem kristallinem Silizium, die optoelektronischen Eigenschaften nach Erhitzen der IWO_x Schichten bis zu 700 °C untersucht. Anschließend widmet sich die Arbeit der charakteristisch niedrigen Zustandsdichte im Valenzband von Methylammoniumbleiiodid und eng verwandter Perowskit-Komposita. Mit Hilfe eines Modells, welches zugleich ein parabolisches Valenzbandmaximum und einen exponentiellen Bandausläufer beschreibt, können zwei Valenzbandmaxima im winkelintegrierten CFSYS Spektrum identifiziert werden. Zusätzlich wird der Effekt unterschiedlicher Beleuchtungsbedingungen (Röntgenstrahlung, UV-Strahlung) sowie von Umgebungseinflüssen (Luftexposition und Vakuumlagerung) auf die Defektdichte des Perowskits untersucht. Auf der Modellierung des Perowskits aufbauend, wird der elektronenselektive Kontakt zum Fulleren C_{60} analysiert. Wobei insbesondere der Effekt einer 1 nm dünnen Zwischenschicht aus Lithiumfluorid zwischen Perowskit und C_{60} auf die betrachtete Grenzfläche Perowskit/LiF/C₆₀ untersucht wird. Es wird klar, dass die Konzentration von Löchern zu beiden Seiten der LiF zwischenschicht stark reduziert ist, sodass trotz erhöhter Defektdichten in den ersten Monolagen des C_{60} die nichtsttrahlende Ladungsträgerekombination vermindert wird.

ABSTRACT

Tandem solar cells consist of two individual solar cells, stacked on top of each other. Using two absorbers with different band gap energies, they permit to reduce both, transmission and thermalization losses. Recently, especially silicon/perovskite tandem solar cells are widely investigated in the research community with power conversion efficiencies (PCE), currently close to 30 %, thus significantly above the respective single junction devices. The PCE crucially depends on the charge carrier transport across the interfaces, which is in a first approximation determined by the energy level alignment of the materials forming the interface and can be analysed by photoelectron spectroscopy (PES). In this thesis, a special variant of PES is applied: The energy of the incident photons is varied between 3 and 7 eV, while the photoelectron yield at one constant final state, thus a specific kinetic energy, is measured (constant final state yield spectroscopy, CFSYS). This method combines two main advantages: A high dynamic measurement range of up to seven orders of magnitude, which allows for the detection of very low densities of states in the valence band region, and a density of defect states in the band gap down to around $10^{15} \,\mathrm{eV^{-1} cm^{-3}}$; furthermore, a high information depth of the photoelectrons of around 5-10 nm is achieved, which enables the observation of buried interfaces and e.g. the direct determination of valence band offsets at heterojunctions. In this thesis, two interfaces between a photovoltaic absorber and a charge carrier selective contact layer are investigated. Firstly, based on the investigation of indium tungsten oxide (IWO_x) as hole selective contact for n-doped crystalline silicon, the opto-electronic properties of IWO_x upon high temperature annealing up to $700\,^{\circ}\mathrm{C}$ are investigated. Thereafter, the focus of the work is on the investigation of the characteristically low density of states at the valence band maximum of methylammonium lead iodide and closely related perovskite compositions. By applying a model which describes both, a parabolic valence band maximum and an exponential band tail in one single equation, two valence band maxima can be distinguished in one angle-integrated CFSYS spectrum. Furthermore, the influence of different illumination (X-ray, UV) and environmental (air exposure, vacuum storage) conditions on the defect density of the perovskite is discussed. Based on the valence band modelling of the perovskite, the interface towards the fullerene C_{60} as electron transport layer is investigated in detail. Hereby, especially, the effect of a 1 nm thin lithium fluoride interlayer between the perovskite and the C_{60} on the considered interface of perovskite/LiF/ C_{60} is investigated. With the LiF interlayer an enhanced defect density is observed in the first monolayers of the C_{60} . However, this is overcompensated by a reduced hole density at both sides of the interface, which decreases the non-radiative charge carrier recombination.

"Die Struktur der Valenzbandkante ist recht kompliziert." Charles Kittel Einführung in die Festkörperphysik 15. Auflage, S.224 2013, Oldenbourg Verlag München

Contents

1	Introduction			1
2	Fun	damer	Itals	7
	2.1	Densit	ty of states in semiconductors	7
	2.2	Semic	onductor interfaces	11
		2.2.1	Metal/semiconductor heterojunctions	12
		2.2.2	Semiconductor/semiconductor heterojunctions	13
		2.2.3	Non-ideal contacts and index of interface behaviour	13
		2.2.4	Charge carrier transport across real interfaces	15
	2.3	Solar	cells	16
		2.3.1	Charge carrier selective contacts	16
		2.3.2	Performance metrics	17
		2.3.3	Silicon heterojunction solar cells	17
		2.3.4	Tandem solar cells	19
3	Met	thods a	and Materials	21
	3.1	Photo	electron spectroscopy	21
		3.1.1	Physics of the photoionization process	22
		3.1.2	Energy scale in photoelectron spectroscopy	25
		3.1.3	X-Ray photoelectron spectroscopy	25
		3.1.4	Ultra-violet photoelectron spectroscopy	27
		3.1.5	Photoelectron spectroscopy in constant final state mode	29
		3.1.6	Probing depth in dependence of the photon energy	32
	3.2	Metho	ods for the investigation of opto-electronic and structural properties	
		of thir	1 films	34
		3.2.1	Grazing incidence X-ray diffraction	34
		3.2.2	Mercury probe conductivity measurements	34
		3.2.3	Spectroscopic ellipsometry	35
	3.3	Invest	igated Materials	36
		3.3.1	Indium tungsten oxide	36
		3.3.2	Metal halide perovskites	38

		3.3.3	C_{60} as electron transporting material	39	
	3.4 Sample preparation		e preparation	40	
		3.4.1	Co-evaporation of mixed indium tungsten oxide	41	
		3.4.2	Fabrication of silicon heterojunction solar cells with IWO_x as hole		
			selective contact	41	
		3.4.3	$Perovskite/LiF/C_{60} \dots \dots \dots \dots \dots \dots \dots \dots \dots $	42	
4	Ind	ium tu	ngsten oxide as hole selective contact for silicon heterojunction		
	sola	r cells		45	
	4.1	Introd	uction	45	
	4.2	2 Density of occupied defect states in mixed indium tungsten oxide layers .		47	
	4.3	Annea	ling of indium tungsten oxide up to $700 ^{\circ}\text{C}$	48	
		4.3.1	Experimental annealing procedure	49	
		4.3.2	Chemical composition	49	
		4.3.3	Crystal structure	51	
		4.3.4	Optical properties	54	
		4.3.5	Conductivity	56	
	4.4	4 Implementation of indium tungsten oxide as hole selective contact in SHJ			
		solar o	cells	58	
	4.5	Chapt	er summary	61	
5	Val	ence b	and structure and defect density of halide perovskites	63	
5	Val 5.1	e nce b Introd	and structure and defect density of halide perovskites	63 63	
5	Val 5.1 5.2	e nce b a Introd Chemi	and structure and defect density of halide perovskites uction	63 63 64	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi Model	and structure and defect density of halide perovskites uction	63 63 64 67	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi Model 5.3.1	and structure and defect density of halide perovskites uction	 63 63 64 67 68 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi Model 5.3.1 5.3.2	and structure and defect density of halide perovskites uction	 63 64 67 68 	
5	Vale 5.1 5.2 5.3	Introd Chemi 5.3.1 5.3.2	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3	and structure and defect density of halide perovskites uction	 63 64 67 68 69 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 Defect	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 81 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 Defect 5.4.1	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 81 82 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 Defect 5.4.1 5.4.2	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 81 82 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 Defect 5.4.1 5.4.2	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 81 82 84 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 Defect 5.4.1 5.4.2 5.4.3	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 81 82 84 	
5	Val 5.1 5.2 5.3	ence ba Introd Chemi 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 Defect 5.4.1 5.4.2 5.4.3	and structure and defect density of halide perovskites uction	 63 63 64 67 68 69 71 73 76 79 81 82 84 85 	

CONTENTS

5.5 Chapter summary			er summary	87	
6	Elec	ctronic	properties of the CsMAFA/C ₆₀ interface	89	
	6.1	Introd	uction	89	
	6.2 X-ray PES analysis of C_{60} thickness variation on CsMAFA		PES analysis of C_{60} thickness variation on CsMAFA $\hfill \ldots \ldots \ldots$.	90	
		6.2.1	Overview	90	
		6.2.2	XPS core level modeling	92	
		6.2.3	Chemical composition of C_{60} on CsMAFA	93	
	6.3 Density of states of C_{60} thin films		by of states of C_{60} thin films	98	
		6.3.1	Energetic positions of the HOMO density of states in C_{60}	98	
		6.3.2	Defect states in C_{60} thin films $\ldots \ldots \ldots \ldots \ldots \ldots \ldots$	101	
	6.4	Measu	rement induced surface photovoltage in near-UV PES measurements	103	
		6.4.1	Estimation of quasi Fermi level splitting in CsMAFA induced by		
			near-UV illumination	104	
		6.4.2	Near UV-illumination induced SPV in C60 with/without absorber $% \mathcal{A}$.	107	
		6.4.3	Influence of the C_{60} thickness on surface photo voltage in PES	110	
	6.5	Energ	y level alignment at the CsMAFA/C ₆₀ interface $\ldots \ldots \ldots \ldots$	112	
		6.5.1	Evolution of density of states with increasing C_{60} thickness \ldots .	113	
		6.5.2	Combined modeling of the density of states of CsMAFA and C_{60}	114	
		6.5.3	HOMO-edge position of C_{60} with increasing thickness $\ldots \ldots \ldots$	118	
		6.5.4	Energetic positions at the CsMAFA/C ₆₀ interface $\ldots \ldots \ldots$	119	
		6.5.5	Determination of band offsets at the CsMAFA/C ₆₀ interface \ldots	122	
	6.6	Influe	nce of LiF as interlayer at the CsMAFA/C ₆₀ interface \ldots \ldots \ldots	123	
		6.6.1	Perovskite valence band maximum and C_{60} HOMO-edge position		
			with/without LiF interlayer	124	
		6.6.2	Influence of LiF at the CsMAFA/C ₆₀ interface on the interface defect		
			density	127	
		6.6.3	Discussion of combined energy level alignment of the		
			$CsMAFA/LiF/C_{60}$ interface	129	
	6.7 Chapter summary		134		
7	Cor	clusio	n and Outlook	137	
Bi	bliog	graphy		143	
\mathbf{A}	Арг	oendix		165	
	A.1	List of	f publications	165	
	A.2	A.2 Modelling of CsMAFA valence band density of states			
	A.3	A.3 Influence of the photon flux on the SPV during the near-UV PES measure-			
		ments for full device stack			

в	Ack	nowledgement	177				
	A.6	Abbreviations and symbols	174				
	A.5	Determination of the optical band gap of C_{60}	. 172				
		ing C_{60} thickness \ldots	. 171				
	A.4	A.4 Modelling parameters of the density of occupied defect states with incr					

Chapter 1

Introduction

It is our decision. If we want to sustain human living on planet earth and enable equal economic living standards in different parts of the world, decentralized, low-cost and environmentally friendly energy conversion is indispensable.

In the past years, climate change has accelerated and is on a trajectory to becoming catastrophic. The previously considered ample remaining time to reduce climate-active gas emissions, so as to minimize their impacts, has shortened rapidly and now requires immediate action. We have grown accustomed to ignore the actual costs of our energy consumption. Theoretically, the fossil resources, formed over millions of years would likely still allow us to continue our established lifestyle for a couple of centuries, since new reservoirs of coal, oil, and gas are being continually discovered. This is not the limiting factor. The most challenging part of fighting our self inflicted climate-catastrophe is thus to prevent ourselves from fully extracting these reservoirs. By continuing the emission of climate active gases, we will intensify the greenhouse effect thereby passing fragile tipping points and climate on earth will dramatically change leading to severe humanitarian catastrophes [1].

One of the most effective options to prevent this scenario is to further reduce the levelized cost of renewable and emission-free energy. Luckily, the sun, as an energy source, combines two important advantages: Firstly, it steadily provides far more power than we currently forecast needing, and, secondly, this power is available independently of the economic wealth of a country and available where human civilization is located [2].

The average power density over land on earth delivered by the sun is 183 W m^{-2} and, with practically usable areas for solar power conversion, 340 TW are potentially accessible [3]. With solar photovoltaics (PV), this energy can be converted into electricity and, by combining it with storage technologies, a reliable and steady supply of energy is possible. With a robust electricity grid equipped to balance effects of weather fluctuations, and day and night cycles, solar PV can be a significant pillar of a renewable energy mix in combination with wind and hydro power.

The largest share $(\sim 95\,\%)$ of the current solar PV production market is dominated

by crystalline silicon (c-Si) wafer-based solar cells, while the rest consists of various thinfilm technologies [4]. The global installed PV capacity in 2020 grew by 127 GW_p (30 % more than in 2019) to a cumulative power of 707 GW_p [5]. A total installed PV power of 4.3-11.1 TW_p, depending on the assumed scenario, could be reached by 2040 [5]. In order to hypothetically supply 100 % of the global electricity demand by 2050, a total installed PV capacity of 25 TW_p would be required [2]. Such a large scale of renewable energy conversion raises the need for efficient resource use in conversion technology as well as a holistic transformation of the grid-system and large energy-storage capacities.

With rapidly growing PV production capacity, their levelized cost of energy per kWh has decreased dramatically throughout the last decades, continually outperforming multiple forecasts, to only $3.12 - 11.01 \in \text{Cent/kWh}$ in germany [5]. Considering the construction of a new power plant in 2021 in Germany, this is the lowest energy cost per kWh among all energy sources, both fossil or renewable [5]. With rising prices for CO₂ certificates, the costs of burning fossil fuels like coal and oil for energy conversion will continue to increase, making solar PV even more attractive.

A key factor in decreasing the energy conversion costs is to increase the power conversion efficiency (PCE) of solar cell devices and modules, as a significant share of the total costs originates from e.g. the mounting and wiring of solar panels (balance of system costs). The PCE of silicon based single junction solar cells is close to its physical limits, which, according to the Shockley-Queisser limit [6] and including Auger recombination, is at 29.4 % [7]. With silicon heterojunction solar cell technology, based on a crystalline silicon wafer and thin amorphous silicon layers, a record PCE of 26.7 % was achieved [8]. Silicon has the intrinsic disadvantage of an indirect band gap, which makes it a rather poor absorber, requiring relatively thick wafers to capture the incoming light effectively. However, historically and due to the abundance of silicon, it is the most important solar PV technology, and most likely will remain so in the foreseeable future.

In the past decade, a new promising material class has raised extensive research interest in the PV community: Metal halide perovskites. Within a few years, by leveraging the knowledge base gained from other thin film technologies such as organic PV, the PCE of perovskite based solar cells has climbed one record to the next. Currently, up to 25.5 % [8] are reached in single junction devices on a laboratory level.

By using only one absorber material, a large fraction of the energy contained in the incoming photons is lost to thermalization, which is determined by the band gap energy of the absorber. This fundamentally limits the PCE. Furthermore, parts of the solar spectrum are not even absorbed, since the photon energy is below the band gap and thus cannot excite charge carriers. With the various and simple possibilities for film deposition and layer growth, in addition to the tunable band gap energies, metal halide perovskites are very suitable to be combined with crystalline silicon in tandem solar cell devices [9]: a medium band gap energy perovskite composition (around 1.7 eV) can be used as an

absorber in the top cell, absorbing the high energy photons, while a large share of the transmitted photons can be absorbed by the crystalline silicon based bottom cell. With this, especially thermalization losses can be minimized. Through the joint work of the research community, the physical limits of single junction silicon solar cells have already been surpassed by a silicon/perovskite tandem device, with a PCE in such tandem solar cells of 29.5% [8]. With the physical limit of the PCE being around 44% [10], there is still a lot of room for further improvement. However, for metal halide perovskites to become interesting for industrial application with silicon bottom cells in a tandem configuration, fundamental challenges need to be addressed, namely the long-term stability and material toxicity due to mostly lead-based material compositions [11, 12].

Both, the device stability and the PCE of silicon/perovskite tandem solar cells are crucially determined by the quality of the various contact layer interfaces [13, 14], as they are found to limit especially the device open circuit voltage and fill factor, and are thus a field of recent and ongoing research [15–17]. The charge carrier transport across interfaces depends on two main aspects: The energy level alignment of both materials forming the interface and the density of defect states at the surfaces and the interfaces.

This thesis aims to contribute to the understanding of two interfaces in the complex layer stack of silicon/perovskite tandem solar cells. The first part focuses on indium tungsten oxide mixtures as a dopant free and easily scalable alternative to p-doped amorphous silicon as hole selective contact for the silicon bottom cell. In the second and third part the density of states in the valence band region of a widely used perovskite absorber composition and its interface to C_{60} as electron selective contact are investigated in detail.

Photoelectron spectroscopy (PES) is one of the most prominent and powerful experimental techniques to study such interfaces [18, 19]. In PES, photons with a known energy are used to excite photoelectrons from a sample surface. The kinetic energy of the photo electrons is measured in an energy selective analyzer, and with this, the initial binding energy of the electrons in the solid can be determined. Depending on the applied photon energy (X-rays, UV-light), this allows for studying the density of occupied states of high binding energy electron core levels, the valence band structure, and defect states in the band gap of semiconductors up to the Fermi level. The material composition and chemical binding environment in the solid are conventionally investigated by using X-ray excitation (XPS), while for the determination of the energy level alignment at interfaces often He-I UV excitation (He-UPS) is used. In this thesis, additionally, a different variant of PES is applied: The incident photon energy, supplied by a Xenon gas pressure lamp, is monochromatized by a double grating monochromator and varied from $\sim 3-7$ eV. The photoelectron yield at one constant final state is measured by an hemispheric electron analyzer, which is why it is named constant final state yield spectroscopy (CFSYS). It combines two main advantages: i) compared to conventional He-UPS it is less surface sensitive with an information depth of around 5-10 nm, and thus also enables studying buried interfaces, and ii) with a very high dynamic range of up to seven orders of magnitude, the density of states in the valence band region including band tails and occupied defects in the band gap can be measured around 3-4 orders of magnitude below typical He-UPS detection limits. CFSYS is thus a suitable method to investigate the energy level alignment and defect density at interfaces, which determine the device functionality of silicon/perovskite tandem solar cells.

The thesis is structured as follows:

In **Chapter 2**, physical fundamentals of semiconductors, heterojunctions, and solar cells, which are necessary for the understanding of the investigated problems are discussed. Thereafter, in **Chapter 3**, the principles of the most important measurement techniques applied in the thesis are presented and the investigated materials are introduced.

Chapter 4 is based on our previous published studies on the energy level alignment of mixed indium tungsten oxide (IWO_x) as a dopant free hole selective contact for silicon heterojunction solar cells. Indium oxide is highly conductive, but has a comparably low work function, while tungsten oxide has a high work function, but low conductivity. By coevaporating both metal oxides, forming mixed indium tungsten oxide, the general goal of this study is to find a trade-off between those characteristics and increase the conductivity of the tungsten oxide while maintaining a sufficiently high work function for the recombination based contact to n-type crystalline silicon. The defect density of mixed IWO_x layers is investigated by means of He-UPS and CFSYS. In order to improve the opto-electronic properties of these mixed oxide layers, the crystallization, parasitic absorption and conductivity of the thin films upon high temperature annealing are studied. Furthermore, the implementation of IWO_x in full silicon heterojunction devices is investigated.

An important part of understanding the electronic interfaces of metal halide perovskites and the respective charge carrier selective layers is to precisely analyse the interface density of states in the valence band region. In **Chapter 5** a detailed study on the valence band maximum of a widely used mixed cation mixed halide perovskite composition $(Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}(PbI_{0.83}Br_{0.17})_3, CsMAFA)$ is presented. With CFSYS, the characteristically low density of states at the valence band maximum of the metal halide perovskite composition can be traced over a very high dynamic range of up to seven orders of magnitude. Using a model, which describes the parabolic band edge and the exponential band tail in a single equation, two valence band edges can be revealed in angle-integrated valence band spectra of such halide perovskites. Furthermore, the influence of different illumination conditions and environmental influences on the defect density of CsMAFA is studied. In **Chapter 6**, the interface between the fullerene C_{60} and the perovskite composition, as discussed in the previous chapter, is investigated. C_{60} is currently the standard electron transport layer (ETL), applied in p-i-n configuration perovskite solar cells. However, this interface is found to limit especially the open circuit voltage of high efficiency perovskite solar cells in p-i-n configuration. By directly measuring the Fermi edge in the respective CFSYS spectra of the sample surface, a substantial surface photovoltage induced by the near-UV illumination is observed and can be quantified. Taking this into account, the energy level alignment of the CsMAFA/C₆₀ interface is derived, including the direct determination of the valence band offset between both materials. Adding a thin LiF interlayer at the interface between CsMAFA and C₆₀ was found to enhance the open circuit voltage of perovskite solar cells with C₆₀ as ETL. Here, the impact of the thin LiF interlayer on the energy level alignment and defect formation of the CsMAFA/C₆₀ interface will be discussed. CHAPTER 1. INTRODUCTION

Chapter 2

Fundamentals

Understanding the electronic properties of semiconductors is essential for understanding opto-electronic devices, such as solar cells. Knowledge of the band structure and density of states of such materials can be used to draw conclusions about their electrical behavior and the formation of electrical contacts at interfaces with other materials. In the following chapter, their physical principles will be introduced. For more detailed elaborations on semiconductor physics the books of Sze [20] and Kittel [21] are recommended, on which the introduction to the density of states in semiconductors (section 2.1) is based. This information will be used afterwards to describe the physical principles of heterojunctions between different semiconductors, as well as their applications as solar cells (section 2.2.2). While the theoretical concepts are important, however, real surfaces and interfaces can differ significantly from the idealized ones, for example due to additional defect states in the band gap, which can influence the Fermi level position and charge carrier transport across those interfaces (section 2.2.3).

2.1 Density of states in semiconductors

An entirely free electron can be described as a plane wave. Within a crystal lattice, however, the interaction of electrons with the periodic potential $V(\vec{r}) = V(\vec{r} + \vec{R})$, with the lattice vector \vec{R} in real space, needs further consideration. To properly describe an electron in this environment, it is necessary to solve the general, stationary Schrödinger equation, which is given by

$$\hat{H}\psi_{\vec{k}}\left(\vec{r}\right) = \left[-\frac{\hbar}{2m}\Delta + V\left(\vec{r}\right)\right]\psi_{\vec{k}}\left(\vec{r}\right) = E_{\vec{k}}\psi_{\vec{k}}\left(\vec{r}\right)$$
(2.1)

with the Hamiltonian \hat{H} , Laplace operator Δ , the reduced Planck constant \hbar , the electron mass m and the energy Eigenvalues $E_{\vec{k}}$. The solution for the wave function $\psi_{\vec{k}}(\vec{r})$ in equation 2.2 is given by Bloch's theorem and is no longer a simple plane wave, but is modulated by a lattice-periodic function $u_{\vec{k}}(\vec{r})$.



Figure 2.1: Fictive band structure of a direct (left) and indirect (right) transition in a semiconductor in kspace. The conduction band (CB) and the valence band (VB) are depicted. In a direct semiconductor, the VB maximum, $E_{\rm V}$, is located at the same k-vector as the VB minimum, $E_{\rm C}$, and in an indirect semiconductor their k-vector differs by $\Delta \vec{k}$.

$$\psi\left(\vec{r}\right) = u_{\vec{k}}\left(\vec{r}\right) \cdot \exp\left(i\vec{k}\vec{r}\right) \tag{2.2}$$

Bragg-reflection at the borders of the Brillouin-zone result in the formation of an energy gap (band gap, $E_{\rm G}$), where no solution of Schrödinger's equation is found [21]. Solids with a non-zero band gap and where the Fermi level in the band gap can be manipulated by doping are generally considered as semiconductors. The electrical conductivity of a solid is proportional to the density of free charges in partially occupied bands, which can contribute to a current flow. The density of free charges depends in first order on the energy gap, separating valence- and conduction band. At absolute zero, the highest and fully occupied band is defined as the valence band (VB), whereas the next fully unoccupied band is known as conduction band (CB). At T > 0 K, electrons are thermally excited into the conduction band and can be considered as fully delocalized charge carriers with an effective mass m_e^* . Each excited electron leaves a *hole* in the valence band, which can similarly be treated as positive charge carrier with effective mass m_h^* .

For a detailed understanding of the electronic processes, the dispersion relation (also known as the band structure) i.e. the dependence of the potential energy on the wave vector, $E(\vec{k})$, needs to be considered. The curvature of the bands depends on the direction of \vec{k} in the crystal and the interaction of charge carriers with the crystal. At the conduction/valence band minima/maxima, it can be approximated by a parabola and is reciprocally proportional to m_e^* and m_h^* . The dispersion relation of electrons and holes in semiconductors at the band edges can be derived as [21]

$$E(k) = \frac{\hbar k^2}{2m_{e,h}^*}.$$
 (2.3)

In Figure 2.1 two different transitions in a semiconductor are shown for a fictive dispersion relation. While, for the direct transition, a photon excites an electron from a valence band maximum to the conduction band minimum without any difference in k-vector, for the indirect transition, an additional phonon accounting for $\Delta \vec{k}$ needs to be involved in order to make the transition happen. The latter one, being a three-particle process, is much less likely to occur, which manifests in the absorption coefficient rising significantly



Figure 2.2: Crystal structure of a two dimensional cubic crystal in reciprocal space. A circle of equal energy in the k_x , k_y plane with radius $|\vec{k}_{\rm R}|$ is shown. The circle area defines all states up to the energy $E(\vec{k}_{\rm R})$. The side length of the cubic unit cell in real space is L. The Brillouin zone is indicated as a square with dimension of $2\pi/L$.

less steep with increasing photon energy, compared to direct transitions.

For the determination of the density of free charge carriers (*n* for electrons and *p* for holes) in a semiconductor, accessing the density of states, D(E), is of essential interest. D(E) describes the available states in an infinitesimally small energy range and is given in units of states per energy and volume. The density of free charge carriers can then be calculated by multiplying it with the respective occupation probability at each energy, given by the Fermi-Dirac distribution, f(E). The product of both needs then to be integrated over the energy from the respective band edge (conduction band edge, $E_{\rm C}$, for electrons) to infinity, as in equation 2.4.

$$n = \int_{E_{\rm C}}^{+\infty} D_e(E) \cdot f(E) \cdot dE$$
(2.4)

To derive the density of states, first, the number of states, N(E), in the crystal needs to be calculated. For an easier perception, Figure 2.2 shows a two-dimensional view of an ideal cubic crystal in reciprocal space with length L in real space, where the Brillouin zone takes the area of $(2\pi/L)^2$. The circle line represents states with the same energy and the area in the circle hence includes all accessible states with a certain energy and below. N(E) can thus be calculated by dividing the circle area with radius $|\vec{k}_R|$ by the area of the Brillouin zone. This can easily be extended towards three dimensions by considering cubic unit cells and a sphere with respective volumes, and leads to equation 2.5. The factor of two is due to the spin degeneracy, which allows every state to be occupied by a spin up and spin down electron.

$$N(E) = 2 \cdot \frac{V_{\text{sphere}}}{V_{\text{unit cell}}} = 2 \cdot \frac{4}{3} \pi |\vec{k}_R|^3 \cdot \left(\frac{L}{2\pi}\right)^3 \tag{2.5}$$

$$=\frac{8\pi \left(2m^{*}E\right)^{3/2}}{3\hbar^{2}} \cdot \left(\frac{L}{2\pi}\right)^{3}$$
(2.6)

As we want to obtain the density of states per energy and volume, the derivation of N(E) with respect to the energy needs to be taken, yielding

$$\tilde{D}(E) = \frac{\partial N(E)}{\partial E} = L^3 \frac{(2m^*)^{3/2}}{2\pi^2 \hbar^3} E^{1/2}.$$
(2.7)

Furthermore, normalized to the crystal volume and thus divided by L^3 , the density of states, D(E), is obtained. By also considering the energy with respect to the conduction band minimum, $E_{\rm C}$, the density of states is described by a square root behaviour with

$$D(E) = \frac{(2m^*)^{3/2}}{2\pi^2\hbar^3} (E - E_{\rm C})^{1/2} = 4\pi \left(\frac{2m^*}{h^2}\right)^{3/2} (E - E_{\rm C})^{1/2}.$$
 (2.8)

The Fermi-Dirac distribution, f(E), depends only on the temperature, T, the Boltzmann coefficient $k_{\rm B}$, and the position of the Fermi level, $E_{\rm F}$. The Fermi level is defined as the energy level, were the occupation probability of the states is at 50 %. For T = 0 K all states below the Fermi energy are occupied and all states above are unoccupied, thus, for this case f(E) is a step function. With increasing temperature, the edge is smoothed out and for energies far away from the Fermi energy $(3k_{\rm B}T < (E - E_{\rm F}))$, it can be approximated by the Boltzmann-distribution.

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_{\rm F}}{k_B T}\right)} \stackrel{3k_B T < E - E_{\rm F}}{\approx} \exp\left(-\frac{E - E_F}{k_B T}\right). \tag{2.9}$$

For the cases, where the Boltzmann-approximation is valid, the integral can easily be solved and the charge carrier density is given as follows:

$$n = 4\pi \left(\frac{2m_e^*}{h^2}\right)^{3/2} \int_{E_C}^{+\infty} \sqrt{E - E_C} \cdot \exp\left(-\frac{E - E_F}{k_B T}\right) \cdot dE$$
(2.10)

$$= \underbrace{2\left(\frac{2m_e^*\pi k_{\rm B}T}{h^2}\right)^{3/2}}_{=:N_{\rm C}} \cdot \exp\left(-\frac{E_{\rm C}-E_{\rm F}}{k_{\rm B}T}\right).$$
(2.11)

In an analogous way the density of free holes is given by

$$p = \int_{-\infty}^{E_{\rm V}} D_h(E) \cdot [1 - f(E)] \cdot dE$$
(2.12)

and we finally get rather simple expressions with the equations 2.13 with the effective densities of holes (with m_h^*) and electrons, $N_{\rm V,C}$. The effective density of states can be understood as the density of states close to the band edge and thus integrated from the band edge over an interval of $k_{\rm B}T$ [22].

$$p \approx N_{\rm V} \cdot \exp\left(-\frac{E_{\rm F} - E_{\rm V}}{k_B T}\right), \quad n \approx N_{\rm C} \cdot \exp\left(-\frac{E_{\rm C} - E_{\rm F}}{k_B T}\right).$$
 (2.13)

To further increase the conductivity of semiconductors, often other atoms than the

material is composed of are introduced in the semiconductor and used as dopants. If the incorporated atom provides an additional electron as compared to the necessary electrons for the chemical binding in the crystal it is called a donor and if the atom provides one electron less than the chemical binding requires, it adds a hole and is called an acceptor. Donors usually posses energy levels just below the conduction band edge, and acceptors just above the valence band edge. Thus, at room temperature, these states can be considered as fully ionized, providing one additional electron (or hole) per dopant atom and the donor- and acceptor density can be assumed to be equal to the density of additional charge carriers in the system. The overall charge carrier density of the majority carriers is then dominated by the density of doping atoms. According to the doping type, "n" (for donors) and "p" (for acceptors), the Fermi level is shifted towards the conduction or valence band edge, respectively.

2.2 Semiconductor interfaces

Interfaces of semiconductors or a metal and a semiconductor are essential to the working principle of each opto-electronic device. The charge transport across an interface is dominated by the energy level alignment of the involved materials. In this section first idealized metal/semiconductor as well as semiconductor/semiconductor heterojunctions will be describes followed by a discussion about non-ideal effects of real interfaces such as interface defect states, liming the applicability of the simplified considerations. The actual formation of such interfaces is very complex and for a detailed theoretical understanding e.g. the work of Mönch can be recommended [23].

In general metals and semiconductors (SC) can be described by their surface potentials, which are indicated in the schematic in Figure 2.3(a). A metal hereby is fully described by it's work function, Φ , which is the minimal energy required to remove an electron from the solid into the vacuum, and free of influences of the solid. It is given by the position of the Fermi level, $E_{\rm F}$, with respect to the vacuum level, $E_{\rm Vac}$. Since the Fermi level in semiconductors is located in the band gap, two additional potentials are introduced: The ionization energy, IE, describes the minimal energy needed to remove an electron from the semiconductor up to the vacuum level, and the electron affinity, χ , which describes the energy gained by adding an electron to the neutral system. The difference between both is the band gap energy, $E_{\rm G}$.

Initially, the potential energy of the charge carriers in each of the two materials is, in general, different. However, once the materials are in electrical contact, the charge carriers at the interface will adjust in order to reach the thermal equilibrium and the Fermi levels of both materials will align. The redistribution of charge carriers obeys the Poisson equation.



Figure 2.3: (a) Surface potentials in a semiconductor (SC) and a metal: work function Φ , electron affinity χ , ionization energy *IE*), (b) Metal/SC contact between an n-type SC with electron affinity χ_{SC} , work function Φ_{SC} and a meal with work function Φ_M , resulting in a Schottky barrier height for electrons $\Phi_{B,n}$ and a band bending qV_{bi} ; (c) Heterojunction between two different semiconductors with their respective surface potentials and the resulting valence and conduction band offsets, ΔE_V and ΔE_C , according to the Anderson rule. See main text for further details. The figures are adapted from Schneikart [24].

2.2.1 Metal/semiconductor heterojunctions

Metal/semiconductor junctions can be distinguished by their charge transport characteristics, i.e. the current-voltage dependence, which is in a first approximation determined by the energy level alignment at the interface. For an n-type semiconductor an ohmic contact, which shows a linear current-voltage dependence, is formed if the metal work function $\Phi_{\rm M}$ is lower than the one of the semiconductor, $\Phi_{\rm SC}$. A rectifying Schottky-contact is formed if $\Phi_{\rm M} > \Phi_{\rm SC}$, which then shows a forwarding or rectifying behaviour depending on the current flow direction. In Figure 2.3(b), a Schottky-contact in thermal equilibrium of an n-type semiconductor and a metal is shown. Electrons, in order to minimize their potential energy, are transferred from the semiconductor (SC) to the metal, which (in the depicted case) has a higher work function than the semiconductor. In the metal, the additional charge carriers do not significantly increase the already very high density of electrons and thus do not affect its work function. However, in the semiconductor a positive space charge is left due to the ionized atoms. This region is thus depleted from electrons and called space charge region. Usually, the width of the space charge region reaches up to several nm, mainly depending on the charge carrier concentration in the semiconductor.

The Schottky-model predicts the energy level alignment of such a metal/semiconductor junction [25]. It is based on the assumption that both vacuum levels align and thus the magnitude of the band bending in the semiconductor, qV_i , is given by the difference between the work function of the metal and the semiconductor. The barrier heigh, $\Phi_{B,n}$, for electrons between both materials is given by the difference between the metal work function and the semiconductor electron affinity, χ_{SC} , as in equation 2.14. Since the work function of the metal equals it's electron-affinity, the Schottky-model is also referred to as electron affinity rule.

$$\Phi_{\mathrm{B,n}} = \Phi_{\mathrm{M}} - \chi_{\mathrm{SC}} = \chi_{\mathrm{M}} - \chi_{\mathrm{SC}} \tag{2.14}$$

2.2.2 Semiconductor/semiconductor heterojunctions

A semiconductor heterojunction is formed, when two different semiconductors are brought into electrical contact. In principle, their energy level alignment can be described similarly to the metal/SC contact by aligning the vacuum levels of both materials, which is depicted in Figure 2.3(c).

Electrons from the semiconductor with the lower work function will migrate over the interface to the semiconductor with the higher work function and leave positive space charges behind, while the same happens inversely for holes - again a depletion region is formed. Depending on the potential energy of the charge carriers, the charge redistribution results in a built-in potential (band bending, $V_{\rm bi}$) and band discontinuities (band offset) in the valence and conduction band, $\Delta E_{\rm V}$ and $\Delta E_{\rm C}$. Both crucially determine the charge transfer across the interface.

Similar to the Schottky-model for metal/SC junctions, an idealized SC/SC heterojunction can be described by the Anderson rule [26] and the band offsets can be calculated according to the equations 2.15.

$$\Delta E_{\rm C} = \chi_1 - \chi_2$$

$$\Delta E_{\rm V} = \chi_1 - \chi_2 + E_{\rm G,1} - E_{\rm G,2}.$$
(2.15)

According to the sign of the discontinuities, two different types of heterojunctions can be distinguished: In type 1 heterojunctions the offsets are positive, and in type 2 both offsets have opposite signs, thus Figure 2.3(c) shows a type 2 heterojunction. The sum of $\Delta E_{\rm C}$ and $\Delta E_{\rm V}$ is given by the difference of both band gaps, and the total band bending by the difference of both work functions.

2.2.3 Non-ideal contacts and index of interface behaviour

The Schottky-model, which is used for Figure 2.3(b) is the most simplistic method to determine the energy level alignment between a semiconductors and a metal. For real interfaces, however, the experimentally observed barrier height is often less dependent on the metal work function than what would be expected from the ideal model. The reason is so-called *Fermi level pinning* due to defect states at the interface or surface of a semiconductor. Here some principle considerations are summarized based on the publications from Robertson [27], Vilan and Cahen [28], and Klein [29].

The simple Schottky barrier height (SBH) model needs to be extended, as actually the SBH for electrons, Φ_n , between a semiconductor with electron affinity χ_{SC} and a metal with work function Φ_M depends on two very different factors: Charge redistribution across

the interface which leads to a depletion region in the semiconductor, or a sudden potential drop, Δ , which accounts for the differences in work function [28] and is not considered in the simple Schottky-model.

$$\Phi_{\mathrm{B,n}} = \Phi_M - \chi_{\mathrm{SC}} - \Delta. \tag{2.16}$$

Thus, there are two extreme scenarios of equation 2.16: In the Schottky-Mott limit, no interface potential drop needs to be considered and the vacuum levels perfectly align without discontinuities. In the situation of very strong Fermi level pinning known as the Bardeen limit [30], the SBH height is essentially independent of the metal work function at the interface. The extent of the existing Fermi level pinning is usually characterized by the index of interface behaviour, S. This quantity tends to be very low ($S \approx 0.1$) for materials with mostly covalent bonds, amongst which is silicon, and large ($S \approx 1$) for materials with mostly ionic bonds, e.g. oxides.

The index of interface behaviour of a semiconductor in between those two extremes and can be defined as the change of the barrier height within an infinitesimal change of the metal electron affinity [23, 28].

$$S = \frac{\mathrm{d}(\Phi_n)}{\mathrm{d}(\chi_M)} \tag{2.17}$$

Most of the discussion of the index of interface behaviour in literature focuses on the nature and origin of the interface states, which determine the value of S. These can be subdivided between *intrinsic states* and *extrinsic states*. Extrinsic states are formed at the interface e.g. by crystal discontinuities, dangling bonds, foreign atoms (adsorbates), or can also be induced by metal deposition on a semiconductor [31]. Intrinsic states, on the other hand are mostly referred to as *metal-induced gap states* (MIGS) [32–34] or *virtual gap states* [35], and are present even for perfectly grown interfaces. They can be understood as electronic states in the metal, which have a wave function with exponentially decaying amplitude into the semiconductor. Thus, the metal states adjacent to the interface induce electronic states in the energetically forbidden band gap of the semiconductor.

According to the linear response model by Cowely and Sze [36], S depends on the density of interface states per unit area, $N_{\rm it}$. The wave function of these states has a certain decay length, λ , into the semiconductor, and with the permittivity ϵ of the semiconductor and the dielectric constant ϵ_0 , S is given by [37]

$$S = \frac{1}{1 + \frac{q^2 \lambda N_{\rm it}}{\epsilon \epsilon_0}}.$$
(2.18)

In an actual interface, both, intrinsic and extrinsic states can be present and the Fermi level pinning is dominated by the one, which induces a higher defect density [27]. Independent of the physical origin of the interface states, they determine a charge neutrality level (CNL): for a neutral surface, the interface states above the CNL are unoccupied and



Figure 2.4: Semiconductor heterojunction between (n)a-Si and (p)c-Si in equilibrium with the illustration of charge carrier transport paths across the interface, drawn on a logarithmic horizontal scale. The individual processes are discussed in the main text. Reprinted from Schulze *et al.* [38], with the permission of AIP Publishing.

below, they are occupied.

Similar to semiconductor-metal interfaces, the energy level alignment between two semiconductors can also be described more precisely than by the Anderson rule by taking the index of interface behaviour into account. Considering two semiconductors, a and b, the barrier height for electrons can be described by equation 2.19 [27].

$$\Delta E_{\rm C} = (\chi_a - \Phi_{\rm CNL,a}) - (\chi_b - \Phi_{\rm CNL,b}) + S(\Phi_{\rm CNL,a} - \Phi_{\rm CNL,b}).$$
(2.19)

The electron affinity rule thus needs to be modified by introducing S, while the physical principles remain similar to the previously discussed semiconductor-metal interfaces.

2.2.4 Charge carrier transport across real interfaces

Defect states in the bulk of semiconductors and at the interface of a semiconductor heterojunction further strongly affect the charge carrier transport across the interface. Depending on the application of the heterojunction, they can be highly detrimental, e.g. by leading to strong non-radiative trap assisted recombination, or they might be actually needed for a trap assisted recombination contact. Here, the most important paths are briefly introduced and illustrated in Figure 2.4.

In Figure 2.4 a specific case a heterojunction of (n)a-Si:H and (p)c-Si is depicted on a logarithmic horizontal scale. The principle transport mechanisms can be understood as more general and thus are valid for other semiconductor heterojunctions. The red arrows indicate non-radiative recombination processes, the blue arrows tunnelling of charge carriers and the black arrows emission paths. Trap assisted recombination, where an electron recombines with a hole, can in principle appear in the bulk of both semiconductors ((c) and (f)) and at their interface (d). Additionally, either the hole or the electron can tunnel from another point in space to that defect state and similarly lead to a non-radiative



Figure 2.5: Energy level alignment of an idealized heterojunction solar cell, consisting of an illuminated absorber material and a hole selective contact (HSC) as well as an electron selective contact (ESC). The quasi Fermi level splitting (QFLS), induced by illumination is indicated with the quasi Fermi level of holes, $E_{\rm F,p}$, and electrons, $E_{\rm F,n}$.

recombination process, which is indicated by the blue arrows towards (f) for a bulk defect and (e) for an interface defect. Furthermore, charge carriers can tunnel via several steps in a row from defect to defect, and then recombine in the bulk of one of the semiconductors, either through defect states energetically deep in the band gap (g) or in the more shallow band tail region (h). By thermionic emission, charge carriers can overcome the band offsets and spikes at the interface (a). Furthermore, charge carriers can also tunnel through these barriers (b). The process of band to band tunnelling via intermediate defect states (i) can assist for an efficient recombination contact, e.g. between the valence band of one semiconductor to the conduction band of another semiconductor.

2.3 Solar cells

The working mechanism of solar cells is based on the photo-excitation of charge carriers and their charge selective separation in the device. Historically, the charge separation in solar cells based on crystalline silicon was ensured by p- and n-type doping of the c-Si, leading to the formation of a homojunction. More recently, high efficiency devices as well as novel solar cell concepts rely on semiconductor heterojunctions, which serve as charge carrier selective contacts. Here the basic concepts are introduced, however, for a detailed understanding the book of Dittrich [22] is recommended.

2.3.1 Charge carrier selective contacts

The absorption of photons in a semiconductor leads to the excitation of excess charge carriers, which induces a splitting of the Fermi levels for holes and electrons into the so-called quasi-Fermi levels, $E_{\rm F,p}$ and $E_{\rm F,n}$. A schematic of an illuminated solar cell with ideal charge carrier selective contacts is shown in Figure 2.5. The photon energy is converted into a higher potential for the electrons, which can then be extracted (on the right hand side in the sketch) and further conducted to supply energy to an external load, and subsequently be transferred back into the system on the left hand side, where they recombine with holes. The charge separation is realized by contact materials that ideally either block electrons and conduct holes (hole selective contact, HSC), or block holes and



Figure 2.6: Current-voltage characteristics of a solar cells with the main performance parameters being the open circuit voltage, $V_{\rm OC}$, the short circuit current $I_{\rm SC}$ and the maximum power point, MPP.

conduct electrons (electron selective contact, ESC). Ideally, the interface is determined by the band offsets and the band bending (which is not depicted in Figure 2.5).

2.3.2 Performance metrics

Solar cells are typically characterized according to their current (I) - voltage (V) characteristic. The *IV*-characteristics of a solar cell including series and shunt resistances ($R_{\rm S}$ and $R_{\rm P}$) is given by [22]

$$I(V) = I_0 \cdot \left[\exp\left(\frac{q(V - IR_{\rm S})}{nk_{\rm B}T}\right) - 1 \right] + \frac{V - IR_{\rm S}}{R_{\rm P}} - I_{\rm ph}.$$
 (2.20)

It can thus be understood as a diode under illumination, where I_0 is the dark saturation current and $I_{\rm ph}$ the photogenerated current. The ideality factor *n* describes the deviation from an ideal diode, where *n* equals one.

Figure 2.6 shows an example I-V curve of an illuminated solar cell. Three main characteristic points are used for its description: The voltage at open circuit condition, $V_{\rm OC}$, the current at short circuit condition, $I_{\rm SC}$ and the maximum power point, MPP, which describes the point on the IV-curve, where the product of current and voltage reaches it's maximum. The fill factor, FF quantifies the current and voltage at the maximum power point ($I_{\rm mpp}$, $V_{\rm mpp}$), relative to the product of $V_{\rm OC}$ and $I_{\rm SC}$.

$$FF = \frac{I_{\rm mpp} \cdot V_{\rm mpp}}{I_{\rm SC} \cdot V_{\rm OC}}$$
(2.21)

The power conversion efficiency, η , of a solar cell is defined as the power output at MPP relative to the incoming power, $P_{\rm in}$, by

$$\eta = FF \cdot \frac{I_{\rm SC} \cdot V_{\rm OC}}{P_{\rm in}}.$$
(2.22)

2.3.3 Silicon heterojunction solar cells

Silicon hetero junction (SHJ) solar cells are based on a crystalline silicon (c-Si) absorber, which is usually passivated by a thin layer of hydrogenated intrinsic amorphous silicon ((i)a-Si:H) on either side of the wafer. On top of the passivation layers, thin n- and pdoped amorphous silicon layers serve as charge carrier selective contacts [39]. The highest



Figure 2.7: Energy level alignment on a silicon heterojunction solar cell in thermal equilibrium. The charge carriers flow is indicated of the electrons (red) and holes (blue), which are selectively extracted by doped a-Si layers from the (n)c-Si absorber. A thin intrinsic hydrogenated a-Si layer on either side of the wafer ensures a good surface passivation and TCOs on both sides assist for lateral charge carrier transport to the metal contacts. The figure is adapted from Mews [48].

efficiencies reached for silicon based single junction solar cells are based on a-Si/c-Si heterojunctions, where both n- and p-contact are deposited in an interdigitated pattern at the back side, reaching a PCE of up to 26.7% [40].

A schematic of the band alignment in a SHJ solar cell is depicted in Figure 2.7. For SHJ solar cells, mostly n-type wafers with a thickness of roughly 200 µm are used as absorbers. Charge carriers are excited in the absorber and are selectively contacted by the (p)a-Si:H on the front side and the (n)a-Si:H on the back side (in the here shown layer stack). The highly recombination active semiconductor/metal junction is separated from the absorber by a 5-10 nm thick (i)a-Si:H layer, which passivates the dangling bonds on the surface of the c-Si crystal. With this, very high open circuit voltages of up to 750 meV can be reached [41]. The (i)a-Si:H/(p)a-Si:H layer stack is mainly optimized between the conflicting objectives of making the layers thicker, to provide a good to excellent surface passivation and contact formation, and make them thinner to reduce parasitic absorption and series resistance losses. As the (p)a-Si:H is not sufficiently conductive, an additional TCO (often indium tin oxide, ITO) is applied on the emitter to ensure good lateral conductivity to the metal contact grid and simultaneously improve the optical incorporation of the photons. As indicated in the schematic in Figure 2.7, a recombination contact is formed at the (p)a-Si:H/TCO interface. The imperfect energy level alignment at this interface can be improved by two different approaches, either by increasing the doping concentration of the (p)a-Si:H, or by applying high work function materials, e.g. metal oxides $(MoO_x \text{ or } WO_x)$ as it will be investigated in chapter 4. In the latter case these materials form the recombination contact with the (n)c-Si due to a substantial charge transfer at the interface, resulting in a high upwards band bending in the (n)c-Si. While the first approach is constrained due to chemical doping limits of the amorphous silicon, for the latter one significant research work has been carried out over the past years [42-44]. Doped layers can even be entirely omitted, when replacing also the (n)a-Si:H on the back side by an electron selective metal oxide contact (e.g. MgO_x [45]), leading to a dopant-free asymmetric silicon heterojunction solar cell, DASH [46, 47]).

2.3.4 Tandem solar cells

With the available solar spectrum, delivered by our sun, the theoretically maximum achievable PCE for a solar cell is fundamentally limited by the band gap energy of the absorber. The two main energy losses, in terms of converting incident sunlight to electricity, in a solar cell are transmission losses (photons that are not absorbed in the material) and thermalization losses (relaxation of potential energy of the electrons into thermal energy, which is transferred to the crystal lattice). According to the Shockley-Queisser limit, which only considers radiative recombination of charge carriers, the maximum PCE of single junction solar cells with a band gap of 1.1 eV (for silicon) is found at 33.4% under AM1.5G illumination condition [6]. AM1.5G describes the global spectral power density delivered by our sun and after passing 1.5 times the optical path length through the earth atmosphere (air-mass, AM). Considering this spectrum, silicon is close to the optimal band gap for reaching the highest possible PCE in single junction devices. Additionally, the intrinsic loss in the absorber due to Auger recombination needs to be considered, yielding a PCE limit of 29.43% for crystalline silicon [7]. Thus, the actual achieved PCE for a siliconbased single junction solar cell is already very close to its physical limits. Therefore, one promising path to surpass this limit is the stacking of several solar cells on top of each other and either contact both cells separately or interconnecting them as monolithic multijunction devices, e.g. tandem solar cells with two absorbers. By combining a low band gap material on the bottom with a high band gap material on the top, thermalization losses can be significantly reduced and the Shockley-Queisser limit can be pushed to 45% with an AM1.5G spectrum and optimal band gaps of $E_{G,Bottom} = 0.94 \text{ eV}$ and $E_{G,Top} = 1.61 \text{ eV}$ [49, 50].

As silicon is by far the most established and abundant material for solar cells, it is worth using the gained knowledge and established industry, and base tandem devices on silicon bottom cells, which restricts the band gap of the bottom cell to $1.1 \,\mathrm{eV}$. In a monolithic interconnection of both cells the highest PCE can then be obtained with a top cell band gap of around $1.7 \,\mathrm{eV}$ [10, 51]. In the past decade metal halide perovskites have raised enormous interest, especially due to the easy fabrication and tunable band gap energy making them interesting partners to combine with silicon in tandem solar cell configurations. CHAPTER 2. FUNDAMENTALS

Chapter 3

Methods and Materials

In this chapter the main applied measurement techniques will be discussed and the investigated materials will be introduced. The most important measurement method, applied in this thesis is photoelectron spectroscopy, which is used in various different variants, and will hence be discussed in more detail in section 3.1. Afterwards, in section 3.2, the measurement principles of the applied methods for opto-electronic and structural analysis will be briefly discussed.

The investigated materials will be introduced in section 3.3 and the sample preparation procedures are described in section 3.4.

3.1 Photoelectron spectroscopy

Photoelectron spectroscopy, also called photoemission spectroscopy (PES), is a widely used class of measurement techniques to investigate the electronic surface properties of semiconductors and heterojunction interfaces. It serves as the main experimental measurement method in this work, and the necessary fundamentals will be discussed in this section. For more detailed explanations, the book by Hüfner [52] is recommended, from which the discussion here is inspired, in combination with the work by Korte [53].

The general principle is based on the photoelectric effect, which was discovered in 1887 by Heinrich Hertz and explained in 1905 by Albert Einstein. As illustrated in Figure 3.1, electromagnetic radiation with a certain photon energy, $h\nu$, impinges on a sample surface under an angle, ψ , and can excite photoelectrons. If the kinetic energy of the excited electrons exceeds the sample work function, Φ_{Sample} , the electrons can leave the material and are measured with respect to their kinetic energy by an energy-selective hemispheric electron analyzer, and in general also depend on the altitude, ϑ , and azimuth (not shown in the sketch), φ , thus the angles in which the photoelectrons escape from the sample. The information about the photon energy of the incident radiation and the kinetic energy of the photoelectrons enables to draw conclusions about the binding energy of the electrons in the material, which is conventionally given relative to the Fermi level of the material.



Figure 3.1: Schematic of a photoelectron spectroscopy measurement. The photons with energy $h\nu$ from the light source impinge on the sample surface with the incident angle ψ and excite photoelectrons, are selected with respect to their kinetic energy by the hemispheric analyzer at an angle ϑ .

Depending on the applied photon energy, it permits on the one hand to investigate core levels and hence the chemical compositions and environment of the different atoms in those compositions by using X-Ray PES (XPS), and on the other hand also the work function and valence band density of states (DOS) by using ultra-violet PES (UPS) with different excitation energies (He-I UPS, He-UPS; Near-UV PES, NUPS). For XPS and UPS, the incident photon energy is kept constant, while the kinetic energy of the photoelectrons is measured. A fundamentally different approach is used for constant final state yield spectroscopy (CFSYS), where the incident photon energy is varied, while photoelectrons with one specific kinetic energy (one final state) are measured. This technique is less widely used in literature, however, compared to the conventionally applied UPS with illumination from a He gas discharge lamp, it allows to investigate the DOS in the valence band and occupied states in the band gap with a very high dynamic range of up to seven orders of magnitude and a high energetic resolution.

3.1.1 Physics of the photoionization process

A schematic of the main energy levels involved in a PES experiment on a semiconductor is presented in Figure 3.2. The physical process of a PES measurement can be divided into three steps, as described by Berglund and Spicer [54], which are indicated by numbers in the energy diagram: First, by photoionization, the impinging photon excites an electron. In the sketch this process is exemplary shown for an electron being excited from a core level and from the valence band region. The energy distribution of the excited electrons replicates in a first approximation the density of occupied states of the material, more exactly, the convoluted DOS of the valence and conduction band and the dipole matrix element, shifted by the photon energy, $h\nu$. The photon energy is then equal to the sum of the binding energy with respect to $E_{\rm F}$, $E_{\rm B}$, the sample work function, $\Phi_{\rm sample}$, and the kinetic energy of the excited electron in the solid. In a second step, the excited electrons are transported to the sample surface. During this process, a part of the excited electrons looses kinetic energy through inelastic scattering in the material. Those secondary electrons are represented by the hatched part of the DOS in Figure 3.2. Finally, in a third step, the electrons need to overcome a potential barrier in order leave the sample into the vacuum under conservation of the component parallel to the surface, k_{\parallel} , of their



Figure 3.2: Energy levels of a photoemission experiment. Photons, with energy $h\nu$, excite electrons from occupied states (e.g. core levels, or valence bands) into unoccupied states. If the energy of the photoelectrons exceeds the sample work function, $\Phi_{\rm sample}$, they can reach the analyzer and their kinetic energy distribution is measured. With this, the binding energy of the electrons in the sample, $E_{\rm B}$ can be determined with respect to the Fermi level. The numbers indicate the corresponding steps in the three-step model of the photoemission process by Berlund and Spicer [54], which is discussed in the main text. The figure was adapted from Korte [53].

momentum. This potential barrier cuts off the spectrum at a certain minimal kinetic energy, referred to as the secondary electron cut-off (SECO), which will later on assist in determining the sample work function. Only electrons with higher kinetic energy than the sample work function can reach the vacuum. Also more complex models, describing the whole process in only one step can be found in literature [52], but here this more intuitive picture should be sufficient for an understanding of the results, which are discussed in this thesis.

Following the three-step model, the primary photoelectron current, $I_{\rm P}$, can be described by the product of the photocurrent due to photoionized electrons, $J(E, h\nu)$, the transmission function, T(E), which describes the energy dependent transport of electrons through the sample, and W(E), describing the escape of photoelectrons into the vacuum [55].

$$I_{\rm P} = J(E, h\nu) \cdot T(E, h\nu) \cdot W(E) \tag{3.1}$$

Let's focus first on the photoionization current, $J(E, h\nu)$. The transition probability rate, w, from the initial state i (wave function Ψ_i) to a final state f (Ψ_f) of an N-electron system due to a small perturbation Δ by an electromagnetic field is described by Fermi's Golden Rule [52]. The transition matrix element $|\langle \Psi_f | \Delta | \Psi_i \rangle|^2$ sometimes is also written in short $|M_{fi}|$ and represents the single electron photoexcitation from the initial to the final state. It can in principle be calculated, but this is mathematically very demanding, and varies for each material.

$$w \propto \frac{2\pi}{\hbar} \left| \langle \Psi_f | \Delta | \Psi_i \rangle \right|^2 \delta \left(E_f - E_i - \hbar \omega \right)$$
(3.2)

Considering equation 3.2 not only for a two energy level system, but integrating over all energy levels, the primary photocurrent can also be written as [53]

$$J(E,h\nu) \propto |M_{fi}(E)|^2 N_{\text{occ.}}(E) \cdot N_{\text{unocc.}}(E)$$
(3.3)

with the density of occupied and unoccupied states, $N_{\text{occ.}}$ and $N_{\text{unocc.}}$, which are given by the density of states multiplied with the Fermi function.

The transmission function is determined by the inelastic mean free path length (IMFP), λ_{imfp} (see also Figure 3.8), and the absorption coefficient α , as [55]

$$T(E,h\nu) = \frac{\alpha(h\nu)\lambda_{\rm imfp}(E)}{1 + \alpha(h\nu)\lambda_{\rm imfp}(E)}.$$
(3.4)

W(E) describes the process of the electron being transferred into the vacuum. Considering electrons as almost free with an inner potential V_0 and with parallel momentum being conserved when escaping the material surface, W(E) is determined by [55]

$$W(E) = \frac{1}{2} \left(1 - \sqrt{\frac{V_0}{E + V_0}} \right).$$
(3.5)

Comparing the different PES modes in terms of the determination of the primary photo current, several advantages and disadvantages become apparent. For XPS and also UPS, the incident photon energy is kept constant, which means that the energy dependence of the dipole matrix element can be neglected. In principle W(E) and $T(E, h\nu)$ would need to be considered. Further, as the density of unoccupied states (thus final states), especially close to the conduction band edge cannot be assumed as constant, the obtained spectrum will be affected by this. This is especially relevant for UPS with near-UV excitation, where the excitation energy is comparably low and the number of final states might be limited. For CFSYS, electrons at one final state are collected, thus W(E) is constant. Even though the density of unoccupied states does not need to be considered, the dipole matrix element, thus the impact of changing photoexcitation cross sections, indeed can have a severe impact on the spectrum. Here, however, a constant matrix element will be assumed, which is a substantial assumption and can give rise to an artificially amplified/diminished DOS, measured by the excitation of photons with varying energy. This will be discussed again in section 5.3.6, where the internal yield, measured by CFSYS is normalized to volume units. A more detailed comparison between the different methods can be found in Korte's work [53].

3.1.2 Energy scale in photoelectron spectroscopy

In Figure 3.2 the relevant energy levels of the photoelectron spectroscopy measurement are shown. Most commonly, energetic positions in PES are given relative to the Fermilevel, $E_{\rm F}$, of the contacted substrate material which is 0 eV, by definition. This is referred to as binding energy scale. In this thesis, binding energies for XPS spectra are given in positive numbers as it fits the convention in literature, while all shallow energetic levels, such as valence and conduction band positions and corresponding spectra are given in the actual sign relative to the Fermi level. As already briefly discussed in the beginning of this section, the kinetic energy of the photoelectrons depends in principle on the incident photon energy, $h\nu$, the binding energy, $E_{\rm B}$, and the sample work function, $\phi_{\rm Sample}$. The kinetic energy of a photoelectron after leaving the sample surface into the vacuum, $E'_{\rm kin}$ is given as equation 3.6 (see also Figure 3.2).

$$E'_{\rm kin} = h\nu + E_{\rm B} - \phi_{\rm Sample}.$$
(3.6)

The analyzer and the sample are brought into electrical contact for the measurement, which leads to an equal Fermi level for both. When the photoelectrons reach the analyzer, they need to overcome the analyzer work function, $\phi_{\text{Spectrometer}}$, which is a tool-specific constant and determined in the calibration procedure of the set-up. The measured kinetic energy of the photoelectrons, E_{kin} , thus differs from the kinetic energy, when leaving the sample, E'_{kin} , by the difference of the work function of the sample and the analyzer. In consequence, E_{kin} is independent of the sample work function and given by

$$E_{\rm kin} = h\nu + E_{\rm B} - \phi_{\rm Sample} - (\phi_{\rm Spectrometer} - \phi_{\rm Sample})$$

$$E_{\rm kin} = h\nu + E_{\rm B} - \phi_{\rm Spectrometer}.$$
(3.7)

3.1.3 X-Ray photoelectron spectroscopy

The binding energies of the core electrons of atoms are characteristic for each element. In a first approximation, they are described by the principal quantum number of the energetic state. The binding energy of each electron, belonging to a certain orbital, depends on the orbital angular momentum (quantum number: l) and the intrinsic angular momentum, the spin (quantum number: s). The spin-orbit coupling connects both quantities with each other. Thus, the core levels of orbitals with l > 0 are split into multiplets. The total angular momentum (quantum number: j) consists of the vector sum of the orbital angular momentum. This leads to physical constrains on the area of each doublet component, as summarized in table 3.1.

The wave functions of the electrons belonging to the core levels interact only to a

Orbital	l	j	Area ratio
s	0	1/2	-
р	1	1/2, 3/2	1:2
d	2	3/2, 5/2	2:3
f	3	5/2, 7/2	3:4

Table 3.1: The area ratio of a doublet core level depends on the total angular momentum, given by $j = s \pm l$, with *l* being the quantum number and *s* the electron spin.



Figure 3.3: Example XPS survey spectrum of anindiumtungsten-oxide mixture with $34\,\%$ indium oxide content 66%and tungsten oxide, measured with non-monochromatized $Al-K_{\alpha}$. The core levels are labelled and the *j*-components of the doublet lines are indicated.

minor extent with each other, thus, the binding energy is only slightly affected by the chemical binding configurations in the material, shifting the core levels by a maximum of a few eV depending on the chemical environment. This can be used to e.g. determine oxidation states of elements. Usually, X-ray tubes using Al-K_{α} ($h\nu = 1486.6 \text{ eV}$) or Mg-K_{α} ($h\nu = 1253.6 \text{ eV}$) serve as radiation sources for XPS. An example for an XPS survey spectrum of a mixture of indium oxide and tungsten oxide on crystalline silicon is shown in Figure 3.3, where the most significant core levels are indicated.

The energy distribution of a core level is physically described by a Lorentzian distribution. The width of the Lorentzian distribution depends on thermionic and statistical scattering as well as the natural line width (i.e. the life time of the electron-hole state). Effects, such as the Doppler broadening or measurement-induced transfer functions lead to a Gaussian broadening of the measured signal. The overall signal can thus be described by a convolution of both, a Lorentzian and a Gaussian distribution, which is called a Voigt profile.

One of the main purposes of XPS is to determine the chemical compositions of thin films and solids. However, the detection limit of the atomic concentrations is limited to around 1%. In order to quantify chemical compositions and for obtaining atomic ratios, the element and core level-specific sensitivity factors need to be considered. The sensitivity factor, $S_{\rm F}$, includes all information of the effective cross-section (σ), the angular efficiency (ξ), the photoelectron energy generation efficiency (y), the illuminated sample area (A), the detection efficiency of the analyzer (β) and the mean free path length of the
photoelectrons (λ_{imfp}) :

$$S_{\rm F} = \sigma \xi y \beta T \lambda_{\rm imfp} \tag{3.8}$$

In literature there are tables of sensitivity factors for most elements. However, each PES system has its own transfer functions, which also depends on the analyzer settings. This always induces a systematic error when evaluating data with tabulated sensitivity factors. An experimental determination of the true sensitivity factor using stoichiometric samples is possible and includes all system-specific factors. Here, a systematic error might be induced by not fully stoichiometric samples for the determination of the sensitivity factor. In general, a large error of around 5% is to be expected when determining atomic ratios. In this work, either experimentally obtained sensitivity factors or relative peak areas are used. The latter needs the fewest pre-assumptions, however it does not permit making any conclusions about the absolute chemical composition, only trends are discoverable comparing different samples.

General approach to core level modelling

The core level spectra obtained by XPS in this thesis were fitted using the least squares fitting procedure of the peak fitting software Fityk (Version 1.3.1.) [56]. A linear background, which results from the inelastically scattered photoelectrons, was assumed as the standard, but for more complex peaks a Shirley background was needed to describe the data adequately [57, 58]. For doublet core levels, the area ratios discussed in the last section were used as constraints. Furthermore, the full width at half maximum (FWHM) was set to be constant for the peaks of the same chemical states, but belonging to the two j-components of the doublet. The energetic positions of the single components of each core level were set as free fitting parameters, while the energetic distance in between individual components of a core level was set to be the same for comparable samples. All components need to be assigned to a chemical state and should not be added without a meaningful model as justification. Note, that the herein used Al-K $_{\alpha}$ source also shows a strong satellite emission line at 1496.3 eV [59]. Thus for each core level a replica shifted about $9.7 \,\mathrm{eV}$ towards lower binding energies is observed. If the higher *j*-component (at lower binding energy) overlaps with these replica, e.g. for core levels with large spin-orbit splitting such as $\ln 3d$, only the lower *j*-component (at higher binding energies) is used for modelling, which already includes all physical information of the core level.

3.1.4 Ultra-violet photoelectron spectroscopy

In order to investigate the valence band region in more detail, conventionally UV-light radiation sources are used for PES, such as Helium gas pressure lamps with a photon energy of $h\nu = 21.2 \text{ eV}$ (He-UPS). Similar to XPS, this mode is not limited to one excitation energy and other radiation sources could be applied. In the present work, besides Helium based



Figure 3.4: Example He-UPS spectrum of an indium tungsten oxide mixture on silicon with (a) the secondary electron cut-off (SECO) and (b) the valence band region. Orange lines show the modelling of the SECO, which is modelled by a sigmoidial Boltzmann function, and the valence band maximum, E_V , which is determined by the intercept of a linear extrapolation of the leading valence band edge and the linear background.

UPS, also a Xenon gas pressure lamp in combination with a double grating monochromator is used to perform UPS measurements with an excitation energy of $h\nu = 6.5 \text{ eV}$ (near-UV PES, NUPS). UPS permits to especially investigate valence band features and its maximum (VBM), and, via the secondary electron cut-off (SECO), also the work function (Φ) of a material, which is given by the energetic distance of the SECO relative to the Fermi level (see also Figure 3.2), as

$$\Phi_{\text{Sample}} = h\nu - E_{\text{SECO}}.$$
(3.9)

Figure 3.4 shows an example of (a) the SECO, and (b) the valence band region (b) of an indium tungsten oxide mixture. In this work, the SECO is modelled by an sigmoidial Boltzmann function. The valence band region, however, is very complex to understand and model correctly. In classical semiconductors (e.g. crystalline silicon) using conventional He-UPS measurements a simple linear extrapolation of the leading edge of the highest valence band feature is carried out and its intercept with the noise level is defined as VBM $(E_{\rm V} \text{ in Figure 3.4})$. For some materials, e.g. metal halide perovskites, this *ad hoc* approach does not sufficiently describe the complexity of this important energetic position. This will be discussed in detail in chapter 5, where a more advanced model is introduced for the determination of $E_{\rm V}$. Note, that all He-UPS data shown in this thesis is corrected for the three main He-I satellite lines, similar to the procedure shown by Zhang et al. [60]. The relative contributions to the measured sum spectrum due to the satellite lines can be determined by measuring e.g. the Fermi edge of a gold film. Since the exact intensity of the signal excited by the satellites might vary slightly depending on the material, the correction in practice is mostly done by manually adjusting the relative intensities of the satellite lines, which is prone to their over- or underestimation. Hence, in conventional UPS occupied gap states are difficult to distinguish from residuals of this correction. In contrast to that, the double grating monochromator used for NUPS (and CFSYS) provides



Figure 3.5: Schematic of the photoelectron spectroscopy set-up, which has been used for the results of this thesis. Three illumination sources are attached to the system: A xenon lamp in combination with a double grating monochromator, a helium gas discharge lamp and an Al- k_{α} X-ray source. The incident photon flux of the Xe-lamp is measured by the beam-splitter sensor. Additionally, the light, reflected by the sample surface is measured by a separate photodiode. The photoelectrons are analyzed by an hemispheric electron analyzer.

a single band of monochromatic light, which makes the correction for the satellite emission lines unnecessary.

3.1.5 Photoelectron spectroscopy in constant final state mode

In UPS and XPS the incident photon energy is kept constant and the photoelectrons are collected at different kinetic energies. In this work, another, less often used PES mode is applied: constant final state yield spectroscopy (CFSYS). Here, the incident photon energy is varied, while electrons at one constant final state, thus a specific kinetic energy, are collected by the analyzer. The binding energy can be similarly obtained as in equation 3.7 by the set photon energy, $h\nu$, the chosen kinetic energy, $E_{\rm kin}$, and the spectrometer work function $\Phi_{\rm Spectrometer}$. Additionally, a bias voltage of $U_{\rm bias} = 7 \,\mathrm{V}$ is applied between the analyzer and the contacted sample, in order to direct the emitted photoelectrons towards the analyzer.

$$E_{\rm B} = E_{\rm kin} - h\nu + \Phi_{\rm Spectrometer} - U_{\rm bias} \tag{3.10}$$

In order to better illustrate the difference of the respective methods, the experimental PES set up, used to acquire the results which are presented in this thesis will be briefly discussed. It is shown in Figure 3.5.

For XPS and He-UPS measurements, the helium gas discharge lamp and the X-ray

tube are directly focused on the sample surface. The hemispheric analyzer selects photo electrons according to their kinetic energy and the detector measures the respective intensity of the emitted photoelectrons which pass the analyzer at the selected kinetic energy. For the near-UV PES measurements a Xenon gas pressure lamp with a broad emission spectrum of 3-7 eV photon energy is used. The optical path is schematically indicated in Figure 3.5. The same lamp and optical path is used for the CFSYS measurements. First, the white light from the Xe-lamp is monochromatized, by the double grating monochromator. A beam shutter ensures that for every measurement point also a dark reference measurement can be recorded and hence helps to improve the sensitivity. The light beam is divided by a beam splitter, which directs around 10% of the photons towards a photodiode (beam splitter sensor). The photon flux, which actually reaches the sample surface is calibrated by introducing a photodiode to the sample position and measuring both photodiode currents in dependence of the photon energy. With the calibrated spectral sensitivity data of the photodiode, placed at the sample position, a calibration factor for the ratio between the photon flux at the beam splitter sensor and at the sample surface can be obtained in dependence of the applied photon energy. According to the reflectivity of the sample, photons might also be reflected and hence do not contribute to the excitation of photoelectrons. The reflected photon flux, $n_{\rm ph,R}$, is therefore monitored by a second calibrated photo diode inside the vacuum chamber.

For recording a CFSYS spectrum, the Cps of the excited photoelectrons are measured in dependence of the photon energy, by simultaneously recording the incident photon flux, measured by the beam splitter sensor, $n_{\rm ph,i}$. This directly provides the external photoelectron yield in units of eV⁻¹ by

$$Y_{\rm ext}(h\nu, E_{\rm kin}) = \frac{Cps}{n_{\rm ph,i}}.$$
(3.11)

As furthermore the photon flux, reflected by the sample, $n_{\rm ph,r}$, is measured during each scan, the reflectivity, R, of sample can be calculated and the internal yield, $Y_{\rm int}$, can be determined, which only considers the excited photoelectrons per absorbed photon.

$$Y_{\rm int}(h\nu, E_{\rm kin}) = \frac{Cps}{(1-R)n_{\rm ph,i}}$$
(3.12)

As the kinetic energy of the electrons is constant, as mentioned above W(E) does not change with energy and also the density of unoccupied states does not need to be considered. Further, the IMFP is constant, which makes the transmission function only depend on the absorption coefficient α . The constant IMFP has the advantage that the measured internal yield is always obtained from the same sample depth profile. Hence, neglecting the dependence of $T(E, h\nu)$ on the absorption coefficient, the internal yield is directly proportional to the density of states and the dipole matrix element. Here, the main difficulty for CFSYS, which is determination of the dipole matrix element becomes



Figure 3.6: Example valence band spectra of a triple cation perovskite composition, measured by three different PES methods. The intensity of the He-UPS spectrum (right scale) is rescaled to match the internal yield of NUPS and CFSYS (left scale).

apparent again.

$$Y_{\rm int}(h\nu, E_{\rm kin}) \propto N_{\rm occ}(E_{\rm kin} - h\nu) \cdot M^2(h\nu)$$
(3.13)

CFSYS has formerly mostly been applied to investigate valence band edges, offsets, and defect states of hydrogenated amorphous silicon (a-Si:H). The two main advantages of this specific variant of CFSYS are a very low detection limit with roughly seven orders of magnitude below the DOS in the valence band and an increased probing depth due to lower kinetic energy of the photoelectrons (see section 3.1.6).

In Figure 3.6 an example of a CFSYS spectrum is compared to the more classical approaches of NUPS and He-UPS for a triple cation perovskite composition as an example: CFSYS enables to trace the DOS over a very high dynamic range of around seven order of magnitude and thus with a noise floor up to four orders of magnitude below typical He-UPS measurements.

Measurement error in near-UV photoelectron spectroscopy

With equation 3.12 the general error of the internal yield is given by error propagation by

$$\sigma_{Y_{\text{int}}} = \sqrt{\left(\frac{\partial Y_{\text{int}}}{\partial Cps}\right)^2 + \left(\frac{\partial Y_{\text{int}}}{\partial n_{\text{i,ph}}}\right)^2 + \left(\frac{\partial Y_{\text{int}}}{\partial n_{\text{r,ph}}}\right)^2}$$
(3.14)

$$\Rightarrow \sigma_{Y_{\text{int}}} = Y_{\text{int}} \sqrt{\left(\frac{\sigma_{Cps}}{Cps}\right)^2 + \left(\frac{\sigma_{n_{\text{i,ph}}}}{n_{\text{i,ph}}}\right)^2 + \left(\frac{\sigma_{n_{\text{r,ph}}}}{1 - n_{\text{r,ph}}}\right)^2}$$
(3.15)

According to the Poisson statistics, the error on Cps is given by

$$\sigma_{Cps} = \sqrt{Cps}.\tag{3.16}$$

As this error is large compared to uncertainties of the photon flux, the total error of the internal yield can be simplified to

$$\sigma_{Y_{\text{int}}} = \frac{Y_{\text{int}}}{\sqrt{Cps}}.$$
(3.17)

Influence of the monochromator slit width on measured internal yield

The entrance and exit slit width of the monochromator can be adjusted to find a trade-off between high light intensity and high energy resolution. Figure 3.7(a) shows the valence band spectra of a triple cation perovskite composition (CsMAFA, as discussed in chapter 5) versus the photon energy, measured with a variation of the monochromator slit widths from 0.2 mm to 4 mm. As shown in Figure 3.7(b), the photon flux of the Xe-lamp generally increases upon decreasing photon energy: For a slit width of 2 mm the photon flux at $E_{\rm Ph} \approx 6.7 \, {\rm eV}$ is around $10^{12} \, {\rm s}^{-1} {\rm cm}^{-2}$ and increases continuously to around $5 \cdot 10^{13} \, {\rm s}^{-1} {\rm cm}^{-2}$ at $E_{\rm Ph} \approx 3.7 \, {\rm eV}$. By adjusting the slit width from 0.2 - 4 mm the photon flux can be changed by around three orders of magnitude. The changing photon flux upon changing photon energy leads to slightly different illumination conditions, which can be relevant when investigating photoactive and well passivated layer stacks (see section 6.4.1). On the other hand, it permits to use comparably low slit width to get a high resolution in the valence band region, and still have a high light intensity in the band gap region, where usually a low density of states (thus low Cps) is expected. Using a slit width of 4 mm reaches a detection limit of $Y_{\rm int} \approx 10^{-14} \, {\rm eV}^{-1}$, but it also leads to a decrease of the energy resolution (see inset of Figure 3.7(a)). In contrast to that, using $0.2 \,\mathrm{mm}$ or $0.5 \,\mathrm{mm}$ leads to a higher energy resolution and hence less broadening of the true physical features, but the noise floor drastically increases to $Y_{\rm int} \approx 10^{-11} \, {\rm eV}^{-1}$. Furthermore, the necessary photon flux for a reliable counting rate is barely reached, which can be seen by the rather noisy signal. For the sake of a compromise between high energy resolution and low detection limit a slit width of 2 mm is chosen as standard value.

For all these measurements, the resolution of the energy analyzer was set to 125 meV, which is itself found as a trade-off between high resolution and high counting rate. As the over all transfer function is determined by both, the monochromator FWHM and the energy analyzer FHWM, it is reasonable to choose both to be set at a similar resolution [53].

3.1.6 Probing depth in dependence of the photon energy

In general, PES is a very surface-sensitive measurement technique. The probing depth is limited by the inelastic scattering of the photoelectrons in the matter, described by the inelastic mean free path length (IMFP), λ_{imfp} . The dependence of IMFP on the kinetic energy of the electrons follows approximately the "universal curve", which is shown in Figure 3.8. The black dots show the experimentally observed IMFP of electrons for a wide



Figure 3.7: (a) CFSYS spectra of typical CsMAFA perovskite layer; (b) Photon flux of the Xenon gas pressure lamp, used for NUPS and CFSYS measurements. Both are shown for a variation of the monochromator slit width from 0.2 mm to 4 mm.



Figure 3.8: Inelastic mean free path length $\lambda_{\rm m}$ (labelled as $\lambda_{\rm imfp}$ in the main text) of electrons according to their kinetic energy (also known as *universal curve*) obtained for a wide range of different elements, as published by Seah *et al.* [61]. The energy range relevant for CFSYS & NUPS (orange), He-UPS (blue) and labsource XPS (green) is highlighted.

range of different materials. Thus, the IMFP is a direct function of the kinetic energy of the electrons, independent of the interacting matter. Using different excitation energies for PES, hence also implies different probing depths. The relevant energy regimes are highlighted in Figure 3.8 for CFSYS (orange), He-UPS (blue), and XPS, with typically available lab-sources (green). With a minimum between 50 and 70 eV at around $\lambda_{imfp} =$ 5 Å, the IMFP rises towards lower and higher kinetic energies. Hence, on the one hand (hard) X-rays enable a higher probing depth, but also near-UV light does increase the IMFP to 10 to 100 Å.

3.2 Methods for the investigation of opto-electronic and structural properties of thin films

3.2.1 Grazing incidence X-ray diffraction

X-ray diffraction (XRD) is a non-destructive measurement technique, which permits to investigate the crystal structure, phases, strain and also preferred orientations of bulk materials or thin films by constructive interference of diffracted X-rays. It most prominently relies on the Bragg-equation $2d = n\lambda \sin \theta$, with the order of the diffraction, n, the lattice constant, d, the incident photon wavelength, λ , and the angle between incident light and the normal to the lattice plane, θ . For the measurement, the intensity of the diffracted light is recorded in dependence of θ . For the measurement of thin films, usually the socalled grazing incidence configuration is chosen. Here, only the detector angle is varied, while for the incident X-rays a very low angle with respect to the sample surface is chosen. This maximises the optical path length in the (thin) layer under investigation and avoids high signal from the substrate. Usually, the pattern quality is however less good then in the typical Bragg-Brentano geometry, where a higher intensity can be reached in shorter time scale. Thus no advanced refinement of the crystal lattice structure is possible (with reasonable measuring times), however by comparing the appearing diffraction peaks to known peak positions from a databases, a simple phase analysis can be performed.

For the measurements in this thesis, a Bruker D8 diffractometer with $Cu-K_{\alpha}$ source and an energy dispersive Sol-X detector was used in a grazing incidence configuration with a small fixed incidence angle of 0.5°. The samples were measured at room temperature and the patterns were detected in a range of $2\theta = 10^{\circ} - 60^{\circ}$ in steps of 0.04° with a counting time of 6 s at each step.

3.2.2 Mercury probe conductivity measurements

The resistivity of the investigated metal oxide layers was measured by a simple set-up allowing to record a current-voltage characteristic of a known contact geometry. For the measurement, the sample is placed on a plate, where two hollow T contacts are below. The sample is pressed on the plate by a vacuum pump, which creates an underpressure and simultaneously the hollow defined area is filled with liquid mercury, directly contacting the thin film. The applied voltage is varied from -1 V to +1 V and with the known geometry and film thickness (determined by using a profilometer), the specific resistivity of the layer can be determined. A lower measurement limit of 10^{-6} S cm⁻¹ for the specific conductivity is given by the internal resistance of the set-up.



Figure 3.9: Measurement principle of spectroscopic ellipsometry, where the incident electric field vector $E_{\rm f,i}$ (under an incident angle θ), consisting of a parallel (p) and perpendicular (s) component gets reflected depending on the complex refractive index (n,k) and thickness of a sample. Experimentally, the change in amplitude (Ψ) and phase (Δ) of both field vector components are measured. Used with permission of Springer, from [62]; permission conveyed through Copyright Clearance Center, Inc.

3.2.3 Spectroscopic ellipsometry

Spectroscopic ellipsometry is a very powerful technique to model the complex dielectric function, ϵ , and can also be used to determine the thickness of very thin layers. Here, only the basic principle will be introduced. The discussion is based on Fujiwara and Collins' work [62], which is recommended as instructive literature. The basic principle is to investigate the change in polarization of electromagnetic radiation, upon reflection at a sample (which can also be a layer stack with several layers). For determining the properties of each single layer an advanced modelling is required.

The measurement principle is depicted in Figure 3.9. Linearly polarized light, which impinges on a sample (i) in general gets reflected as elliptically polarized light (r), depending on the complex refractive index, and the sample thickness. The incident electric field vector $E_{\rm f,i}$ can be describes by the superposition of its two components, perpendicular (s) and parallel (p) to the incident plane ($E_{\rm f,is}$ and $E_{\rm f,ip}$). Both components get reflected differently and depending on the complex refractive index $\tilde{n} = n + ik$, with n being the refractive index and k the extinction coefficient and the thickness of the sample. The reflected electric field vector components change in their amplitude and phase, resulting in general in an elliptical polarization with the components of the reflected electric field vector $E_{\rm f,rs}$ and $E_{\rm f,rp}$. Experimentally, the polarization can also be described by the two ellipsometric angles Ψ and Δ . Where tan Ψ describes the ratio of the amplitudes and Δ the phase difference of the s- and p-component of the electric field vector of the incident and reflected electromagnetic radiation.

$$\rho = \tan \Psi \cdot \exp\left(i\Delta\right) = \frac{E_{\rm f,rp}/E_{\rm f,ip}}{E_{\rm f,rs}/E_{\rm f,is}} \tag{3.18}$$

Using ρ , the complex dielectric function ϵ can be determined by

$$\epsilon = \epsilon_1 + i\epsilon_2 = \sin^2(\theta) \left(1 + \tan^2(\theta) \left(\frac{1-\rho}{1+\rho} \right) \right)$$
(3.19)

with the incident angle of the light θ . The complex refractive index is given by the square root of the dielectric function. The absorption coefficient of a material, α , can be calculated by its extinction coefficient, k, and the wavelength, λ :

$$\alpha = \frac{4\pi}{\lambda}k.\tag{3.20}$$

For the measurements, conducted in this thesis, a wavelength range of 180 to 850 nm was chosen and the spectra were recorded with three different incident angles relative to the surface normal (50° , 60° and 70°). The applied dispersion model for mixed indium tungsten oxide layers was a combination of a Drude-Lorentz [63] and a Tauc-Lorentz [64] oscillator. By applying such a dispersion model, the film thickness can be determined from the effective dielectric function.

3.3 Investigated Materials

In this section the investigated contact materials will be briefly discussed. First, both co-evaporated metal oxides, indium oxide and tungsten oxide are introduced. Afterwards, metal halide perovskites and the fullerene C_{60} as electron selective contact layer for perovskite based solar cells will be discussed.

3.3.1 Indium tungsten oxide

As already mentioned in section 2.3.3, high work function metal oxide thin films have been investigated and applied as charge selective contacts in solar cells and are established as transparent conductive oxides (TCO) in various opto-electronic devices. In order to optimize the hole selective contact in SHJ solar cells, which is usually realized by a thin (p)a-Si:H layer, high work function metal oxides, such as MoO_x [43, 65–67], VO_x [68], and WO_x [43, 69, 70] have been investigated, with the goal to improve the carrier selectivity and thus the device V_{OC} and FF, while ensuring simple deposition methods, yielding promising results.

Tungsten(VI) oxide (WO₃) is known from various applications besides charge selective contacts for solar cells, such as electrochromic windows [71], water splitting devices [72], and also as buffer layer in e.g. perovskite solar cells [73], or in light emitting diodes [74]. It has a large band gap of 2.6-3.3 eV [75, 76], good thermal stability and a high work function of up to 6.5 eV [77]. However, due to it's poor conductivity, the application of WO_x as hole selective contact in SHJ has been shown to significantly increase series resistance losses [69, 78].

Indium(III) oxide (In₂O₃) on the other hand is known for its high conductivity when doped with different dopants. The most prominent dopant is tin (ITO), yielding low electrical resistivity of up to $\rho = 10^{-4} \Omega \text{cm}$ [79–81], and low absorption in the wavelength



Figure 3.10: Energy levels (vacuum energy $E_{\rm vac}$, valence $E_{\rm V}$ and conduction band edge $E_{\rm C}$) of IWO_x thin films on silicon versus the InO_x content in the indium tungsten oxide mixture. Reprinted from Menzel *et al.* [88], with the permission of AIP Publishing.

region of the solar spectrum. Therefore, it is one of the most commonly used TCOs. Furthermore, indium oxide was also doped with other materials, such as hydrogen [82], molybdenum [83, 84], zinc [82] or tungsten [85, 86], where either the charge carrier mobility or the charge carrier concentration is increased in order to increase the specific conductivity as compared to In_2O_3 . Pure indium oxide has a work function of around $4.4 \, \text{eV}$ [87], which is an intermediate value as compared to other metal oxides. As seen above, indium oxide and tungsten oxide have contrary characteristics, which might enable a trade off by keeping the high work function of tungsten oxide with simultaneously increasing its conductivity when mixing both materials. In our previous publication on mixed indium tungsten oxide spanning the whole range from pure indium oxide to pure tungsten oxide it could be shown, that the work function of IWO_x on (n)c-Si and also the band bending induced in the (n)c-Si could be manipulated by varying the indium oxide content in the mixture as shown in Figure 3.10 (reprinted from the original publication [88]).

However, due to Fermi level pinning and an index of interface behaviour, S, of 0.1 for crystalline silicon (see section 2.2.3), the high difference in work function does not directly translate into a similarly high band bending, but is reduced by a factor of 10. The maximum measured band bending for pure tungsten oxide was found to be around 600 meV, thus the Fermi level is pinned by interface states close to mid-gap of the crystalline silicon. The energetic distance, which is then left between the (n)c-Si valence band and the IWO_x conduction band needs to be overcome by e.g. trap assisted recombination (see section 2.2.4). While the band bending in combination with trap assisted recombination might be sufficient for a decent carrier selectivity, the conductivity for pure tungsten oxide is too low to enable a reasonable application as charge selective contact, even with using very thin layers.

In this work, the aim is to investigate the opto-electronic properties of indium tungsten oxide mixtures in an attempt to improve the conductivity on the one hand by the mixed composition and on the other hand by high temperature annealing. By combining both materials, different mechanisms might play a role and lead to the aimed result of a decent conductivity, while keeping a high work function. Either, a more conductive amorphous



Figure 3.11: Crystal structure of a perovskite with composition ABX_3 , exemplary for MAPbI₃, with A: CH₃NH₃, in the very center of the structure; B: Pb, in the center of the octahedra; and X: I, at the corners of the octahedra. The figure is reprinted from Eames *et al.* [94] under CC-BY 4.0 license.

mixture, or mixed segregated phases, that possess a higher conductivity than the materials on their own might be formed. In recent years also several studies on tungsten doped indium oxide (also named IWO_x) were published [86, 89, 90]. However, those persue a different aim: There, the idea is to enhance the conductivity by adding small amounts of tungsten to In_2O_3 , the conductivity should be enhanced. As the percentages of tungsten were very low in these studies (in the order of several percent), the work function is not significantly increased [86].

3.3.2 Metal halide perovskites

The perovskite crystal structure was first discovered in 1840 for the composition $CaTiO_3$ [91]. However, it took over 150 years until the first solar cells, with a metal halide perovskites absorber, were developed by Kojima *et al.* in 2009 with a PCE of 3.8 % [92]. The research field has developed very quickly, reaching record PCE of over 25.5 % nowadays [93].

One of the main advantages of perovskites is their wide range of opto-electronic properties depending on their composition, and hence a large variety of perovskite compositions is investigated in the research community. For solar cells, usually hybrid organic-inorganic metal halide perovskites are used. The general formula for perovskites is ABX₃ and its crystal structure is shown in Figure 3.11: A (depicted in the very center) is a monovalent cation, B (in the center of the octahedra) a divalent metal cation and X (at each corner of the octahedra) a monovalent halide anion. In the still most prominent and widely investigated composition, methylammonium (MA, $CH_3NH_3^+$, specifically depicted in Figure 3.11) is introduced as the cation, A; lead is used as the divalent metal (Pb²⁺), B; and the anion iodine (Γ) as the halide, X, yielding the composition MAPbI₃. Typically, in more recently investigated perovskites compositions however usually, A, B and X are each combinations of different elements. A is often a combination of the organic MA, FA (formamidinium, $CH_3(NH_2)_2^+$) or inorganic Cs. As metal, B, mostly Pb²⁺, Sn²⁺ or Ge²⁺ are used and as halide, X, Cl⁻, Br⁻ or Γ .

Metal halide perovskites show a number of useful properties, which make them very interesting partners for silicon in tandem solar cell applications. The first important feature is the tuneable band gap, which is mainly manipulated by adjusting the composition of the halides [95–98]. Furthermore, as direct semiconductors, they show a very sharp absorption edge [99] and can thus be used as thin film absorbers and semitransparent top-cells in tandem configurations. They are unusually defect tolerant [100, 101] and can be deposited easily by a variety of deposition methods. Most commonly in a lab-scale fabrication spin coating is used, but also e.g. thermal evaporation [102], laser evaporation [103], spray deposition [104] or inkjet printing [105] are possible and ensures industrial upscaling possibilities. However, there are substantial challenges to overcome for perovskites, mainly the long-term stability, hysteresis and toxicity. The toxicity is mostly tackled by the attempt to replace Pb with Sn, however Sn-based perovskites still strongly lag behind Pb-based ones in terms of both, efficiency and stability [106]. With their low band gap, Sn-based perosykites might not be compatible to silicon based bottom cells, but can serve themselves as bottom cells in perovskite-perovskite tandem solar cells. As ionic materials, metal halide perovskites tend to strong hysteresis, which is due to ion migration [107] and has been tackled mostly by interface engineering with promising progress [108]. The long term stability has been significantly enhanced over the past years, but is still one of the major challenges and now under increasing research focus. This is especially the case since the PCE has reached already very high values. Metal halide perovskites tend to degrade under various conditions. The thermal instability is mostly due to the loss of the volatile MA [109] and can be improved by replacing MA with other cations, such as FA or going towards fully inorganic compositions with Cs as cation [110]. However, for a trade off between stability and still reasonable PCE, combining several cations has become state of the art for achieving high efficiency, stability and reproducibility [111]. Not only high temperatures $(> 100^{\circ} \text{ C})$ are detrimental to the photovoltaic properties, but also exposure to air, as this combines both, humidity [112] and oxygen exposure [113]. This is usually prevented by encapsulating the final devices [114]. Besides improving the stability through different compositions, it has also been found, that the interfaces to the charge selective contacts play an important role [115].

Perovskite solar cells are heterojunction devices and usually consist of the absorber material (perovskite, considered as intrinsic) and additionally an electron selective (n) and a hole selective contact (p). As single junction devices, there are different device architectures: n-i-p ("regular") and p-i-n ("inverted"), which describe the layer stack in the order of deposition. Both yield good efficiencies in single junction solar cells, however, the inverted structure is preferred over the regular structure for silicon/perovskite tandem solar cells due to the reduced parasitic absorption [116].

3.3.3 C₆₀ as electron transporting material

For perovskite solar cells, optimizing the bulk properties is important, however, the device performance at the end is crucially determined by the contact layers, which have an



Figure 3.12: Chemical structure of the *Buckminsterfullerene* C_{60} . The carbon atoms are located at the vertices. The figure is reprinted from reference [119].

influence on both, device stability and the classical performance parameters leading to the PCE [13]. In the present work, the interface formation and energy level alignment with the electron transporting material C_{60} is investigated (chapter 6).

 C_{60} belongs to the group of fullerenes and is an organic semiconductor which consists of molecules with 60 carbon atoms arranged in a football-like structure, as depicted in Figure 3.12 [117, 118].

It has been well known as electron acceptor material in organic photovoltaics [120, 121]. Since it has been shown that thin organic layers are well compatible as charge selective contacts with metal halide perovskite absorbers [122, 123], it became the standard electron transporting layer for "inverted", i.e. p-i-n metal halide perovskite solar cells, but is sometimes also applied in regular architecture [124]. Also other closely related derivates of the C_{60} fullerene, such as $PC_{61}BM$ (Phenyl- C_{61} -butyric acid methyl ester) are used as electron accepting materials. The lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) in organic semiconductors usually have well defined energy levels and less dangling bonds are observed than in inorganic semiconductors such as e.g. amorphous silicon, which make them attractive for interface engineering. However, it is found, that in p-i-n perovskite solar cells, the interface between the perovskite and C_{60} as electron transport layer limits the device open circuit voltage, which is attributed to non-radiative recombination at the interface [125]. The insertion of a thin ($\approx 1 \text{ nm}$) layer of LiF as passivation between the perovskite and C₆₀ has been shown to reduce non-radiative recombination [125, 126], thus increase the open circuit voltage, while keeping a high FF [17, 125] and will be investigated in section 6.6.

3.4 Sample preparation

The description of the layer deposition of indium tungsten oxide thin films used in chapter 4 and the according experimental details are partially taken from Menzel *et al.* [127]. The description of the preparation of the glass/ITO/MeO-2PACz/CsMAFA layer stack investigated in chapter 5 layer stack is taken from Menzel *et al.* [128]. The deposition of the glass/ITO/MeO-2PACz/CsMAFA samples (investigated in chapter 5) and additionally

the samples for both C_{60} thickness variation series with and without LiF interlayer (investigated in chapter 6) was conduced by Amran Al-Ashouri according to the implemented base-line procedure in the HySPRINT lab at Helmholtz-Zentrum Berlin.

3.4.1 Co-evaporation of mixed indium tungsten oxide

For the thermal co-evaporation, In_2O_3 - (99.994%) and WO₃-powder (99.99%) purchased from Sigma-Aldrich were evaporated from aluminum oxide and tungsten crucibles, respectively, in an ultrahigh vacuum chamber (base pressure $<10^{-9}$ mbar). During the deposition, the substrate was rotated with about 1.3 rotations per second. By independently setting the temperature of both crucibles, different evaporation rates, thus compositions, ranging from pure tungsten oxide to pure indium oxide could be obtained. For the tungsten oxide the crucible temperature was varied from 930 °C to 1020 °C and for the indium oxide from 1280 °C to 1325 °C.

For the samples used for the high temperature annealing study in chapter 4, the IWO_x was deposited on 1.2 mm thick, 1x1 inch Corning glasses. With deposition rates of 0.2 to 0.8 nm/min a final layer thickness of 19 nm to 30 nm was reached. The layer thickness was determined *ex-situ* by means of a Bruker Dektak XT profilometer.

The IWO_x layers for the investigation of the defect density by CFSYS in section 4.2 and the implementation of IWO_x as hole selective contact in SHJ solar cells were deposited with the above mentioned settings. For the first one 2" n-type c-Si wafer from TOPSIL with a specific resistivity of $1-2\Omega$ cm were used and the latter one is described below. The layer thickness for IWO_x on silicon was determined by spectroscopic ellipsometry (see section 3.2.3).

All substrates were not intentionally heated; however, a slightly elevated substrate temperature caused by the heated crucibles, which are at a distance of about 20 cm to the substrate, cannot be entirely excluded. Since the applied temperature range of the crucibles is small, the resulting effect should be comparable for all samples and is therefore neglected.

3.4.2 Fabrication of silicon heterojunction solar cells with IWO_x as hole selective contact

In chaper 4 the implementation of mixed indium tungsten oxide layers in silicon heterojunction solar cells is investigated in order to replace the (p)a-Si hole selective contact. Here, the experimental procedure of the SHJ cell fabrication with IWO_x contact layer is described. The layer stack is similar to the one depicted in Figure 2.7.

Polished n-type float zone silicon wafers $(1-5 \,\Omega \text{cm})$ with a thickness of 280 μ m were used as substrates, cleaned according to the RCA procedure [129] and dipped in 1% diluted hydrofluoric acid for 2 minutes to remove the chemical oxide grown on the surface in the last RCA cleaning step. They were passivated by a thin layer of hydrogenated intrinsic amorphous silicon $(d_{\text{Front}} = 6.95 \text{ nm}, d_{\text{Back}} = 6.45 \text{ nm})$. On the back side, 10.6 nm (n)a-Si was deposited as electron selective contact. All a-Si:H layers were deposited by plasma enhanced chemical vapour deposition. The intrinsic layers were deposited at 0.8 mbar, $210 \,^{\circ}\text{C}$, with radio frequency (RF) plasma with 18 W and gas flow rates of 13 sccm SiH₄ and 7 sccm H_2 , followed by a hydrogen plasma treatment at 1.25 mbar, with 30 W, and 30 sccm H₂. The (n)a-Si layers were deposited at 1 mbar, 240 °C, 40 W RF, and gas flow rates of 15 sccm SiH₄, 40 sccm H₂, and 4 sccm PH₃. Afterwards 70 nm of ITO were deposited on the rear side by RF-sputtering and the samples were annealed at $200 \,^{\circ}\text{C}$ for 5 min in atmosphere. The samples were transferred into the vacuum system, where the indium tungsten oxide mixtures with different indium oxide fraction and a thickness of 4-7 nm were evaporated on the front side according to the procedure described in section 3.4.1. The stoichiometry was determined by reference samples, with the same evaporation conditions, and deposited right before the actual samples in order to not damage the passivation nor the metal oxide layers by the harsh X-ray illumination. The deposition rate of tungsten oxide was found to decrease slightly from deposition to deposition, which might lead to a slight underestimation of the indium oxide content in the solar cells. Again, the samples were annealed at $200 \,^{\circ}$ C for 5 min under nitrogen rich atmosphere after the deposition and before the RF-sputtering of the front side ITO. For the sputtering of the front side ITO a mask was used to define the cell area of $1 \,\mathrm{cm}^2$ and the samples were annealed at 200 °C for 5 min in ambient atmosphere to cure the sputter damage. Finally, for the metal contacts, on the full rear-side 500 nm silver and on the front side a metal grid with $1.5 \,\mu \text{m}$ silver were thermally evaporated.

3.4.3 Perovskite/LiF/C₆₀

To prepare the samples for investigating the valence band maximum of the mixed cation mixed halide perovskite (chapter 5) and the energy level alignment to the electron transporting layer C_{60} (chapter 6), the following procedure was pursued. The investigated layer stacks are shown in Figure 3.13(a) for the investigation of the bare perovskite surface, and (b) and (c) for the investigation on the perovskite/ C_{60} interface.

Glass substrates, fully covered with indium tin oxide (ITO, $15 \Omega \text{ sq}^{-1}$ sheet resistance), supplied by Automated Research GmbH, were first washed in an ultrasonic cleaner, subsequently in detergent (Mucasol), water, acetone and isopropanol and then cleaned using UV-O₃ just before the next preparation steps, which were conducted in an N₂-filled glovebox. For the hole-selective layer, a self-assembling monolayer (SAM) molecule, MeO-2PACz [130], was spincoated at a concentration of 0.3 mg ml⁻¹ following a previously published procedure [130]. The perovskite precursor powders were dissolved in a 4:1 mixture of dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), aiming for a perovskite precursor composition of Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})₃. The solution was spin-



Figure 3.13: Device layer stacks as investigated (a) in chapter 5; (b) and (c) in chapter 6, with ITO/Glass substrates, MeO-2PACz as hole selective self assembling monolayer and spin coated CsMAFA. The perovskite surface (a) as well as the interface towards C_{60} without (b) and with (c) 1 nm LiF as interlayer were investigated. For the PES measurements, the samples were contacted via the ITO substrate, i.e. with $E_{\rm F,ITO}$ as reference for the binding energy scale.

coated with a rotation speed of 3500 rpm (5 s acceleration, 35 s constant) and 250 μ l Anisole was used as an antisolvent (drop 28 s after the start of spinning). The same perovskite has proven to be well reproducible [111, 125], while showing a decent optoelectronic quality ($\approx 1 \%$ photoluminescence quantum yield without further passivation). With C₆₀ as electron transport layer and the exact same layer stack as investigated here, power conversion efficiencies of 21 % for single junction solar cells were shown on SAMs [130], and a similar formulation with slightly higher Br amount has been used in high efficiency (PCE = 29.2 %) perovskite/silicon tandem solar cells [17]. This perovskite composition was chosen, due to its good batch-to-batch reproducibility and is widely used in multiple laboratories, with most of them yielding fairly similar results.

In order to investigate the working mechanism behind the insertion of LiF by determining the energy level alignment and interface formation (chapter 6) two sample series with varying C_{60} thickness, with and without 1 nm LiF interlayer have been prepared.

 C_{60} (sublimed, 99,999%, CreaPhys GmbH) was evaporated (T = 355-380 C°, base pressure $5 \cdot 10^{-5} - 1 \cdot 10^{-6}$ mbar) with a deposition rate of 0.01 nm/s. For the samples with 1 nm C_{60} a lower deposition rate of 0.005 nm/s was chosen. A variation of the film thickness with d = 1, 2, 3, 5, 10, and 20 nm was prepared. The layer thickness has been controlled by a quartz crystal. For a second sample series, a thin layer (≈ 1 nm) of LiF has been evaporated between the perovskite and the C_{60} with a deposition rate of 0.005 nm/s without breaking the vacuum in between the LiF and C_{60} deposition.

The coverage and homogeneity of the layer growth, especially for such thin layer thicknesses in the order of the information depth of the applied PES techniques, is important to consider. Figure 3.14 shows secondary electron microscopy (SEM) cross sections of exemplary two layer thicknesses a) 3 nm and b) 20 nm. A layer thickness in the single digit nm range (especially, when the layer is not very conductive) is at the resolution limit of the used SEM. Thus, thin layer of 3 nm C₆₀ is difficult to resolve clearly. As far as it can be seen here, the C₆₀ forms an homogeneous coated thin layer on the perovskite and not clusters are observed. Note, that the diameter of a C₆₀ molecule is around 0.7 nm and thus



Figure 3.14: SEM images of the ITO/MeO-2PACz/CsMAFA/C₆₀ layer stack on glass with a nominal layer thickness of C₆₀ of (a) 3 nm and (b) 20 nm C₆₀ thickness. The self-assembled monolayer, MeO2-2PACz, is not visible in the image and thus noted in parentheses.

only several mono layers of the molecules form these very thin layers. A very slow evaporation rate is needed to ensure a well controlled layer thickness. The C_{60} thin film with 20 nm thickness is already well observable in the SEM picture with full and homogeneous coverage of the perovskite grains.

Each sample was transferred into the photoelectron spectroscopy (PES) vacuum setup using an inert transfer unit filled with dry, pure nitrogen and has hence not been exposed to ambient atmosphere at any time. PES measurements were started directly after transferring the samples into the vacuum system as soon as the necessary base pressure $(<10^{-9} \text{ mbar})$ was reached. For the measurement, the sample was electrically grounded by two metal contacts which were pressed onto the ITO (as indicated in Figure 3.13) at the edge of the sample, where the perovskite had been scratched off beforehand. The ITO substrate assists here for lateral charge transport and ensures that severe charging effects can be excluded.

Chapter 4

Indium tungsten oxide as hole selective contact for silicon heterojunction solar cells

Section 4.3 is based on the publication [127]:

<u>D. Menzel</u> and L. Korte.

Evolution of Optical, Electrical, and Structural Properties of Indium Tungsten Oxide upon High Temperature Annealing.

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Contribution of Dorothee Menzel: Experiment planning, sample preparation, measurement execution, data evaluation and interpretation, manuscript writing.

4.1 Introduction

In this chapter indium tungsten oxide will be investigated regarding its suitability as hole extraction layer for silicon heterojunction (SHJ) solar cells (see also section 2.3.3) and thereby replacing the standard (p)a-Si:H hole selective contact.

In our previously published study [88], the energy level alignment between (n)c-Si and IWO_x , covering the whole composition range from pure indium oxide to pure tungsten oxide was investigated. The obtained energy level alignment is depicted in Figure 4.1.

The work function of indium tungsten oxide mixtures can be varied from 6.25 eV for pure tungsten oxide over a range of 2 eV to 4.25 eV for pure indium oxide. Concomitantly, the band bending in the crystalline silicon at the IWO_x/(n)c-Si interface decreased from 600 meV to 400 meV. From this, the index of interface behaviour (see section 2.2.3) is determined to $S \approx 0.1$, which is in accordance with S reported in literature for crystalline



Figure 4.1: Energy level alignment of $InO_x/(n)c$ -Si compared to $WO_x/(n)c$ -Si. The work function (WF) and valence band maxima (E_V are obtained by He-UPS, while the band bending in the crystalline silicon was measured by SPV measurements. The band gap energy was determined from a Tauc-plot. The Figure is reprinted from Menzel *et al.* [88].

silicon [23]. With the large difference in work function of the (n)c-Si and the high work function tungsten oxide a significant dipole at the interface is formed.

It was found that the work function rapidly decreases from 6.25 eV for pure tungsten oxide to a level of around 4.5 eV already at an indium oxide fraction, C_{In} , of 40%, as it is also shown in Figure 3.10. Therefore, in further experiments, the focus of the investigated layers is on tungsten oxide rich mixtures. For a decent selectivity, and good hole extraction, two mechanisms need to inter play: First, the electrons need to be rejected by the interface and second, holes need to be extracted fast and without additional barriers by the IWO_x layer.

The rejection of electrons, generated in the crystalline silicon and reaching the interface is ensured by both the high band bending of 600 meV and the repelling interface dipole. Photogenerated holes on the other hand, should be extracted by a recombination based contact between the IWO_x conduction band to the (n)c-Si valence band. The energetic offset between the conduction band of WO_x and the valence band position in the inversion layer of (n)c-Si was found to be 580 meV. The band bending in the (n)c-Si is thus not high enough to directly contact the IWO_x conduction band and defect states in between are needed for an efficient hole extraction, as described in section 2.2.4, and also discussed e.g. by Battaglia *et al.* [131] or Gerling *et al.* [132].

In the present work, the density of occupied defect states at the (n)c-Si/IWO_x interface will be investigated by means of CFSYS and He-UPS (section 4.2). Afterwards a detailed investigation of the opto-electronic properties of IWO_x thin films upon high temperature annealing up to 700 °C will be presented (section 4.3) and finally the implementation of IWO_x as hole selective contact layer in SHJ solar cells will be discussed (section 4.4).

4.2 Density of occupied defect states in mixed indium tungsten oxide layers

In order to investigate the density of defect states in the band gap of co-evaporated IWO_x, thin films with different InO_x -fraction (C_{In}) have been deposited on float zone n-doped c-Si wafers according to the procedure, as described in section 3.4.1. They have been characterized by means of XPS in order to determine the indium oxide fraction in the mixture and further by means of He-UPS and CFSYS to investigate the density of defect states in the band gap region.

In Figure 4.2(a) and 4.2(b) the spectra of the valence band and band gap region for different C_{In} are compared, obtained by a) He-UPS and b) CFSYS. For the He-UPS measurements a selection of the sample set also used in ref. [88] is shown on a semilogarithmic intensity scale, and was corrected for the helium satellite excitation lines. The CFSYS spectra are measured in a separate sample series. Note, that the IWO_x film thickness is slightly different for both sample series with around 10 nm for the He-UPS measurements and around 20 nm for the CFSYS measurements. From both, He-UPS and CFSYS, for pure WO_x a low level of defect states is observed. With increasing C_{In} up to 14% a distinct defect band with a width of around 1 eV and located at -0.8 eV with respect to the Fermi level appears in the He-UPS spectra. For further increase of C_{In} over 18%, occupied states throughout the whole band gap can be seen. For pure indium oxide there are almost equally distributed states all over the band gap with a clear drop at the Fermi edge, as it would be expected for a metal. This is in accordance with the large metallic fraction found in indium oxide rich mixtures of IWO_x [88].

For a different series of C_{In} variation on (n)c-Si, also CFSYS measurements were conducted and are shown in Figure 4.2(b). As the work function strongly increases for higher WO_x fraction also the final state kinetic energy, which is set just above the SECO, had to be set accordingly at increasingly high values. To illustrate the limits of the measurement here, the incident photon flux of the Xe-lamp is shown in addition for the four different measurements. The increasing photon flux towards higher binding energies highlights the strength of CFSYS to investigate occupied states in the band gap with increasing photon flux, where usually a low density of states is expected. However, the photoelectrons, excited by the near-UV light need to overcome the sample work function in order to reach the analyzer and thus, for high work function materials, the range down to which the density of states can be traced by near-UV CFSYS is limited. If the ionization energy, hence the work function plus the valence band edge is too high, the valence band maximum cannot be observed. However, the DOS just below the Fermi level can still be accessed. For tungsten oxide the low defect density, as observed in the He-UPS measurement, can be verified. Only below -1 eV binding energy, the internal yield slowly starts to increase. However, as the photon flux in this regime is very low, there is a large



Figure 4.2: Valence band spectra of indium tungsten oxide with varying InO_c -fraction on a logarithmic yscale, obtained by (a) He-UPS and corrected for helium satellite lines, and (b) CFSYS. In panel (b) additionally the incident photon flux for the CFSYS measurement is shown with varying photon energy (right axis) spectra and incident photon flux for different indium oxide fraction in IWO_x on (n)c-Si, on a logarithmic yscale.

uncertainty on the actual internal yield, as the calibration is less accurate for such highly fluctuating and low photon fluxes. The almost metal-like DOS for pure InO_x is even more apparent in the CFSYS spectra than measured with He-UPS. For $C_{In} = 17\%$ and 28% the density of defects is at an intermediate level between both extreme compositions.

Hence, pure tungsten oxide might not supply enough defect states between the Fermi level and the valence band maximum of the (n)c-Si at the interface, which in combination with its low conductivity can make it unsuitable for the application as hole selective contact for (n)c-Si on its own. However, for small indium oxide fractions up to ~14%, the defect peak right below the Fermi level could indeed serve for an efficient trap assisted recombination. The density of occupied states being below the detection limit of He-UPS between -3 eV and -2 eV for $C_{\rm In}$ up to 14% could be further beneficial to suppress unintended non-radiative recombination at the interface.

4.3 Annealing of indium tungsten oxide up to 700 °C

From the PES results above, it can be concluded that simply co-evaporating the higher conductive and low work function InO_x with the low conductive and high work function WO_x significantly influences the density of occupied states in the band gap. However, we will also see at the end of this chapter that, in solar cells reaching reasonable efficiencies without strong extraction barriers is not possible with such as-deposited films. Therefore, in the following, for a range of different IWO_x compositions, deposited on glass-substrates, the evolution of the opto-electronic properties upon high temperature annealing will be investigated. The study of the material properties will be presented in four sections. First, the chemical composition will be discussed in order to find the exact stoichiometry of the co-evaporated samples. Afterwards the crystallization temperature as well as the crystal structure of the thin films will be analyzed, which leads to a deeper understanding of the film compositions. Last, optical and electrical properties of the indium tungsten oxide films and their potential application as material for carrier selective contacts will be evaluated.

4.3.1 Experimental annealing procedure

For the annealing study the eight samples with different compositions were heated sequentially from 200 °C to 600 °C in steps of 50 °C for 5 min on a high precision hotplate in ambient atmosphere in the dark. Two further annealing steps were conducted in a high temperature tube furnace with nitrogen atmosphere at 700 °C and 800 °C for 10 min. After every annealing step the samples cooled down to room temperature and were measured afterwards.

4.3.2 Chemical composition

In order to determine the exact film stoichiometry and the In-to-W ratio of the metal oxide mixtures, XPS was carried out directly after deposition, without breaking the vacuum. The XPS analysis was focused on the W4f and In3d core levels. A Shirley background was assumed for all core levels. The model used for fitting the W4f spectra consists of Voigt profiles, representing the doublet with spin orbit splitting of 2.12 eV and area ratio of 3:4 and the different oxidation states, 6+, 5+ and 4+ [133, 134]. The model for $\ln 3d_{3/2}$ consists of individual peaks for metallic indium (In), indium with oxidation state 3+ (In⁺³) and indium hydroxide species [135, 136] (In(OH)). For each core level, the full widths at half maximum for all individual peaks were constrained to be identical. For more detailed information about the fitting models, see also ref. [88]. The In and W fraction of the metal oxide mixtures were calculated using sensitivity factors obtained from WO_3 and In_2O_3 samples, which have been oxidized post-deposition by an oxygen plasma at 10^{-5} mbar for 10 min and were therefore considered as fully stoichiometric. The ratio of the metal peak area to the O1s peak area, each divided by the known number of the respective atom in the chemical formula of the metal oxide, was used as sensitivity factor. The sensitivity factors of 17.07 for In 3d and 3.83 for W4f were used in order to determine the fraction of InO_x in the mixture of indium oxide and tungsten oxide, $C_{\rm In} = A_{\rm In3d}/(A_{\rm In3d} + A_{\rm W4f})$, where A is the area of the respective core level normalized by the determined sensitivity factor. As already mentioned above, the aim is to keep the work function as high as possible. Since the work function of the mixture decreases from $6.3 \,\mathrm{eV}$ to $4.5 \,\mathrm{eV}$ for pure tungsten oxide and $\approx 50\%$ indium oxide fraction, respectively [88], the study is consequently focused on tungsten-rich layers.



Figure 4.3: XPS spectra of IWO_x thin films on glass with different indium oxide fraction, $C_{\rm In}$, in the mixture. A Shirley background was subtracted and the data was normalized with the sum of both, the In 3d and W 4f core level peak areas. To compensate for charging of the sample surface, the core level positions were shifted by the indicated $E_{\rm B}$ shift. The figure was reprinted from Menzel *et al.* [127].

The measured data, after subtraction of a Shirley background and normalized with the sum of the In 3d and W4f core level peak area, is shown in Figure 4.3. The data shown here is not yet weighted with the sensitivity factors. It can be observed that the binding energies of the same core level deviate up to 10.7 eV in between the different samples. The core level spectra might be shifted due to different reasons: a) The Fermi level position relative to the band edge changes, thus also the energetic distance of the core level to the Fermi level, $E_{\rm F}$ - $E_{\rm B,CL}$, in the "rigid bands" model, b) the sample surface gets charged, or c) the chemical state of the investigated materials changes. Here, glass substrates were used with no additional conductive layer on the substrate. For thin, non-conductive films, this is likely to lead to severe surface charging effects. Note, that the peak area, which is used to determine the layer composition, is not affected by this. To allow an easier visualization of peak area changes, the spectra in Figure 4.3 were shifted along the binding energy axis (shown as " $E_{\rm B}$ shift" in the graph). The core level position of the sample with 26% indium oxide fraction was set as an arbitrary reference point. The investigated layers cover the whole range from pure tungsten oxide to pure indium oxide with the intended closer spacing for high tungsten oxide fractions. For the layer with an indium oxide fraction of $C_{\text{In}} \approx 7\%$ the XPS spectra were accidentally measured with a larger step width (as visible from the plotted data points), and also with a shorter measuring time per spot. This is why the uncertainty of the stoichiometry for this layer is assumed to be much larger (10%) than for the other layers (5%). The uncertainty of 5% is reasonable for a quantitative determination of the composition by XPS, and results out of a plethora of origins,



Figure 4.4: (a) Grazing incidence XRD pattern of a pure WO_x thin film on glass with increasing annealing temperature, measured at room temperature. (b) Crystallization temperature, $T_{\rm C}$, of IWO_x with different indium oxide fraction, $C_{\rm In}$, in the mixture. $T_{\rm C}$ is obtained by the appearance of diffraction peaks in the XRD pattern, as exemplary shown in panel a). The figure was reprinted from Menzel *et al.* [127].

such as mean square deviation between raw data and fitted model or inhomogeneity in the layer itself, but also systematic errors introduced by uncertainties in the sensitivity factors.

4.3.3 Crystal structure

Next, the crystallization process of the indium tungsten oxide thin films will be investigated. First the crystallization temperature will be discussed and then the crystal structures after crystallization for different compositions of the layers will be analyzed.

As an example, Figure 4.4(a) shows the obtained XRD-patterns of the pure tungsten oxide layer for all post-annealed states. As deposited, the layer showed an amorphous structure, i.e. no diffraction peaks were visible in the pattern. After annealing at a temperature of T = 450 °C, this layer crystallized in the monoclinic crystal structure with the most intense diffraction peak at $2\theta \approx 24^{\circ}$. Since the annealing was conducted in steps of 50 °C, the actual crystallization temperature ($T_{\rm C}$) lies between 400 °C and 450 °C. This is in accordance with other studies, where temperatures of $T \approx 400 \,^{\circ}\text{C}$ were found for the crystallization of pure tungsten oxide [137]. All other IWO_x layers were analyzed in the same way and the resulting crystallization temperatures are shown vs. the indium oxide fraction, C_{In} , in Figure 4.4(b). The pure indium oxide phase crystallized at 200 °C, which is in accordance with other studies of In_2O_3 [138, 139]. The as-deposited indium oxide also showed slight indications of the presence of the known monoclinic In_2O_3 phase with a much less pronounced 222 peak; at 200 °C it is then fully crystallized. This might result from small crystallites, which form already during the deposition process. For the mixed oxide layers, the range of crystallization temperatures is divided into two parts. For layers with $C_{\text{In}} < 50 \%$, i.e. tungsten oxide rich mixtures, high crystallization temperatures of $T_{\rm C} = 450 \,^{\circ}\text{C}$ are observed and 500-600 $^{\circ}\text{C}$ for the layers with $C_{\rm In} = 7 \,\%$ and $C_{\rm In} = 41 \,\%$, respectively. For the three indium oxide rich layers with $C_{\text{In}} > 50 \%$, significantly lower crystallization temperatures of $T_{\rm C} = 200 \,^{\circ}{\rm C}$ to $250 \,^{\circ}{\rm C}$ are obtained. Since the passivation



Figure 4.5: Grazing incidence XRD patterns of IWO_x thin films on glass with varying indium oxide fraction, $C_{\rm In}$, after annealing at 700 °C. Also shown: diffraction patterns taken from the ICDD database [140]. The figure was reprinted from Menzel *et al.* [127].

quality of intrinsic amorphous silicon is very sensitive to temperatures above 200 °C, it can be concluded that tungsten-rich indium tungsten oxide in its unannealed amorphous state would only be suitable for application in (i)a-Si passivated silicon heterojunction solar cells.

It is important to understand whether the thin films form a phase composition with superposition of different mixed phases, or whether they segregate into pure phases. Therefore, the X-ray diffraction patterns after annealing at 700 °C are compared with the Powder Diffraction File (PDF) 4+ data base provided by the International Center for Diffraction Data (ICDD) [140]. Depending on the stoichiometry, three or four different phases can be found, as shown in Figure 4.5(a)-(d): Layers contain either a single phase, or they segregate into a combination of two phases, depending on C_{In} . Note, that the patterns are all normalized to their maximum intensity. For some layers, especially the one with $C_{\rm In} = 41$ %, the intensity was lower than for others, which is why in the normalized data the pattern appears more noisy than for others. Since the film thickness was similar for all layers between 19 and 30 nm this can be ascribed to a reduced fraction of crystallized material and a larger amorphous part in the thin film. According to the ICDD powder pattern, the resulting phases match the composition determined by means of XPS, as it can be seen in Figure 4.5. The monoclinic tungsten oxide phase (WO₃, space group P21/n, PDF 04-005-4272) appears in layers with $C_{\rm In} \leq 22 \%$. The layer with $C_{\rm In} = 26 \%$ crystallizes in the pure monoclinic indium tungstate phase $(In_2(WO_4)_3, space group P21/c, PDF)$ 04-007-5763), which also makes up a part of the layers with slightly lower ($C_{\text{In}} = 22 \%$) and



Figure 4.6: Crystallization diagram based on GIXRD measurements of thin film mixtures of IWO_x thin films on glass with varying indium oxide fraction, $C_{\rm In}$, in the mixture. The measurements were conducted at room temperature and the annealing was conducted in ambient conditions. The black dots indicate the chemical composition and the crystallization temperature, T_C, of the thin films. The coloured areas show the different obtained phases in the mixtures after crystallization. The figure was reprinted from Menzel *et al.* [127].

higher ($C_{\text{In}} = 41\%$) indium oxide fraction. For $C_{\text{In}} = 41\%$ a composition of two phases can be observed. The -204 and 115 diffraction peak of $\ln_2(WO_4)_3$ are still visible, where additionally two other reflexes appear at $2\theta = 31^\circ$ and $2\theta = 36^\circ$. Since the pattern of the rhombohedral hexaindium tungsten oxide phase (\ln_6WO_{12} , space-group R-3, PDF 04-007-6814) is very similar to the pure cubic indium oxide phase (\ln_2O_3 , space group I213, PDF 01-073-6440) it is hard to distinguish these phases with the low intensity obtained from the measurements of the thin films. One indication is the small peak close to 12-1 towards smaller angles which broadens the 12-1 peak as compared to the 222 peak of the pure indium oxide phase. However, the resolution at these low intensities is not sufficient to clearly distinguish these two phases in the pattern.

Richard *et al.* investigated powder samples of solid state reacted indium tungsten oxide mixtures and found four different phases: In_2O_3 , In_6WO_{12} , $In_2(WO_4)_3$, WO_3 [141]. Here, the thermally evaporated thin films crystallize in combinations of these phases and no additional phases could be detected from the XRD measurements. However, for $C_{In} > 50 \%$ it is not clear, if only In_2O_3 and no In_6WO_{12} is present, or if a combination of both phases is present in the layers. The tungsten oxide fraction in these mixtures either stays amorphous, or the W⁶⁺ ions partially substitute the In^{3+} ions in the crystal structure, which is conceivable due to their similar ionic radii of 0.74 Å and 0.94 Å.

In Figure 4.6 a tentative crystallization diagram, based on these observations is shown. Note, that the layers were annealed at T_{Anneal} first and then measured at room temperature. The data on which the crystallization diagram is based on, is obtained from the eight samples of this series, marked as black dots in Figure 4.6. Additionally, there might also appear the rhombohedral In₆WO₁₂ phase, which could not be resolved in the XRD pattern obtained in this series and is hence not indicated in the diagram.



Figure 4.7: Reflection (dashed lines) and transmission (solid lines) spectra for IWO_x thin films with varying indium oxide fraction, C_{In} , in the mixture: (a) after deposition, and (b) after annealing at 200 °C, (c) at 250 °C and (d) at 800 °C. The quartz glass substrate reference is shown as black line. The figure was reprinted from Menzel *et al.* [127].

4.3.4 Optical properties

In order to apply the IWO_x thin films on the front side of solar cells, a low optical absorption is necessary, since such parasitic absorption would lead to a current loss in the device. The reflection (dashed lines) and transmission (solid lines) spectra of the different mixtures of indium oxide and tungsten oxide are shown in Figure 4.7 for as-deposited (a) as well as annealed layers, with annealing temperatures of 200 °C (b), 250 °C (c) and 800 °C (d). The black curve in Figure 4.7 indicates the transmission and reflection of the bare glass substrate (Corning). The investigated layers all have a device relevant thickness of 19 to 30 nm. The reflection and transmission measurements were performed using a UV/VIS photospectrometer in a wavelength range from 250-1200 nm in steps of 5 nm.

In general, but especially for low annealing temperatures and as-deposited layers, a decrease in transparency (solid line) for increasing indium oxide fraction in the mixture over the whole wavelength range is observed. After annealing at 200 °C (Figure 4.7(b)) the poor transparency of the indium oxide rich layers between 350 nm and 1200 nm is already improved, whereas the mixed oxides as well as the pure tungsten oxide show almost no change. After 250 °C annealing (Figure 4.7(c)) the crystallization of the In₂O₃ phase is completed and the transparency in the lower wavelength range increases further. The same holds for the mixed oxide layers, which also show a further increased transmission. Note, that the tungsten oxide rich layers already show a high transmission for the as-deposited

amorphous thin films and only improve slightly. After complete crystallization (Figure 4.7(c), after 800 °C annealing), according to the XRD measurements, all layers similarly show a very high transparency.

The reflection data is shown as dotted lines. For the as-deposited layers, the reflection decreases with increasing indium oxide fraction. The reflection does not significantly change upon annealing up to an annealing temperature of 250 °C. With further increasing annealing temperature the reflection decreases, especially for the tungsten oxide rich layers.

In order to assess the applicability of indium tungsten oxide as a front contact in a solar cell, an estimate of the loss in short circuit current density due to parasitic absorption can be calculated. To that aim a stack of the glass substrate and the indium tungsten oxide layer on top is modeled using the software SpectraRay/3 by Sentech Instruments. The reflection and transmission data was fitted using Swanepoel's method [142] with a model of up to three Tauc-Lorentz oscillators and one Drude term. From the fitted extinction coefficient, the absorption coefficient was calculated. The resulting spectrally resolved absorption for a 10 nm thick layer was calculated, multiplied with the AM1.5g solar spectrum and integrated over the wavelength range of 280 to 1200 nm. A film thickness of 10 nm as the upper limit for application as carrier selective contact was assumed. This yields an upper limit of the possible loss in short circuit current density of c-Si solar cells by parasitic absorption for the given films and preparation conditions in the single pass limit. Figure 4.8 shows this equivalent $j_{\rm SC,loss}$ for films with different indium oxide fraction in dependence of the annealing temperature.

For as-deposited 10 nm thick indium oxide layers, applied as a front side layer on a solar cell, the short circuit current density might decrease by up to $j_{\rm SC,loss} = 3.2 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ due to parasitic absorption in the indium oxide. Increasing the tungsten oxide fraction, leads to a strong decrease of parasitic absorption to $j_{\rm SC,loss} \approx 0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ for the layers with $C_{\rm In}$ of 53 % and 64 %. The four mixtures with $C_{\rm In} = 7$ %, 22 %, 26 % and 41 % show a slightly higher $j_{\rm SC,loss}$ of around $j_{\rm SC,loss} = 0.7$ -0.9 mA cm⁻². As-deposited, the pure tungsten oxide shows the lowest $j_{\rm SC,loss}$.

Now, considering the parasitic absorption after annealing the layers, the pure tungsten oxide does not change significantly up to $T_{\rm Ann} = 700$ °C. For all other layers the short circuit loss is decreased significantly by the first annealing steps, at $T_{\rm Ann} = 200-250$ °C. For high indium oxide fraction, this is probably due to the crystallization of the indium oxide rich phases. Since the tungsten oxide rich phases only crystallize at higher temperatures, the decrease of $j_{\rm SC,loss}$ cannot result from crystallization of the main phase. Instead, the improved transparency might be due to further oxidation of the initially slightly understoichiometric layers, as shown in section 4.3.2. For an annealing temperature of 200 °C, as it will be applied for the solar cells in section 4.4, a $j_{\rm SC,loss}$ of $0.2 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ is found for WO_x and $2.2 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ for InO_x. As the assumed layer thickness here is around twice the actual layer thickness in section 4.4, the observed decrease in $j_{\rm SC}$ from $34.4 \,\mathrm{mA}\,\mathrm{cm}^{-2}$



Figure 4.8: Estimated loss in short current density, $j_{SC,loss}$, due to parasitic absorption in IWO_x thin films for varying indium oxide fraction in the mixture and versus the annealing temperature. The estimate was obtained by modelling the absorption coefficient to reflection and transmission data, assuming an IWO_x layer thickness of 10 nm, and front side application on a solar cell with AM1.5G spectrum. The figure was reprinted from Menzel *et al.* [127].

to $33.2 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ is in good agreement with the estimations, elaborated here. For higher annealing temperatures than 250 °C, all mixtures show a low parasitic absorption, which would make them in principal suitable for application on the front side of solar cells. Since high annealing temperatures might be critical in a combination with other, more temperature sensitive layers, it is an advantage of the tungsten oxide rich layers, that their parasitic absorption is at a low level even in the as-deposited state and for low annealing temperatures. Compared to the standard p-type amorphous silicon hole-selective contact for silicon heterojunction solar cells, this low parasitic absorption on the front side can be a large advantage: Holman *et al.* determined the loss in short circuit current for a 10 nm thick (p)a-Si:H layer to be about 1.6 mA cm⁻² [143]. Hence, about 1.4 mA cm⁻² might be gained in j_{SC} by replacing the a-Si:H selective contact with a thin layer of indium tungsten oxide.

4.3.5 Conductivity

The lateral conductivity of the thin films with mixtures of indium oxide and tungsten oxide will be further analyzed in order to investigate whether mixing the tungsten oxide with the more conductive indium oxide or an annealing step can increase the conductivity of the pure tungsten oxide. In Figure 4.9 it can be seen, that the conductivity for the tungsten oxide containing mixtures in the as-deposited state is at least about three to four orders of magnitude lower than the conductivity of the pure indium oxide. The lower limit of the



Figure 4.9: Lateral conductivity, in dependence on the annealing temperature of the thin films. $T_{\rm C}$ indicates the crystallization temperature of the layer, determined by XRD (Figure 4.4). Conductivity was measured at room temperature after the annealing steps. The figure was reprinted from Menzel *et al.* [127].

measurement is at $\sigma = 10^{-6}$ S cm⁻¹, due to the internal resistance of the measurement setup. Only for three of the eight layers, i.e. with $C_{\rm In} = 100\%$, 22% and 26%, a measurable conductivity could be obtained with $1.2 \cdot 10^{-2}$, $3.4 \cdot 10^{-6}$ and $4.0 \cdot 10^{-6}$ S cm⁻¹, respectively. The mixed oxide layers with $C_{\text{In}} = 7 \%$, 41 %, 53 % and also the one with the highest indium oxide fraction $(C_{\text{In}} = 64 \%)$ are not conductive enough for this measurement method. The difference in composition from pure indium oxide to $C_{\text{In}} = 64\%$ is quite high, however, the main gain in terms of applicability as hole selective contact (high work function) is observed for $C_{\rm In} < 40\%$ [88], which makes the indium rich stoichiometries less interesting for the application as charge selective contact. The pure indium oxide shows an overall increasing conductivity up to $0.39 \,\mathrm{S \, cm^{-1}}$ after annealing at 700 °C. For $T > T_{\rm C}$ the pure tungsten oxide also shows an increasing conductivity of up to $1.6 \cdot 10^{-4} \,\mathrm{S \, cm^{-1}}$, while the conductivity of all mixed oxide layers stays below $10^{-6} \,\mathrm{S \, cm^{-1}}$. Table 4.1 shows the measured specific conductivity, σ , for three different compositions (pure indium oxide, pure tungsten oxide and $C_{\text{In}} = 22 \%$) and two different annealing states (as-deposited and after annealing for 10 minutes at 700 °C). From these results the specific resistivity, ρ , can be calculated. For a layer with $10 \,\mathrm{nm}$ thickness, which is a relevant assumption for an application as charge selective contact in solar cells, also the series resistance contribution, $R_{\rm s}$ is estimated. Note, that additionally, for a real layer stack, the contact resistance needs to be taken into account. The series resistance of the pure indium oxide in both annealing states, as-deposited and after 700 °C, is negligible compared to other contributions in series resistance in a solar cell. Contrary to that the as-deposited indium tungsten oxide mixture with $C_{\rm In} = 22\%$ shows a significant $R_{\rm s}$ contribution, so a trade off would need to be found in terms of layer thickness and a still functional hole selective contact. For the crystallized pure tungsten oxide the $R_{\rm s}$ contribution is again negligible. However, these films require an annealing step at at least 450°C, as it was shown above.

	$T_{\rm Ann}$	InO _x	$C_{\text{In}}=22\%$	WO_x
Thickness [nm]		27	21	19
$\sigma \left[\text{S cm}^{-1} \right]$	as dep.	$1.2 \cdot 10^{-2}$	$3.4 \cdot 10^{-6}$	-
	$700^{\circ}\mathrm{C}$	0.39	-	$1.6 \cdot 10^{-4}$
$\rho \left[\Omega \cdot \mathrm{cm} \right]$	as dep.	81	$3.0.10^{5}$	-
	$700^{\circ}\mathrm{C}$	2.6	-	$6.4 \cdot 10^{3}$
$R_{\rm s}\left[\Omega\right]$	as dep.	$8.1 \cdot 10^{-5}$	0.3	-
	$700^{\circ}\mathrm{C}$	$2.6 \cdot 10^{-6}$	-	$6.4 \cdot 10^{-3}$

Table 4.1: Measured conductivity, σ and specific resistance, ρ of indium oxide, tungsten oxide and a mixed indium tungsten oxide with an indium oxide fraction C_{In} of 22%. Calculated nominal series resistance contribution, R_{s} for an assumed layer thickness of 10 nm for three different compositions in the as deposited (as dep.) state and after annealing at 700 °C.

4.4 Implementation of indium tungsten oxide as hole selective contact in SHJ solar cells

The evaporated indium tungsten oxide mixtures were further investigated in order to replace the (p)a-Si as hole selective contact in the complete layer stack of SHJ solar cells as depicted in Figure 4.10(a). The experimental procedure is described in section 3.4.2. The indium oxide fraction, $C_{\rm In}$, was varied in the indium tungsten oxide mixture and the obtained IV-characteristics for different $C_{\rm In}$ under standard test conditions (25 °C, 1000 Wm⁻²) are shown in Figure 4.10(b).

For all compositions a severe S-shaped behaviour of the IV-curve is observed, which indicates insufficient charge carrier collection, most likely due to a poorly working rectifying contact and strong extraction barriers at the IWO_x contact. The band bending induced in the (n)c-Si substrate can be obtained by a surface photovoltage experiment. Hereby, the sample is illuminated with a short laser pulse (905 nm, 150 ns), which excites excess charge carriers in the silicon, an thus reduces the band bending by accumulating charge carriers until (almost) flat-band conditions are reached. This directly translates into a difference of the measured surface photovoltage (SPV) in a metal-insulator-semiconductor structure (see e.g. the work of Korte [53] for more details). With assuming flat band conditions in the illuminated case, the difference in SPV between the dark and the illuminated case equals the band bending in dark conditions. The band bending of the herein presented solar cells (thus including the (i)a-Si:H passivating layer) was measured before the deposition of the ITO and is shown in Figure 4.10(c). For pure WO_x it is significantly lower as compared to the direct interface of (n)c-Si/IWO_x, which was as high as 594 meV [88]. The maximal band bending is observed for $C_{\rm In} = 16 \%$.

The performance parameters of the IV-characteristics are shown in Figure 4.10(d) - (g). The short circuit current density, $J_{\rm SC}$, decreases from 34.4 to 33.2 mA cm⁻² for increasing $C_{\rm In}$, indicating an enhanced parasitic absorption in the IWO_x, which is in agreement with the results discussed in section 4.3. It is found that the composition which shows the highest SPV (thus band bending), also yields the highest $V_{\rm OC}$, *FF* and PCE. However,



Figure 4.10: (a) Schematic layer stack of the SHJ solar cells with indium tungsten oxide replacing the (p)a-Si:H hole selective contact. (b) IV-characteristic for different indium oxide fraction in the mixture of IWO_x under standard test conditions. (c) Surface photovoltage amplitude measured on (n)c-Si/(i)a-Si:H/IWO_x. (d)-(g) Obtained IV-parameters from the IV-characteristics shown in (b).

as the pure tungsten oxide shows the highest work function of the whole composition range, also the highest band bending would have been expected here, but was observed differently. The fill factor follows the trend of the measured SPV with the highest value of 59%. The strong S-shaped IV-characteristics also clearly influences the $V_{\rm OC}$, which reaches a maximum of 657 mV, yielding an over all PCE of 13.3% for an indium oxide fraction of 16% in the IWO_x mixture. As no reference cell with (p)a-Si instead of IWO_x as hole contact was fabricated in this batch, possible losses related to the back side cannot be excluded. However, the strong correlation between the SPV and the *FF* indicates, that indeed the low *FF* is a result of poor selectivity at the front side.

To investigate, whether the origin of the reduced band bending, measured for the pure tungsten oxide, as mentioned above, could result from an insufficient WO_x thickness, the thickness of pure WO_x in the same layer stack as above was varied from 3.2-8.5 nm. Thereby, a high band bending of over $570 \,\mathrm{meV}$ was already reached for $3.2 \,\mathrm{nm}$ WO_x and did not increase for higher thickness. However, the FF increased from 45% for $3.2\,\mathrm{nm}$ WO_x to 50 % for 8.5 nm WO_x and so did the V_{OC} increase from 454 meV to 522 meV. Thus, even though the maximum band bending was already reached, further increasing the WO_x thickness was beneficial for the device efficiency, even though the IV-characteristics were still very poor in general, especially with a very low fill factor. Hence, for pure tungsten oxide, even though a high band bending is achieved, the absence of defect states (section 4.2), serving as recombination center for the recombination based contact might make it unsuitable here. For mixed oxide layers, there are defect states observed in the band gap, which could facilitate the charge carrier transport, but still severe S-shaped IV-characteristics are observed. We have seen in section 4.3.5 that the mixed IWO_x thin films show a very low conductivity, which in combination with the lower band bending as compared to tungsten oxide rich layers could be the reason for the observed extraction losses.

Furthermore, for WO_x and MoO_x, it was found that they form a thin interfacial silicon oxide layer, when they are directly deposited on amorphous or crystalline silicon, leading to substoichiometric compositions of the metal oxide layer close to the interface [144, 145]. For tungsten oxide, this native thin SiO_x layer stays stable up to 500 °C and forms an intermixed zone with the silicon at higher temperatures [144]. On the one hand, if the (uncontrolled) thickness of the interfacial silicon oxide exceeds typical tunnel distances for charge carriers, this can lead to an additional extraction barrier [146]. On the other hand, the substoichiometric tungsten oxide shows a lower work function, which also reduces the band bending in the crystalline silicon [78]. This was found similarly for MoO_x, when applied as hole selective contact for SHJ solar cells on both c-Si and a-Si substrates [145]. Thus, instead of using (i)a-Si as a passivation layer, one path to a promising application of IWO_x could be to combine it with a thin SiO_x passivation layer instead. A controlled saturation of the surface with oxygen in addition to a good defect passivation, might enable a stoichiometric growth of even very thin tungsten oxide rich IWO_x layers. With this a higher band bending in the (n)c-Si could be reached and simultaneously the low conductivity would be less detrimental. For other high work function metal oxides such as MoO_x a defined growth of a SiO_x passivation layer has already been shown to yield promising results, by enabling a stoichiometric growth and lower contact resistances [147]. This could further allow for very thin tungsten oxide layer thickness, making the low conductivity less detrimental. Mixing the high work function tungsten oxide with low amounts of indium oxide below around 10 %, could then additionally be beneficial by introducing a defect band close to the Fermi level, and hence forming traps to assist the recombination contact.

4.5 Chapter summary

In this chapter, the suitability of indium tungsten oxide (IWO_x) as hole selective contact for SHJ solar cells and its opto-electronic properties upon high temperature annealing up to 700 °C have been investigated.

The energy level alignment of $IWO_x/(n)c$ -Si, especially the band bending induced by the high work function tungsten rich mixtures, can be varied by manipulating the indiumto-tungsten ratio in the mixture by thermal co-evaporation [88]. Here, the defect density at the interface was investigated by means of He-UPS and CFSYS. It was found, that the defect density close to the Fermi level of pure tungsten oxide is below the sensitivity limit of CFSYS, which is of the order of 10^{15} cm⁻³eV⁻¹. This might hinder the trap assisted recombination contact to (n)c-Si. With the addition of small fractions of indium oxide up to 14%, a distinct defect peak at -0.8 eV below the Fermi level was observed, while between -2 eV and -3 eV binding energy, the density of states was below the detection limit of He-UPS. For higher indium oxide fractions, the large amount of metallic indium led to occupied states equally distributed all over the band gap.

With the aim to improve the opto-electronic properties of the IWO_x mixtures, their structural, optical and electrical properties were investigated upon high temperature annealing up to 700 °C, spanning the composition range from pure indium oxide to pure tungsten oxide. Layers containing less than 50 % indium oxide showed crystallization temperatures of $T_{\rm C} = 400-600$ °C, while for layers with more than 50 % indium oxide $T_{\rm C} = 200-250$ °C was found. Optical reflection and transmission as well as the electrical conductivity were measured at room temperature after each annealing step. An estimate for the loss in short current density due to parasitic absorption was calculated, assuming a device relevant film thickness of 10 nm. The high parasitic absorption of up to $3.2 \,\mathrm{mA}\,\mathrm{cm}^{-2}$ for as-deposited indium oxide was found to decrease with increasing tungsten oxide fraction, and with increasing annealing temperatures. Layers with up to around 50 % tungsten oxide, as well as all layers annealed above 250 °C showed low parasitic absorption with

estimated photocurrent losses $< 0.5 \,\mathrm{mA}\,\mathrm{cm}^{-2}$. Even though the initial motivation was to increase the conductivity by adding highly conductive indium oxide to the lowly conductive tungsten oxide, this could not be demonstrated for the mixed oxide layers. Their conductivity stayed mostly below the lower measurement limit at $\sigma = 10^{-6} \,\mathrm{S}\,\mathrm{cm}^{-1}$, which restricts their application as charge carrier selective contact to a very thin layer thickness.

The attempt of introducing the co-evaporated IWO_x layers as hole selective contacts instead of (p)a-Si in a SHJ solar cell structure with thin intrinsic amorphous silicon passivation was presented. However, simply increasing the fraction of the more highly conductive InO_x in the IWO_x is not sufficient to ensure a well working hole selective contact with good selectivity and conductivity. A pronounced s-shaped IV-characteristics was obtained for all investigated compositions, with an indium oxide fraction of 16% being the most promising composition by yielding a power conversion efficiency of 13.3% but a poor fill factor of only 59%. Both, the low band bending (for high InO_x -fraction) and the low conductivity (for high WO_x fraction) limit the hole extraction and thus the fill factor. Further, for pure WO_x , a high band bending might still not enable a good charge extraction as the trap densities between the c-Si valence band and the WO_x conduction band, required for the recombination contact, are too low.

However, here, the IWO_x mixtures were only investigated in a layer stack, with an (i)a-Si passivation layer, which can lead to the formation of an interfacial silicon oxide layer [144], and with this to substoichiometric tungsten oxide close to the interface with a lower work function [78]. One promising path for a successful implementation of IWO_x as hole selective contact would thus be to use very tungsten oxide rich layer compositions in combination with a thin SiO_x passivation layer [148]. This could enable the stoichiometric growth with high work function, which allows for thinner layers and thus reduced losses in series resistance. A low indium oxide fraction in the mixture up to 10% could ensure the necessary trap states for the recombination contact, while maintaining a high work function of over 5.5 eV.
Chapter 5

Valence band structure and defect density of halide perovskites

This chapter is based on the publication [128]:

<u>D. Menzel</u>, A. Tejada, A. Al-Ashouri, I. Levine, J. A. Guerra, B. Rech, S. Albrecht and L. Korte.

Revisiting the Determination of the Valence Band Maximum and Defect Formation in Halide Perovskites for Solar Cells: Insights from Highly Sensitive Near-UV Photoemission Spectroscopy.

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Contribution of Dorothee Menzel: Experiment planning, measurement execution, data evaluation and interpretation, manuscript writing.

The polylogarithmic fitting model was developed by Jorge Andres Guerra and Alvaro Tejada, the script for the modelling was written by Alvaro Tejada, while the actual modelling was conducted in collaboration of Dorothee Menzel and Alvaro Tejada.

The investigated samples in this chapter, were prepared by Amran Al-Ashouri.

5.1 Introduction

Despite strong interest and notable achievements in optimizing halide perovskite (HaP) absorber materials as well as the charge-selective contact layers, a detailed understanding of the energetics (band edge energies, band alignments) at surfaces and interfaces is still an area of ongoing research. For such materials UPS is a well-established tool to investigate electronic properties such as the work function and the energy position of the valence band maximum (VBM), i.e. quantities which determine in a first approximation the band line-up and charge carrier redistribution upon the formation of electronic interfaces. However,

conventional UPS with He-I excitation at 21.2 eV is of very limited use when it comes to the characterization of occupied defect states in the band gap, between the VBM and Fermi energy. Standard UPS is only capable of measuring a density of states (DOS) 2-3 orders of magnitude lower than the valence band DOS, which is not sufficient to detect typical defect densities in the band gap of HaPs. Additionally, very careful analysis is needed to correct for existing satellite lines [60]. Due to the characteristically low DOS of HaPs at the VBM [149], the correct evaluation of the valence band edge is particularly difficult. Occupied trap-states in the band gap have been observed before, e.g. by Zhang *et al.* [150] and Wu *et al.* [151] using conventional He-UPS. However, the resolution is limited and a quantification not easily achievable.

Here, by applying near-UV PES with excitation energy of 4-7 eV in UPS and constant final state mode, on the one hand the probing depth can be increased and on the other hand the noise floor is orders of magnitude below the one of typical helium based UPS as elaborated in the methods section 3.1.5. In literature only few studies using near-UV PES on HaPs are found, but the very first ones already demonstrate those advantages, by using such light sources with an excitation energy up to 8 eVs. for NUPS [151–153]. Recently, it further has been shown that such near-UV PES with varying excitation energies from 3.8 eV to 7.7 eV is a powerful technique, capable of probing very low densities of gap states in bromide-rich wide band gap mixed halide perovskites [154]. Here additionally, the observed defects are quantified and several valence band edges can be resolved by an advanced model of two parabolic band edges in one angle integrated spectrum.

In the first part of this chapter, the chemical composition of the herein investigated triple cation triple halide perovskite (CsMAFA) will be discussed (section 5.2). Afterwards the state of the art modelling of the VBM of metal halide perovskites will be revised and a new approach for modelling the DOS of the the valence band edge will be proposed (section 5.3). This model will be used to quantify and compare the reproducibility and reliability of CFSYS measurements (section 5.3.3) as well as the influence of different precedent illumination conditions, short exposure to air (< 10 min), and two weeks vacuum storage (section 5.4).

The perovskite was spin-coated on a layer stack of glass/ITO/MeO-2PACz/CsMAFA with a precursor composition of $Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$. The experimental procedure is described in section 3.4.3.

5.2 Chemical composition of CsMAFA

X-ray photoelectron spectroscopy was performed, in order to investigate the chemical composition of the CsMAFA perovskite. Detail spectra of the most prominent core levels for four different, but nominal identically processed samples are shown in Figure 5.1(a)-(e) for comparison. The intensity is normalized relative to the area of the Pb $4f_{5/2}$ core



Figure 5.1: XPS core level spectra of four nominally identical CsMAFA layers (Sample 1 to Sample 4) in a layer stack of glass/ITO/MeO-2PACz/CsMAFA and modelling results of (a) $I3d_{3/2}$, (b) Pb $4f_{5/2}$, (c) N 1s, (d) C 1s and (e) Br 3d. A linear background was assumed for all spectra and already subtracted in the shown data. Reprinted with permission from Menzel *et al.* (supporting information) [128]. Copyright 2021 American Chemical Society.

level to account for slight variations in intensity within the sample series and compare peak areas in between samples. The fitting was performed using the software fityk [56]. A linear background was assumed for all spectra. For each core level the FWHM was set to be the same within all samples. For $I3d_{3/2}$, Pb $4f_{5/2}$ and N 1s the peak position was a free fitting parameter. Similarly, for C 1s and Br 3d the overall binding energy position was used as free fitting parameter, whereas the second (or third) component was fixed to the same distance relative to the position of the first one for all samples.

The resulting fitting parameters for all components are listed in Table 5.1. The C 1s core level model consists of three main components, where the first one at the lowest binding energy represents C–(C,H) bonds (at $\approx 283.8 \text{ eV}$), the second one represents C–N bonds at 1.29 eV higher binding energy and the third one represents C–O–C bonds with 3.8 eV higher binding energy relative to the C–(C,H) peak position [155, 156]. The resolution of these core level spectra is not high enough for any more advanced modelling including any further bonds. However, a clear indication of C–O–C bonds on the surface of the CsMAFA is observed. Hence, the sample handling in gloveboxes, i.e. in inert nitrogen atmosphere, does not entirely prevent the sensitive film surface from a minor oxidation. The Br 3d core level consists of the two doublet components 3/2 and 5/2 with a peak area ratio of 2:3. The binding energy is in good agreement to the Br–Cs bond [157, 158]. The spin orbit splitting was set as free fitting parameter and resulted in 1.04 eV, which is in accordance with literature [155], and shows that even though the resolution is rather poor for some of the core levels, they can still serve for a rough comparison.

Core level	Sample	$E_{\rm B}$ [eV]	FWHM [eV]	Area [Counts s ⁻¹]	Assigned bond
L 3d3/2	1	629.89	1.40	1557.3	I-Ph
	2	630.03	1.40	1340.7	I–Pb
	3	630.11	1.40	1465.9	I–Pb
	4	630.24	1.40	1390.2	I–Pb
Pb 4f5/2	1	142.44	1.16	437.5	Pb–I
,	2	142.55	1.18	403.8	Pb–I
	3	142.61	1.18	406.8	Pb–I
	4	142.76	1.17	389.1	Pb–I
C 1s	1	283.67	1.77	17.5	C-(C,H)
	2	283.83	1.77	30.9	C - (C, H)
	3	283.78	1.77	17.0	C - (C, H)
	4	283.99	1.77	12.2	C - (C, H)
C 1s	1	284.96	1.17	10.5	C–N
	2	285.12	1.17	2.3	C–N
	3	285.06	1.17	2.0	C–N
	4	285.27	1.17	3.6	C–N
C 1s	1	287.47	1.17	24.7	C-O-C
	2	287.63	1.17	20.9	C–O–C
	3	287.57	1.17	22.1	C-O-C
	4	287.78	1.17	18.9	C–O–C
Br 3d5/2	1	67.64	1.22	27.0	Br–Cs
	2	67.70	1.22	32.3	Br–Cs
	3	67.79	1.22	25.1	Br–Cs
	4	67.90	1.22	27.5	Br–Cs
Br $3d3/2$	1	68.67	1.22	17.8	Br–Cs
	2	68.73	1.22	21.3	Br–Cs
	3	68.82	1.22	16.5	Br–Cs
	4	68.93	1.22	18.1	Br–Cs
N 1s	1	399.76	1.31	84.1	(C=O)-N-C
	2	399.89	1.31	73.5	(C=O)-N-C
	3	399.97	1.31	82.0	(C=O)-N-C
	4	400.12	1.31	75.2	(C=O)-N-C

Table 5.1: XPS Fitting results of four nominally identical CsMAFA layers (Sample 1 to Sample 4) in a layer stack of glass/ITO/MeO-2PACz/CsMAFA. The resulting binding energy position, full width at half maximum (FWHM), the peak area and the assigned bond are listed for the respective sample and core level.

N 1s core level model consists of one single component corresponding to N–C bonds with a binding energy around 400 eV. The Pb 4f core level here can be fitted with one single peak of Pb $4f_{5/2}$ corresponding to the Pb²⁺ oxidation state at $E_B \approx 142.5 \text{ eV}$ [157, 159]. No additional component indicating PbI₂ (at higher E_B) or Pb⁰ (at lower E_B) was found to be present. Similarly, $I3d_{3/2}$ could be fully described with one peak corresponding to Pb–I bonds, located at $E_B \approx 630 \text{ eV}$ [155, 160].

A slight shift of the spectra can be observered, where relative to sample 1, the other samples are shifted by roughly 0.1, 0.2 and 0.3 eV for sample 2, 3 and 4, respectively, as also indicated by the dotted lines in Figure 5.1. Since for the evaluation of the valence band region further down in this chapter, it will be possible to refer to the measured Fermi edge, the shift does not in general hinder the comparison in between the samples. The overall signal intensity is rather low for the N1s, C1s, and Br3d core levels, thus no detailed quantitative analysis is shown here. Note, that the excitation cross sections of the specific elements are not considered and hence no atomic ratios are given. The doublet peak area of the core levels with only one j-component fitted can be easily calculated by the known area ratio of d and f orbitals and the values shown in Table 3.1. The resulting doublet peak area ratio of I3d compared to Pb 4f is found to be around ≈ 3.88 , which is in accordance with other XPS studies of comparable HaP-compositions [155]. Sample 2 however, shows a slightly lower iodine-to-lead ratio, which might be due to loss of the rather volatile MAI and could indicate starting degradation of the perovskite during the measurement. However, no Pb⁰ component is visible in the Pb 4f core level detail spectra in Figure 5.1(b), which would be an indication for strong degradation of the investigated layer [159, 161]. It is important to keep in mind, that all XPS measurements were conducted after the He-UPS, NUPS and CFSYS valence band spectroscopy. A damage of the perovskite film by X-rays and/or vacuum storage can be expected as it is found in various other studies as summarized by Béchu *et al.* [18]. As it will be shown later in this section, X-rays indeed induce an elevated density of defect states in the band gap, even though no Pb⁰ could be detected by means of XPS.

5.3 Modelling of the valence band edge in metal halide perovskites

Determining the energetic position of the VBM for HaPs is not straightforward and remains widely discussed in the community [60, 149, 162]. Angle resolved PES (ARPES) measurements as well as DFT calculations of the dispersion relation of MAPbI₃ point to a strong dispersion of the energetically highest valence bands [103, 152]. Thus, when measuring angle integrated PES, it is challenging to correctly account for the very low DOS at the VBM, which is not located in the center of the Brillouin zone, but at the R-point in reciprocal space [103, 152, 163]. There are two main evaluation methods to obtain the VBM from valence band spectra measured by UPS found in literature: It is usually determined from the intercept of linear extrapolations of the leading edge of the energetically highest valence band feature and of the noise level, either a) on a linear $(E_{V,Lin})$, or b) on a semi-logarithmic $(E_{V,Log})$ scale. The former is the traditional approach for materials like Ge or GaAs [164], which is also applied e.g. for the evaluation of the valence band position of indium tungsten oxide in chapter 4. The latter one was first proposed by Endres et al. to account for the low DOS at the valence band onset [149]. This method circumvents the unphysically high values for the distance of the VBM to the Fermi level, which sometimes even exceeds the known optical band gap, when using method (a). On the other hand, Yang et al. found that, by using method (b), the energetic position strongly depends on the applied UPS excitation energy [152]. They state that using method (a) on spectra recorded at the M-point and adding a fixed energetic distance to the R-point, known from DFT calculations, leads to the most reliable results.

CHAPTER 5. VALENCE BAND STRUCTURE AND DEFECT DENSITY OF HALIDE PEROVSKITES



Figure 5.2: Example for the VBM evaluation for CsMAFA on glass/ITO/MeO-2PACz/ substrate. The spectra are shown on a linear (blue, right, bottom) and a semi-logarithmic (red, left, top) scale with the intensity of (a)the He-UPS and the internal yield of (b) NUPS and (c) CFSYS spectra normalized. The He-UPS spectrum was further corrected for satellite lines. The red and blue shaded areas indicate the data fitting regions used for the fits on the semilogarithmic or the linear scale, respectively. Reprinted with permission from Menzel *et al.* [128]. Copyright 2021 American Chemical Society.

5.3.1 Comparing different UV-PES modes

Both evaluation methods (intercept between linear fit and noise on either linear or semi-log scale, here $E_{\rm V,Lin}$ and $E_{\rm V,Log}$, respectively) are compared in Figure 5.2(a)-(c) for three different PES methods.

Extrapolating the DOS on a semi-logarithmic scale gives greater weight to the characteristically low DOS at the VBM (which in HaPs is found to not be located at the origin of the Brillouin zone) and therefore also leads to energetically higher VBM positions. Zu *et al.* compared ARPES measurements with angle integrated He-UPS measurements supported by DFT calculations on a MAPbI₃ single crystal. They evaluated the valence band spectra on a linear scale at different points in the Brillouin zone. Comparing them with VBM positions extracted on a semi-logarithmic scale from angle integrated UPS on thin films, they find good agreement between both methods [163]. However, as discussed in more detail below, this exponential tail is caused by the specific shape of the dispersion relation between the highest VBM and the lower lying bands in the valence band region.

Figure 5.2(b) and (c) show the VBM measured with NUPS and CFSYS (on the same sample as Figure 5.2(a), and exemplary fits on a linear (right) and semi-logarithmic (left) scale, similar to the He-UPS evaluation. Indeed, as also found by He-UPS, a long exponential tail over roughly two orders of magnitude can be observed, but by decreasing the detection limit using NUPS and CFSYS, it is revealed that the noise level of He-UPS intersects with this low DOS at an arbitrary energetic position. However, it is obvious that a consistent determination of the energetic position of the VBM should not depend on the measurement technique, as also suggested by Yang and Yang [152]. Additionally, the modelling of the noise itself by an exponential function is not justified by any physical reason. Comparing the results on the linear and the semi-log scale, more consistent values in between the different measurement techniques by fitting on a linear scale are found, as also observed by Yang and Yang [152].

It can be seen that, as the signal-to-noise ratio increases from the He-UPS to NUPS and CFSYS, $E_{\rm V,Log}$ approaches the Fermi level. Measured with He-UPS (and corrected for satellite lines), the valence band maximum is found at $E_{\rm V,Log} = -1.19 \,\mathrm{eV}$. With NUPS, and thus intermediate signal-to-noise ratio, $E_{\rm V,Log} = -0.81 \,\mathrm{eV}$ is found and using CFSYS yields by far the energetically highest VBM position at $E_{\rm V,Log} = -0.68 \,\mathrm{eV}$. With a perovskite band gap of 1.63 eV the latter one would indicate a slight p-type character of the surface. Evaluated on the linear scale, the deviation between the fitted VBM positions is much smaller with $\approx 150 \,\mathrm{meV}$ in between the different measurement techniques. Comparing both evaluation methods on a linear and semi-logarithmic scale for CFSYS, a difference of 850 meV is found which is quite tremendous and would result in completely different interpretations of the doping-type of the material.

The same trend can be observed for four different, but nominally similar processed samples, with a slight variation of the Fermi-level position in the band gap, which will be discussed in section 5.3.5.

In practice, the arbitrarily defined $E_{V,Log}$ found by evaluating He-UPS on the semilogarithmic scale matches quite well with E_V obtained by ARPES [163]. However, the mentioned inconsistencies demonstrate clearly that a more elaborated modelling of the valence band maximum including a physical interpretation of the fitted parameters is required and one possible method will be discussed in the next section.

5.3.2 Combined modelling of the valence band edge and exponential band tail

The strong dispersion and *soft* onset of the valence band signal in UPS spectra measured on HaPs [149] requires careful modelling of the valence band region. To this end, here a model initially published by Guerra *et al.* [165, 166] for optical absorption measurements is adapted to describe the DOS of the valence band, measured by CFSYS. It assumes parabolic band edges and their energetic fluctuation due to varying local disorder. Structural and/or dynamic disorder induces exponential band tail states, also known as Urbach tails, which are observed in the band edge of all materials. The inverse of the exponential slope is defined as the Urbach energy, in agreement with universally observed Urbach rule [167]. In He-UPS measurements on HaPs, a similar exponential region has been found at the top of the valence band region [149, 163]. Since there are fundamental differences between optical absorption measurements and near-UV PES methods, a more general parameter to describe the slope of this exponential tail caused jointly by the structural disorder and integration of the dispersion relation over the whole Brillouin zone, $E_{\rm t}$, is defined. The model function as in equation 5.1 describes the density of occupied states, $N_{\rm OCC}$, in dependence of the binding energy, $E_{\rm B}$, and is based on a 1/2-degree polylogarithm function, ${\rm Li}_{1/2}$, with only three fitting parameters: the valence band edge ($E_{\rm V,PLog}$), the inverse slope of the exponential band tail ($E_{\rm t}$), and an arbitrary amplitude scaling parameter (a_0),

$$N_{\text{OCC}}\left(E\right) = -\frac{a_0}{2}\sqrt{E_{\text{t}}} \operatorname{Li}_{\frac{1}{2}}\left(-\exp\left(\frac{E + E_{\text{V,PLog}}}{E_{\text{t}}}\right)\right)$$
(5.1)

Note, that such parameterizations of the valence band/tail region are often divided in two separate equations, being the assumed linear valence band edge and the exponential Urbach tail [168]. The model describes both, the parabolic and band tail region consistently in one single equation, without relying on arbitrary continuity conditions to join the two. For binding energies far below the valence band edge, $E \ll E_{V,PLog}$, it reproduces the conventional models for a square root DOS in the valence band, and for $E >> E_{V,PLog}$ an exponential tail into the band gap. See Guerra *et al.* in ref. [165] for a more detailed mathematical discussion of the model. The measured spectra were modelled with a linear combination of 1) two Polylogarithm functions $N_{OCC,1} + N_{OCC,2}$, each according to Equation 5.1 representing two parabolic band edges and corresponding to two different parabolic VBM in reciprocal space, which will be elaborated in the discussion section. $E_{\rm V,PLog,Low}$ and $E_{\rm V,PLog,High}$ then describe the respective valence band maxima and their amplitudes are fitted independently of each other. Here, $E_{\rm t}$ of both valence bands, are assumed equal since both parabolic band edges experience the same fluctuation broadening. 2) Three Gaussian functions (as commonly assumed for localized defect bands [169]) are used for modelling the occupied gap states in the band gap. All three defect bands are assumed to have the same FWHM, while the energetic position, $E_{\rm Di}$, and the amplitude $a_{\rm Di}$ were free fitting parameters. The fitting parameter of the defect amplitude can easily be converted into the area under the Gaussian by

$$A_{\rm Di} = a_{\rm Di} \cdot FWHM \cdot \sqrt{\frac{\pi}{4 \cdot \ln\left(2\right)}}.$$
(5.2)

Those two general parts of the model are convoluted with the Fermi distribution at 298 K with $E_{\rm F}$ also as a free fitting parameter with an upper limit of $+0.2 \,\mathrm{eV}$ relative to the reference Fermi level $E_{\rm F,ITO}$. However, for some samples, a reliable fit of the Fermi edge to the measured data is not possible, even though it is included in the model: For samples with low defect densities, the gap state density at the Fermi-edge is close to the detection limit and can thus not always be fitted consistently. Occasionally, the fit converges to modelling the drop of the DOS, which is actually attributed to the Fermi edge, instead



Figure 5.3: CFSYS spectrum of a CsMAFA layer on glass/ITO/MeO-2PACz/ in a selected energy region around the Fermi level of the contacted substrate $E_{\rm F,ITO}$. The Fermi edge was modelled with a sigmoidial Boltzmann function and the edge position is considered as the electron Fermi level at the surface $E_{\rm F}^*$. Reprinted with permission from Menzel *et al.* (supporting information) [128]. Copyright 2021 American Chemical Society.

as the high-energy side of the defect Gaussian D3. Therefore, additionally a sigmoidial Boltzmann function was fitted to the Fermi edge (as shown in Figure 5.3) and the obtained values are reported as $E_{\rm F}^{*}$ and used as consistent reference position.

For the least-square fitting routine of the combined model to the measured DOS by CFSYS, the instrumental broadening needs to be considered, which is ensured by the convolution of the model function with the instrument transfer function, which was evalaborated in detail by Korte [53].

5.3.3 Modelling of CsMAFA valence band region by combined polylogarithmic model

The large spread in E_V values obtained by the two conventionally applied modelling approaches in literature as described in section 5.3.1 calls for a reliable model to describe the valence band structure and to consistently quantify the energetic position of the respective band edges, which is presented in the following section by using the model described in section 5.3.2.

Figure 5.4(a) shows an exemplary valence band DOS of a CsMAFA thin film, measured by CFSYS. The model introduced above is used to describe the density of occupied states, N_{OCC} , and fitted to the measured internal yield. The model basically consists of a polylogarithm function (blue line, *VBM*, *PLog*, *High*) and trap states, modeled tentatively by three Gaussian functions (D1-D3). These peaks only serve to extend the modelled DOS into the band gap and to include the trap states in the model in a physically meaningful way. For the sake of completeness, the modelled parameters are shown in the appendix (Appendix A.1). The data here is normalized to the amplitude scaling parameter of the respective band edge, a_0 . Note, that the actual N_{OCC} (red line) is broadened by the transfer function of the PES setup, resulting in the convoluted DOS (black line). As mentioned above, the model assumes parabolic band edges, which lead to a square root energy dependence of the N_{OCC} , in combination with an exponential band tail described by the slope parameter E_t .



Figure 5.4: Internal yield of CsMAFA on glass/ITO/MeO-2PACz/ and measured by CF-SYS. Modelling of the highest observed valence band edge(s) by (a) one parabolic band edge $(E_{\rm V,PLog,High})$ with an exponential tail (slope = $1/E_{\rm t}$), jointly described by a polylogarithm (PLog) function and (b) two PLog functions belonging to two different transitions in k-space. The gap state density is modelled by three Gaussian functions. The data was fitted with this model DOS convoluted with the instrumental broadening of the PES set-up, and $E_{\rm V,PLog,High}$ is chosen as the origin of the energy axis. Reprinted with permission from Menzel *et al.* [128]. Copyright 2021 American Chemical Society.

For $E \ll E_{V,PLog,High}$ the measured data clearly exceeds the modelled DOS. This is accounted for by a second polylogarithm function as shown in Figure 5.4(b), which can be attributed to the next lower VBM in the dispersion relation. Further, the (unoccupied) conduction band is indicated as a guide to the eye by adding another polylogarithmic function at an energetic distance of 1.63 eV corresponding to the optical gap as measured by UV-Vis spectroscopy, and with a tail parameter of 15 meV and thus close to the Urbach energy.

The Urbach energy can be evaluated by a linear fit on a semi-logarithmic scale of the sub-bandgap absorption measured by various methods, which are usually based on optical spectroscopy. Metal halide perovskites typically show low Urbach energies below 16 meV [170]. For the herein used composition 15.5 meV was found by measuring external quantum efficiency (EQE) [130] and 14.3 meV by calculating the absorptivity from photoluminescence (PL) following a procedure by Ledinský *et al.* [170]. To justify the suitability of polylogarithmic model for quantifying the band tail slope, additionally the absorption calculated from the complex refractive index, \tilde{n} , measured by spectroscopic ellipsometry (SE) and spectral transmittance was fitted, with the same polylogarithm model as by Guerra *et al.* [165]. A tail-parameter of $E_{\rm U} = 15.3$ meV was found, here representing the Urbach energy, which again, is in good agreement with the previously mentioned methods [128]. In previous studies on hydrogenated amorphous silicon, it has been shown, that CFSYS serves as reliable method to quantify the Urbach energy, yielding values in good agreement with literature [169].

However, the band tail slope, $E_{\rm t}$, which is fitted to the CFSYS data is around 40-50 meV and hence over three times higher compared to the Urbach energy measured by sub-bandgap absorption spectroscopy methods.

There are three principal differences of those methods compared to NUPS and CFSYS which need to be considered when comparing both tail parameters: i) PES is very surface sensitive, while both EQE and PL are averaging over the bulk of the HaP films. Disorder and defect states at the surface are expected to be enhanced compared to the bulk [171], which can be expected to result in an increased Urbach energy as measured by PES; ii) the energetic resolution of optical measurements is usually better than the herein used electron energy analyzer resolution of 125 meV. Although this is considered for the modelling, the broadening by the analyzer increases the uncertainty especially for very steep tails [53]; iii) For the CFSYS measurements, the sample has not been exposed to any ambient air and was measured under ultra-high vacuum conditions, whereas most optical spectroscopy measurements are recorded in ambient air. In the section 5.4 it will be shown, that on the one side even short exposure to ambient air affects the sample surface, such that the actual valence band structure is smeared out and E_t strongly increased. On the other side, also degradation and enhanced trap state densities upon vacuum storage are observed. As the bulk of the film is expected to be less affected by the exposure to air or vacuum than the surface, the comparison between PES and the optical methods is not straight-forward and deviations between E_t and E_U need to be expected.

5.3.4 Attribution of valence band maxima to different k-vectors

In literature, several DFT studies of the dispersion relation for MAPbI₃ single crystals can be found [103, 163, 172]. The angle resolved DFT calculations by Shirayama *et al.* on MAPbI₃ single crystals [103] here assist as an approximated reference to the experimental data, despite the fact, that the obtained dispersion relation will deviate from the one of the herein used perovskite composition. Philippe *et al.* compared DFT calculations for CH₃NH₃PbI₃ and CH₃NH₃PbBr₃ and showed that the uppermost valence bands are dominated by I-related states, whereas the Br-related valence band states are found to be at lower binding energies [172]. Since for the more complex crystal structure of mixed metal-halide perovskite, no comparable studies are published so far, a comparison to CH₃NH₃PbI₃ is the only option. According to Shirayama *et al.*, the highest valence band has a global maximum at the R-point in reciprocal space and a second local maximum towards lower binding energies at the M-point with an energetic distance of $0.32 \,\text{eV}$.

The two main transitions that are observed here in the measured data, and which are modeled by the two polylogarithm functions can be attributed to two different valence band edges, according to the respective parabolic VBM in the dispersion relation. While the attribution of $E_{\rm V,PLog,High}$ to the R-point is reasonable since no energetically higher



Figure 5.5: CFSYS spectrum of a CsMAFA layer on glass/ITO/MeO-2PACz/ (Sample 1) compared to integrated ARPES data on MAPbI₃ as published by Zu *et al.* [163], which was shifted by +1.48 eV on the x-axis and normalized the internal yield on a semi-logarithmic scale (left) and a linear scale (right). Reprinted with permission from Menzel *et al.* (supporting information) [128]. Copyright 2021 American Chemical Society.

VBM with significant DOS is measured by CFSYS, the lower VBM with an energetic distance of around -0.38 eV cannot be assigned with certainty. As in both DFT [103] and angle resolved PES (ARPES) [163] the energetically next lower VBM of MAPbI₃ in the dispersion relation is found at the M-point, one could speculate that also for CsMAFA the energetically lower VBM can be attributed to the M-point.

The fact, that here indeed the very highest VBM is observed is further supported by ARPES measurements on MAPbI₃ performed by Zu *et al.* [163], who quantified the VBM at the R-point by a linear extrapolation of the spectrum recorded at the R-vector and found $E_{\rm V,Lin,R} = -1.41 \, \rm eV$. When aligning their ARPES data to the herein measured CFSYS spectrum (see Figure 5.5), the modelled $E_{\rm V,PLog,High}$ is found 70 meV below $E_{\rm V,Lin,R}$ evaluated by Zu *et al.* and is thus in very good agreement, additionally considering that a slightly different material is investigated.

In angle-integrated PES on spin-coated HaPs thin films, where the small crystallites are oriented in arbitrary directions, the detected photo electrons in general originate from the whole Brillouin-zone [18]. In case of any preferential orientation, the different k-vectors might not be weighted equally and suppress or enhance emission in certain directions. While the attribution and correlation to the DFT calculated DOS needs to be taken very carefully, the fact of observing two separate VBM with an energetic distance of around 0.38 eV, resulting from different points in the Brillouin zone can be stated more confidently.

All PES measurements are carried out under illumination, namely by the UV light or X-rays used to excite the measured photoelectrons. In decent photovoltaic absorbers such as our HaPs, this should lead to both, a) a splitting of the quasi Fermi levels (QFLS), and b) a change of band bending due to charge redistribution in the perovskite arising from a combination of inhomogeneous depth profiles of photogeneration, recombination and charge extraction at contacts. Specifically, in the herein investigated sample structures, photoelectrons are emitted on the front, and holes are extracted through the rear contact. The surface Fermi level which is modeled, $E_{\rm F}^{*}$, is then the quasi Fermi level of the electrons under measurement illumination conditions: $E_{\rm F}^{*} = E_{\rm F,n,front}$. The induced QFLS under the specific illumination conditions during the near-UV PES measurements and the resulting SPV will be further discussed in the evaluation of the CsMAFA/C₆₀ contact in chapter 6 in section 6.4.1, where also the QFLS is illustrated in Figure 6.7. Since the rear contact is a very efficient hole extraction layer, as evidenced both by high solar cell fill factors [17] and in direct measurements [130], a relatively flat quasi Fermi level of the holes throughout the perovskite film can be assumed, thus $E_{\rm F,ITO,back} \approx E_{\rm F,p,rear} \approx E_{\rm F,p,front}$. Thus, $E_{\rm F,ITO} - E_{\rm F}^{*}$ is equal to the QFLS between $E_{\rm F,p}$ on the back of the perovskite film and $E_{\rm F,n}$ on its front, i.e. it is the surface photovoltage under these specific illumination conditions [173]. With $E_{\rm V,PLog,High} = -1.41 \,\mathrm{eV}$ relative to the surface quasi Fermi level and a band gap of 1.63 eV (also indicated by the sketch of the conduction band, which should not be surprising in a highly efficient photoabsorber under illumination.

However, the observed difference of $E_{\rm F,ITO}$ - $E_{\rm F}^{*}$ is much less compared to the expected QFLS, which is in the order of several hundreds of meV under these illumination conditions. Thus, a significant drop of $E_{\rm F,n}$ from the illuminated bulk to the surface in combination with a downwards band bending needs to be present. Considering the large amount of defects created under the illumination and the vacuum conditions, affecting the perovskite's surface, such a drop due to recombination at these defects is easily conceivable. It is important to note, again, that actually the Fermi edge of the electrons, $E_{\rm F}^{*}$, is observed while in conventional He-UPS measurements, this edge is not visible because it is below the noise floor. Therefore, $E_{\rm V}$ from He-UPS is usually reported on the binding energy scale, thus relative to the contact's Fermi level (in this case, this would be $E_{\rm F,ITO}$ on the rear of the sample), which can lead to an unrecognized SPV as a result of quasi Fermi level splitting. Indeed, in some He-UPS measurements, the sample is illuminated with very low photon fluxes in order to minimize this effect as well as changes in band bending [174]. Importantly, SPV and changes in band bending might also occur in other PES measurements, which could be a reason for the widely observed "n-type"-character of the surface of HaPs [173] as well as other inconsistencies e.g. when comparing parameters extracted from XPS and UPS measurements which use very different illumination, thus charge generation conditions.

To sum up the discussion of the modelling approach: It was shown that, with a higher resolution and lower detection limit, two distinct valence band edges can be observed. Different to conventional angle integrated He-UPS, CFSYS can trace the DOS of the very highest VBM, assumed to be at the R-point in reciprocal space from DFT on the similar HaP MAPbI₃. The ad-hoc evaluation method of a linear extrapolation on a semilogarithmic scale has been shown to strongly depend on the detection limit and thus an advanced model was adapted to consistently quantify the VBM. Thus, near-UV highresolution PES can assist to better understand the valence band structure of complex multi-cation multi-halide perovskites. Knowing which band edge exactly is experimentally probed by He-UPS and either calculating the energetic distance of the highest VBM to the measured one with the support of DFT calculations, or experimentally determining the energetic distance (e.g. by a method with a low noise floor such as CFSYS) seems to be the most exact approach for determining the Fermi level position in the band gap (as also suggested by Yang and Yang [152]). However, if no high sensitivity PES such as CFSYS is available, support by precise DFT calculations for each specific material might be necessary to assess the position of the highest VBM with high confidence. However, these are very demanding for complex multi cation and multi halide perovskites.

5.3.5 Reproducibility of CsMAFA with similar sample history

After discussing in detail the energetic positions of an exemplary sample, here four samples with the very same sample history and precursor composition, produced in different batches or even within the same batch yield slightly different results. The respective XPS measurements have already been discussed in section 5.2. The obtained fitting parameters for four different, but nominally identical CsMAFA layers are summarized in Table 5.2. Note, that all samples are in the condition of "after NUPS", since they have all been illuminated with 6.5 eV for around 15 min, in order to record the NUPS spectrum, to set the final state kinetic energy to the best value for each sample.

Sample	Precedent	$\Delta E_{\rm V,PLog}$	$E_{\rm V,PLog,High}$	$E_{\rm F}^{*}$	$E_{\rm t}$	D_{it}	D_{it}
	condition	, ,	$-E_{\mathrm{F}}^{*}$	$-E_{\rm F,ITO}$			
		[eV]	[eV]	[eV]	$[\mathrm{meV}]$	[rel. to a_0]	$[\mathrm{cm}^{-3}]$
1	NUPS	0.37	-1.41	0.03	43	$1.5 \cdot 10^{-4}$	$7.9 \cdot 10^{16}$
2	NUPS	0.39	-1.50	0.13	48	$1.8\cdot10^{-4}$	$9.2\cdot10^{16}$
3	NUPS	0.38	-1.42	-0.12	44	$3.8\cdot10^{-4}$	$2.0\cdot 10^{17}$
4	NUPS	0.36	-1.37	-0.17	41	$1.3\cdot 10^{-4}$	$6.8\cdot10^{16}$
Mean	NUPS	0.38(1)	-1.43	-	44(3)	$2(1) \cdot 10^{-4}$	$1.1 \cdot 10^{17}$

Table 5.2: Obtained fitting parameters for four different CsMAFA layers with nominally identical processing history. The defect density, D_{it} per volume unit is estimated by normalization based on DFT calculations for MAPbI₃.

The energetic position of the highest detectable valence band edge, $E_{\rm V,PLog,High}$, with respect to the surface Fermi level, $E_{\rm F}^{*}$ varies from -1.37 eV to -1.50 eV with a mean value of -1.43 eV. The distance from $E_{\rm V,PLog,High}$ to $E_{\rm V,PLog,Low}$ is consistently about 0.36-0.39 eV. The calculated distance between $E_{\rm V,R}$ and $E_{\rm V,M}$ for MAPbI₃ taken from literature, is found to be around 0.32 eV [103, 152], thus slightly below these experimentally found values, which are for CsMAFA. This can be attributed to the different composition of the samples.



Figure 5.6: Valence band edge of a CsMAFA layer on glass/ITO/MeO-2PACz/ (Sample 2) obtained be He-UPS and corrected for satellite lines on a semi-logarithmic scale (left) and a linear scale (right). The spectrum was modelled with one polylogarithmic, function as described in the main text. It represents the energetically lower parabolic valence band edge, $E_{\rm V,PLog,Low}$, as compared to the modelling of CFSYS data. Reprinted with permission from Menzel et al. (supporting information) [128]. Copyright 2021 American Chemical Society.

As an example, the He-UPS spectrum of Sample 2 was additionally modelled with the polylogarithm function used for the CFSYS modelling and is shown in Figure 5.6. Because of the higher noise level only the energetically lower VBM can be modelled and no measurement induced broadening is considered. For $E_{\rm V,PLog,Low}$ an energetic position of -1.9 eV relative to the substrate Fermi level and a band tail parameter of $E_{\rm t} = 167 \,\mathrm{meV}$ was obtained. The large tail parameter is partially due to the instrument broadening not being considered and partially due to the hidden VBM, which here cannot be resolved. As $\Delta E_{\rm V,PLog} = 0.39 \,\mathrm{eV}$ is known from the CFSYS modelling, $E_{\rm V,PLog,High} = -1.51 \,\mathrm{eV}$ can be estimated and is in very good agreement with the values obtained by modelling the CFSYS data.

To summarize, the situation for this or closely related materials appears to be as follows: in He-UPS only the region between the very highest and the next lower VBM is visible, whereas the actual VBM itself and an eventual disorder related Urbach tail are hidden below the noise floor. This, in turn, may lead to the extraction of $E_{\rm F}$ - $E_{\rm V}$ values which are larger than the band gap, which are clearly unphysical. In contrast CFSYS clearly reveals the VBM, with a square-root shape as expected from theory for a parabolic band edge.

Turning now to the Fermi level position relative to the substrate Fermi level ($E_{\rm F,ITO}$ - $E_{\rm F}^{*}$) a shift of up to 300 meV in between the samples is observed. This however is not attributed to inconsistent modelling, but to a shift of the whole spectrum relative to $E_{\rm F,ITO}$, which can be attributed to three main reasons:

1. During the measurement, the samples are illuminated by UV-light. Charge carriers that are photogenerated during the measurements lead to a splitting of the quasi Fermi levels, which results in a surface photovoltage (SPV), i.e. a potential difference between the Fermi level positions at the top and the bottom of the layer stack. In fact, the situation is similar to a solar cell with the HaP film as the absorber, being held close to open circuit conditions. (Not exactly at $V_{\rm oc}$ conditions, however, since there is a small current flow due to the photoemitted electrons, balanced by the extraction of holes at the SAM/ITO rear contact. These holes then recombine with electrons supplied through the sample contact. This leads to a charge carrier imbalance across the film, thus a photovoltage. Since these non-intended charge separations happen to a different extent for every sample, also a slightly different SPV $\neq 0 \text{ eV}$ is expected. As it will be shown in chapter 6, the effect of SPV is greatly enhanced once an electron selective layer is applied to the front side and charges can accumulate in that layer [175].

- 2. Positive charging of the surfaces might occur when photoelectrons are generated at a higher rate than the corresponding states can be refilled by electrons from the sample contact. This leads to a shift of the spectrum towards lower binding energies. From the evaluation of the Pb 4f and I 3d peak position of the XPS spectra, a slight charging was indeed observed with 0.1 - 0.3 eV for samples 2 - 4 compared to sample 1, which is shown in section 5.2. Since the charging (observed in the core levels with XPS illumination) does not directly correlate to the observed shifts of E_V on the binding energy scale (observed in the VB region with UV illumination) and, at least for sample 4, is even larger than the observed deviation of the surface Fermi level, it cannot be the only reason.
- 3. The sample surface condition can be different between samples for a variety of reasons. First the processing history, including the solution mixing, spin coating timing, minor changes in the atmosphere surrounding the sample and the sample transfer influence the surface conditions of the respective sample [18]. Also other mechanisms, such as the usage of DMSO in the solvent mixture of the perovskite are discussed in literature to induce surface trap-states [150], which influence the Fermi level position in the band gap due to charge redistribution between bands and gap states ("Fermi level pinning"). Additionally, the measurement-induced degradation due to UV-light leads to increased defect densities, which will be discussed in section 5.4.

Since all these physical reasons (charge carrier generation and separation, charging and Fermi level pinning) shift the spectrum along the binding energy axis, thus relative to $E_{\rm F,ITO}$, it is not possible to distinguish the exact underlying mechanism. However, the alignment to the modelled $E_{\rm F}^*$ is at least free of the first two, while still a slightly different Fermi level relative to the band edge can be explained by different sample surface conditions.



Figure 5.7: CFSYS spectrum of a CsMAFA layer on glass/ITO/MeO-2PACz/ compared to the density of states (DOS) as obtained by DFT calculations for MAPbI₃ by Shirayama and co-workers [103]. Both were modelled with the polylogarithm model as describes in the main text and aligned to the energetically highest valence band edge. The amplitude scaling parameter of the CF-SYS model fit, a_0 , is scaled to match the one of the calculated DOS at $5.13 \cdot 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$. Reprinted with permission from Menzel et al. (supporting information) [128]. Copyright 2021 American Chemical Society.

The slope of the exponential tail, quantified by the tail parameter $E_{\rm t}$, varies from 41 meV to 48 meV for the four measured samples. The true value might be slightly lower, because the obtained values are at the limit of the energetic resolution with this experimental setup. The shape of the DOS in the valence band should be consistent in between different samples and only shift relative to $E_{\rm F,ITO}$, as elaborated above.

With the low detection limit of CFSYS it is possible to measure and even quantifying the density of occupied states above the modeled band edges, $D_{\rm it}$, using a convolution of the gap states DOS modeled as three Gaussian functions (D1-D3), multiplied with the Fermi distribution and convoluted with the instrument transfer function. There is explicitly no physical interpretation of the nature or total number of defect bands provided. Relative to the amplitude scaling parameter, a_0 , belonging to $E_{\rm V,PLog,High}$, the defect density varies from $1.3 \cdot 10^{-4}$ to $3.8 \cdot 10^{-4}$ with a mean value of $2.1 \cdot 10^{-4}$. Since the measured internal yield is directly proportional to the density of occupied states, assuming a similar excitation cross section over the whole spectral range, a rough estimate for the density of occupied gap states per volume unit by normalizing the internal yield to a known DOS at a defined position can be obtained.

5.3.6 Normalization of internal yield to DOS in volume units

Since the measured internal yield is directly proportional to the density of occupied states in units of eV^{-1} cm⁻³, assuming a similar excitation cross section over the whole spectral range, a density of occupied gap states per volume unit can be estimated by normalizing the internal yield to a known charge carrier density at a defined position. Shirayama *et al.* calculated the effective density of states in the valence- and conduction bands for MAPbI₃ by means of DFT [103].

Considering the volume of the unit cell $V = 250.3 \cdot 10^{-24} \text{ cm}^{-3}$, as obtained by the lattice

parameters provided in the publication and assuming a cubic unit cell, the charge carrier density per eV and volume unit can be calculated from the DFT data. The data from Shirayama *et al.* [103] is shown in Figure 5.7. By fitting one poly-logarithmic function according to equation 5.1, however without considering any measurement induced broadening, the amplitude a_0 of the energetically higher valence band ("VBM, PLog, High") is found to be $a_0 = 5.13 \cdot 10^{20} \text{ cm}^{-3} \text{ eV}^{-1}$, which is used for rescaling the internal yield from CF-SYS and should be considered as an approximation. Note, that this normalization is thus based on MAPbI₃, while for the herein presented data CsMAFA is investigated. Further, and very importantly, for the determination of the density of defect states with respect to the valence band DOS, a constant matrix transition element was assumed, which may not be the case for the photon energies used (3.6 - 7.3 eV).

The effective density of states (for MAPbI₃ $N_V \approx 2.5 \cdot 10^{18} \text{ cm}^{-3}$ [176]) can be approximately considered as the integrated DOS from the valence band edge down to the valence band edge plus $k_B T$ [177]. As a proof of concept, it was found that $N_V/k_B T$ roughly matches the DOS the internal yield was normalized to, shown as the small arrow in Figure 5.7.

The obtained density of occupied trap states of the four CsMAFA samples varies between $6.8 \cdot 10^{16} \,\mathrm{cm}^{-3}$ and $2.0 \cdot 10^{17} \,\mathrm{cm}^{-3}$ with a mean value of $1.1 \cdot 10^{17} \,\mathrm{cm}^{-3}$.

Note, that these estimated defect densities are very high considering the high PCE in solar cells obtained with this exact material. Indeed, a combination of several factors may lead to an overestimation of the defect densities found here $(10^{16} - 10^{17} \text{ cm}^{-3})$ compared to those reported in literature $(10^{13} - 10^{16} \text{ cm}^{-3})$ [178–181] for high-quality polycrystalline $MAPbI_3$ and CsFAMA films: i) Depending on the measurement method (e.g. for deep level transient spectroscopy [179] or time-resolved microwave conductivity [180]) the defect density is estimated from modelling recombination processes, which provide an indirect way of determining the defect density also including assumptions about the capture cross section; it can be speculated that even though the defect states are present in the material in the amounts we report on here, their charge carrier capture cross sections could be lower than assumed in the electrical measurements. Thus they would not contribute strongly to trap-assisted non-radiative recombination in the working device; ii) the assumption of a constant matrix element in the studied photon energy range $(4 - 7 \,\mathrm{eV})$ might be invalid, and the matrix element decreases significantly as the photon energy increases, implying that the signal in the defect region is "amplified" with respect to the signal originating from the VB [177]; Note, that the excitation cross sections for extended (VB) states and localized (defect) states might differ; iii) the obtained defect densities are only relevant to the surface region, and the actual amount in the bulk is much lower [171]; and iv) the actual surface density is further strongly influenced by a variety of sample conditions as well as the measurement itself, which will be discussed in the next section.



Figure 5.8: CFSYS spectra of CsMAFA on a layer stack of glass/ITO/MeO-2PACz/ for different sample histories: (a) and (d) with two sequential CFSYS scans, (b) and (e) after measurements with varying illumination (NUPS, He-UPS, XPS), (c) and (f) after two weeks of vacuum storage and < 10 min exposure to ambient air. (a) - (c) are the spectra as measured and aligned to the lower valence band edge, $E_{\rm V,PLog,Low}$; (d) - (f) show the measured internal yield minus the two modeled valence bands. Here, the modeled Fermi level $E_{\rm F}^*$ is used as origin of the energy axis. Reprinted with permission from Menzel *et al.* [128]. Copyright 2021 American Chemical Society.

5.4 Defect generation in CsMAFA upon sample illumination and handling

The exact shape of the valence band DOS and especially the defect density crucially depends on the specific sample history. In this section, those changes upon different illumination conditions and sample handling, e.g. such as transfer and storing conditions precedent to CFSYS measurements are investigated. In Figure 5.8(a) - (c) the spectra of the internal yield for different sample histories are shown. The most important resulting modelling parameters are summarized in Table 5.3 and supplementary parameters and full spectra are shown in the Appendix A.2. Additionally, the residuals of the measured data minus the two polylogarithm functions in Figure 5.8(d) - (f) are plotted on the binding energy scale relative to the surface Fermi level, $E_{\rm F}^{*}$. The area below these residuals is a direct measure of the occupied defect density per volume unit in the band gap, and is modeled by the defect peaks D1-D3.

5.4.1 Influence of near-UV Irradiation on the defect density in CsMAFA

First, the influence of the near UV irradiation during UPS and CFSYS measurements on the valence band region and on defect generation in the band gap is assessed.

In Figure 5.8(a), the internal yield spectra of two sequential scans obtained from a typical CsMAFA layer (Sample 2 from the previous section) aligned to the modelled $E_{\rm V,PLog,Low}$ are shown. Usually, the sample is first illuminated for the NUPS measurement for 15 min with a photon energy of 6.5 eV, which is necessary to find a suitable final state kinetic energy for the CFSYS measurement. For each CFSYS scan the UV-illumination time is 60 min with photon energies varying from 3.7 eV to 7.3 eV. Considering the fitting results in Table 5.3 the high DOS valence band positions ($E_{V,PLog,High}$ and $E_{V,PLog,Low}$) are not affected by this prolonged near-UV irradiation. In contrast, the slope parameter decreases and the defect density in the energy region of $E - E_{\rm F}^{*} = -0.6 \, {\rm eV}$ up to the Fermi energy increases with illumination time (see also Figure 5.8(d)). The decrease of the slope parameter can be attributed to a change in the energetic position of D1, which is a free parameter of the fit: if D1 shifts towards the valence band edge, it includes more states in the exponential band tail region, which thus can decrease the slope parameter slightly. Considering Peaks D1-D3, between the 1st and 2nd CFSYS scan, the total density of gap states is significantly increased from $1.8 \cdot 10^{-4}$ to $4.6 \cdot 10^{-4}$ relative to $a_0 (9.2 \cdot 10^{16} \text{ to})$ $2.4 \cdot 10^{17} \,\mathrm{cm}^{-3}$). However, this is partially attributed to a fitting artifact due to the shift of D1 towards the valence band edge. Considering only D2 and D3, which can be fitted reliably since they are not influenced by the valence band parameters, the increase of the combined gap state density in these peaks is slightly lower with $2.4 \cdot 10^{-5}$, from $2.3 \cdot 10^{-5}$ to $4.8 \cdot 10^{-5}$ relative to a_0 and thus around $1.2 \cdot 10^{16}$ cm⁻³, and can indeed be attributed to defect generation during the near-UV illumination, induced by the measurement.

To investigate the dynamics of the formation of those trap states upon illumination with less pre-assumptions from the advanced modelling of the whole spectrum, CFSYS in a very small photon energy range (4.9 eV to 5.0 eV) was measured repeatedly on a previously not illuminated area of the sample, directly after the transfer into the vacuum system.

In order to investigate the defect formation kinetics a small range CFSYS measurement with a photon energy of 4.9 eV to 5 eV was performed before any other illumination of the sample, hence also before the spectrum shown in 5.9(a). The result is shown in 5.9(b): Immediately after starting the illumination, gap states start to increase by about half an order of magnitude and saturate at an internal yield of $Y_{\rm IN} = 2.5 \cdot 10^{-12} \, {\rm eV^{-1}}$. By considering the entire spectrum, recorded afterwards and the according modelling this can be attributed to a DOS of $3.3 \cdot 10^{16} \, {\rm cm^{-3} \, eV^{-1}}$ after 20 min illumination time.

Figure 5.9(a) shows the valence band spectrum of sample 4 in dependence of the photon energy, which is directly convertible to the binding energy.

Since all other samples experienced initially 15 min of UV irradiation, the formation



Figure 5.9: (a) Valence band spectrum of CsMAFA on a layer stack of glass/ITO/MeO-2PACz/ (sample 4) measured by CFSYS. (b) Initial small range CFSYS measurement of the same sample as in panel (a), obtained directly after the transfer into the vacuum system without precedent illumination. Reprinted with permission from Menzel *et al.* (supporting information) [128]. Copyright 2021 American Chemical Society.



Figure 5.10: Valence band spectra of CsMAFA on a layer stack of glass/ITO/MeO-2PACz/ (sample 1) obtained by CFSYS. Shown are four out of 10 sequential scans. Reprinted with permission from Menzel *et al.* (supporting information) [128]. Copyright 2021 American Chemical Society.

of the gap states is already close to its saturated value when the CFSYS measurement starts and thus, no difference between scan 1 and 2 is observed for most samples. Since the incident photon flux is also recorded and the measurement spot size is known approximately, it can be directly correlated to the applied photon dose. To confirm that the saturation persists upon longer illumination time, a sequence of 10 scans was performed and no further defect formation could be observed (see Figure 5.10). This implies that for this specific material an intrinsic gap state density below roughly $10^{16} \,\mathrm{cm}^{-3} \,\mathrm{eV}^{-1}$ (depending on the dipole matrix element) will not be detectable by the herein used CFSYS set-up. However, the defect densities above this saturated value can be approximately quantified, while being confident to not further degrade the sample with the irradiation required for the measurement itself. Considering the broadly observed degradation of lead based halide perovskites upon UV-illumination in literature, especially in combination with ETL or HTL materials [182], the saturation of defect formation as observed here is remarkable.

Sample	Precedent	$\Delta E_{\rm V,PLog}$	$E_{\rm V,PLog,High}$	$E_{\rm F}^{*}$	E_{t}	$D_{ m it}$	$D_{ m it}$
	condition		- $E_{\rm F}^{*}$	$-E_{\rm F,ITO}$			
		[eV]	[eV]	[eV]	[meV]	[rel. to a_0]	$[\mathrm{cm}^{-3}]$
2	NUPS	0.39	-1.50	0.13	48	$1.8 \cdot 10^{-4}$	$9.2 \cdot 10^{16}$
	initial scan						
2	NUPS	0.39	-1.50	0.13	43	$4.6 \cdot 10^{-4}$	$2.4\cdot 10^{17}$
	second scan						
3	NUPS	0.38	-1.42	-0.12	44	$3.8 \cdot 10^{-4}$	$2.0 \cdot 10^{17}$
3	He-UPS	0.37	-1.46	-0.15	51	$3.0 \cdot 10^{-4}$	$1.6 \cdot 10^{17}$
3	XPS	0.25	-1.65	-0.15	109	$7.7 \cdot 10^{-3}$	$3.9\cdot 10^{18}$
-	air	0.42	-1.52	-0.15	76	$1.2 \cdot 10^{-3}$	$6.1 \cdot 10^{17}$
	exposure						
-	vacuum	0.38	-1.41	-0.13	45	$2.2\cdot10^{-3}$	$1.1\cdot10^{18}$
	storage						

Table 5.3: Valence band and defect parameters obtained from fitting the developed model to CFSYS measured on CsMAFA, with different sample histories. The defect density, D_{it} per volume unit is estimated by normalization based on DFT calculations for MAPbI₃.

5.4.2 Influence of He-I and X-ray illumination on the defect density in CsMAFA

With its low measurement-induced damage, CFSYS may assist to investigate the degradation of perovskite absorber materials under harsher illumination conditions, such as He-I and X-rays.

Figure 5.8(b) shows the CFSYS spectra of a CsMAFA film (sample 3), which has been measured after NUPS (same as all samples in the previous section), after He-UPS (21.2 eV, $t_{\rm ill.} = 40 \text{ min}$) and after XPS (Al-K_{α}, 1486.6 eV, $t_{\rm ill.} = 3 \text{ h}$). The respective residuals after subtracting both polylogarithm model functions, i.e. the gap states, are shown in Figure 5.8(e).

The exposure to He-I irradiation had a comparably minor impact on the sample. The observed valence band structure, especially the clear distinction between $E_{\rm V,PLog,High}$ and $E_{\rm V,PLog,Low}$ was maintained, but their energetic distance slightly decreased from 0.38 eV to 0.37 eV. Relative to the substrate Fermi level, $E_{\rm V,PLog,High}$ is shifted towards higher binding energies by 40 meV. $E_{\rm t}$ also slightly increased from 44 meV to 51 meV, which might indicate partial degradation of the crystal structure. The decreasing total gap state density from $3.8 \cdot 10^{-4}$ to $3.0 \cdot 10^{-4}$ ($2.0 \cdot 10^{17}$ to $1.6 \cdot 10^{17}$ cm⁻³) is somewhat misleading and again attributed to the energetic position of D1, which moved further away from $E_{\rm V,PLog,High}$. This fitting artefact here leads to a concomitant decrease of its area. Considering the measured spectra in Figure 5.8(b) the increase in defect density is better quantified by the area of D2 and D3, which slightly increased from $6.9 \cdot 10^{-5}$ to $8.8 \cdot 10^{-5}$ ($3.6 \cdot 10^{16}$ to $4.4 \cdot 10^{16}$ cm⁻³) after NUPS and He-UPS, respectively. With this, it can be concluded that aside from the possible initial damage that may have occurred upon the initial exposure of the sample to UV irradiation, the additional damage induced by additional He-I radiation

in the investigated time scale is negligible. This is an important finding, since He-UPS is widely applied as the standard method for valence band spectroscopy.

Exposure to X-rays for about 3 h however changed the shape of the DOS in the whole valence band region, such that it is hardly possible to model both high DOS valence band maxima as done for all other samples. For both, $E_{\rm V,PLog,High}$ and $E_{\rm V,PLog,Low}$, the energetic position relative to the substrate Fermi level shifted towards higher binding energies and at the same time their energetic distance decreased to $0.25 \,\mathrm{eV}$. The exponential tail slope parameter $E_{\rm t}$ strongly increased to $109 \,\mathrm{meV}$, which can be interpreted as a significant structural damage on the sample surface. The density of gap states was also further increased by more than one order of magnitude to $7.7 \cdot 10^{-3} (3.9 \cdot 10^{18} \,\mathrm{cm}^{-3})$ as compared to after He-I and Near-UV illumination.

5.4.3 Influence of sample environment conditions on the defect density in CsMAFA

Last, the influence of different sample environment conditions will be discussed: short exposure to air (<10 min) and storage in vacuum for two weeks. The corresponding spectra shown in Figure 5.8(c) and (f).

While both conditions do not severely affect the high DOS valence band region, as the energetic position relative to the Fermi level as well as the energetic distance between $E_{\rm V,PLog,High}$ and $E_{\rm V,PLog,Low}$ stay almost constant, the DOS in the band tail region as well as the gap state density are very sensitive to those conditions. Interestingly, the short exposure to air led to a similarly severe formation of gap states as the long illumination with X-rays, up to $1.2 \cdot 10^{-3}$ relative to $a_0 (6.1 \cdot 10^{17} \text{ cm}^{-3})$, being almost equally distributed up to the Fermi level. Furthermore, the exponential tail slope parameter, $E_{\rm t}$, increases significantly to 76 meV. The equal distribution of the gap states up to the Fermi level and amount of gap states relative to the valence bands at lower binding energy is reminiscent of the spectra obtained by Levine *et al.* obtained for mixed APbBr₃-perovskites [154], where similarly, the layers have shortly been exposed to ambient air. The interaction of lead halide perovskites with humid air has been shown to enhance the degradation of lead halide pervoskites [183] with a supposed decomposition into PbI₂ and other species. Thus, observed trap states in HaPs, especially with highly sensitive PES methods, need to be evaluated carefully, and any exposure to air should be avoided. Since the amount of gap states is still below the detection limit of most He-I based PES systems, this conclusion could not be drawn until now.

It is worth paying special attention to the sample, which had been stored in vacuum for two weeks. While for most samples the gap states seem to be rather equally distributed throughout the band gap (up to the Fermi level), here the appearance of a distinct and localized defect band D1 at +0.38 eV relative to $E_{\text{V,PLog,High}}$ is observed and the overall defect density was increased to $2.2 \cdot 10^{-3}$ relative to $a_0 \ 1.1 \cdot 10^{18} \text{ cm}^{-3}$. However, the prolonged storage in vacuum did not affect the exponential tail slope, which remained rather low at 45 meV. The volatile methylamine is known to leave the HaP material during annealing at 100°C [184] ("outgassing") and a slowed down, but similar behavior should to be expected in ultra-high vacuum [159]. Note, that also in finalized HaP-based solar cells, a degradation in reduced ambient pressure has been observed, and was linked to outgassing and phase separation [185]. Thus, the observed appearance of a distinct defect band might be caused by an intermediate decomposition state. This data in general supports the approach of quantifying the gap states by Gaussian distributions but would need further systematic study to enable the determination of the energetic position of the defect band relative to the valence band edges and further clarification of the defect formation time scales under different environmental conditions.

5.4.4 Degradation processes in lead-halide based perovskites

The chemical origin of the defect formation might be linked to a combination of several decomposition routes. As discussed e.g. by Lin et al. for CH₃NH₃PbI₃, two main routes might play a role, where either the perovskite is decomposed into PbI₂ and CH₃NH₃I or into PbI_2 combined with out-gassing of the volatile methylamine and HI species [186]. Then, PbI_2 can be further decomposed into metallic Pb^0 and iodine (I₂). Often the appearance of Pb^0 - states in the Pb 4f core level is thus used as an indication of degradation of HaP surfaces, as mentioned when evaluating the XPS results in section 5.2 [159, 184, 186], where however no indication of metallic lead could be found in all of the samples within the detection limit. Hence, the observed gap states might be attributed to either decomposed perovskite and thus PbI_2 , or already show the appearance of a low amount of Pb^0 , which is not observable by XPS yet. Since the herein used analyzer is not very sensitive at the high kinetic energies used for XPS, the measurement time of 3 h for all detail spectra is rather long. However, several studies confirm, that this is still below the X-ray illumination time, where metallic lead is usually observed [159, 186]. CFSYS measurements on a pure PbI_2 film confirm that indeed it shows a similar, almost constant density of occupied states in the band gap up to the Fermi level as presented in Figure 5.11, which might originate from the lead-iodine composition or already from metallic lead formed by photolysis. In further studies by Wu et al. on lead-iodine based perovskites, a similar distribution of trap states throughout the band gap up to the Fermi level was observed by means of near-UV PES [151].

The here presented results are proof, that even though no indication of degradation or decomposition of the lead halide perovskites film might be observed by means of XPS, a partial decomposition of the perovskite is to be expected. Further studies, e.g. with varying amounts of excess PbI_2 in the HaP precursor solution, different solvents and



Figure 5.11: CFSYS spectrum of a spin-coated PbI_2 film on ITO/glass substrate. The binding energy is given relative to the Fermi edge, fitted by a sigmoidial Boltzmann function. The figure is reprinted from the supporting information of Menzel *et al.* [128].

compositions as well as systematic variation of X-ray illumination time would be needed for a clear assignment and understanding of those gap states. For example, Zhang *et al.* investigated the influence of different solvents used in the perovskite precursor solution and found that a chemical reaction between DMSO and methylammonium (MA⁺) within the perovskite precursor is linked to the formation of defect states related to DMA⁺ and NH₄⁺ [150].

5.5 Chapter summary

Near-UV excited constant final state yield spectroscopy (CFSYS) was applied to halide perovskites (HaP) and combined with a modelling of the valence band edge to systematically determine the VBM as well as investigate the evolution of gap states systematically and quantitatively. It could be demonstrated that CFSYS enables deep insights into the valence band structure of HaPs and can directly trace the density of occupied states over a high dynamic range of up to seven orders of magnitude.

By comparing CFSYS to conventional He-I and near-UV ($h\nu = 6.5 \text{ eV}$) based UPS on CsMAFA ($Cs_{0.05}(MA_{0.17}FA_{0.83})_{0.95}Pb(I_{0.83}Br_{0.17})_3$) metal-halide perovskite thin films, it was demonstrated that a substantial part of the DOS in the valence band region is hidden below the noise floor of conventional He-I UPS. It was found that evaluating the leading edge of the energetically highest valence band feature on a semi-logarithmic scale gives inconsistent results, especially when methods with higher signal-to-noise ratio are applied. Additionally, the definition of a consistent energetic position on the exponential tail slope is not possible.

To solve this issue, a new model to describe the HaPs was introduced, which considers parabolic band edges and energetic band fluctuations. Until now, only angle-resolved methods could provide information about the strong dispersion of valence bands in HaPs. With the new fitting approach applied to Near-UV CFSYS data, it was possible to resolve two features in the valence band DOS, resulting from local maxima at different points in the Brillouin zone, with a mean energetic distance of 0.38 eV, from which only the energetically lower one is observable in classical He-UPS due to the higher density of states. Further, the Fermi edge could directly be observed and thus a reliable energetic position of -1.50 eV to -1.37 eV relative to the surface Fermi level is found for four different samples of CsMAFA. Occupied gap states with a density of states around four orders of magnitude below the density of states at the highest valence band edge, and which are partially generated by the UV-illumination used for the measurements, could be quantified. By normalizing the density of states to DFT calculations of MAPbI₃ from literature, those defect states could roughly be estimated in volume units to be in the order of 10^{16} cm^{-3} .

Furthermore, the effect of different sample environments and illumination conditions on the valence band DOS of CsMAFA was investigated: Near-UV illumination induces a total density of occupied gap states up to a mean value of $2.2 \cdot 10^{-4}$ ($1.1 \cdot 10^{17}$ cm⁻³), which was not significantly enhanced by further He-I irradiation, while the characteristic energy, describing the slope of the exponential band tail, E_t , slightly increased. X-ray illumination had an enormous impact on the valence band DOS with both a strongly increased density of occupied gap states and increased E_t . Short exposure to ambient air had a similar severe influence on the gap state density, however E_t was less affected. A prolonged storage in ultra-high vacuum mainly led to the appearance of a distinct defect band at + 0.38 eV relative to the highest modeled valence band edge with an approximate density of $2 \cdot 10^{-3}$ (10^{18} cm⁻³).

With the herein provided results, it was demonstrated that CFSYS with near-UV excitation is a useful and suitable tool to investigate the characteristically low density of states at the valence band edge of HaPs. Even very low electronic defect densities can be directly traced and hence important information about the energetics, as well as a quantification of defects on or close to the HaP film's surface, can be obtained. The lack of similarly sensitive PES measurements, combined with the strong dispersion of HaPs, might partly explain the large spread of energetic values for the VBM found in literature for perovskites and charge-selective layers. The high information depth of several nm also enables the investigation of buried interfaces as employed as it will be presented in chapter 6 for the interface of CsMAFA/C₆₀.

Chapter 6

Electronic properties of the $CsMAFA/C_{60}$ interface

6.1 Introduction

The fullerene C_{60} is widely applied as electron selective contact in organic solar cells and has become the standard electron transporting layer in p-i-n metal halide perovskite solar cells (PSCs). Further, it is applied in silicon/perovskite tandem solar cells with p-i-n structure of the perovskite top cell, yielding high efficiency devices [17]. However, the obtained open circuit voltage for PSCs is found to be limited by this interface due to non-radiative recombination losses at the interface [125, 126], which raises interest to thoroughly study the energetic formation of the perovskite/ C_{60} interface including the energy level alignment and density of gap states (D_{it}). The insertion of an ultra thin (1 nm) LiF interlayer has been shown to significantly enhance the open circuit voltage [17] presumably by reducing the non-radiative recombination losses at the interface. However the exact passivation mechanism is poorly understood so far.

In this chapter, some evidence will be shown that points towards a reduced hole concentration at both sides of the perovskite/ C_{60} interface in combination with an electrostatic decoupling of the perovskite and the C_{60} , and an increased valence band offset with the insertion of the thin LiF interlayer.

The interface between the triple cation perovskite CsMAFA with a composition of $Cs_{0.05} (MA_{0.17}FA_{0.83})_{0.95} Pb (I_{0.83}Br_{0.17})_3$, which already has been studied in chapter 5, and thin films of C_{60} will be investigated by means of near-UV photoelectron spectroscopy. Further, the influence of a thin (1 nm) LiF buffer layer on the electronic structure of the interface will be discussed. In order to compare the interface formation of CsMAFA with C_{60} with and without the thin LiF interlayer, two main sample series with varying thickness of C_{60} in a full solar cell-like layer stack (glass/ITO/MeO-2PACz/CsMAFA/C₆₀)

are investigated: C_{60} was thermally evaporated with a stepwise variation of the thickness from 0 to 20 nm either directly on the perovskite (abbreviated as "no LiF") or with an ultra thin LiF interlayer of 1 nm in between the perovskite and the C_{60} (abbreviated as "LiF") according to the procedure described in section 3.4.3.

First, the chemical properties of the evaporated thin films of both sample series will be investigated by means of XPS (section 6.2). This is followed by discussing the density of states of the C_{60} HOMO level and occupied gap states (section 6.3), measured by various (near-) UV-PES methods. Different to the investigation of the bare perovskite as it was shown in the previous chapter 5, here complete photoactive devices, including both contact layers (HTL and ETL) are measured with UV-light, which results in a significant photovoltage throughout the layer stack. This will be evaluated in detail. A significant amount of gap states in C_{60} thin films attributed to structural disorder [187] is known from conventional as well as high resolution UPS measurements [187–189] and will here be investigated by means of CFSYS. This non-vanishing DOS permits to trace the occupied gap states up to the Fermi edge, which becomes clearly visible in the spectra. After discussing the properties of C_{60} thin films, the formation of the CsMAFA/ C_{60} contact will be investigated (section 6.5). While He-UPS usually is limited to the investigation of the material surfaces and for evaluations of interfaces one needs to rely on assumptions about the possible occurrence of charge transfer and band bending at the interface to obtain an estimate for the band alignment, the high information depth of CFSYS enables to observe the formation of electronic states and evolution of energetic positions directly at the interface. The combined model for describing the perovskite valence band edge used in the previous chapter (section 5.3.2) is further adjusted to directly quantify the energy offset between the perovskite VBM and the C_{60} HOMO-edge using a sample with intermediate C₆₀ layer thickness of 5 nm. Last, the effect of an ultra-thin LiF interlayer on the interface formation between CsMAFA and C_{60} will be evaluated and discussed (section 6.6).

6.2 X-ray PES analysis of C₆₀ thickness variation on CsMAFA

In order to investigate the chemical composition of the investigated interface, the core level spectra and composition of the two series "LiF" and "no LiF" with varying C_{60} thickness on CsMAFA with and without a 1 nm LiF interlayer, respectively, will be discussed in the following.

6.2.1 Overview

In Figure 6.1 the spectra of (a) F 1s, (b) I 3d, (c) C 1s and (d) Pb 4f core levels of the entire thickness variation of C_{60} are shown with the series "no LiF" presented on the bottom and CsMAFA/LiF/C₆₀ in the top half of the graphs.



Figure 6.1: XPS (Al-K_{α}) core level spectra for a thickness variation of C₆₀ on Glass/ITO/MeO-2PACz/CsMAFA (bottom) and Glass/ITO/MeO-2PACz/CsMAFA/1 nm LiF (top) for (a) F 1s, (b) I3d, (c) C 1s and (d) Pb 4f. The applied fitting models for the core levels are shown here and discussed in the main text. *) core levels spectra, which have been taken with a larger step width and smaller dwell time.

As the C_{60} thickness increases, the intensity of the perovskite related core levels, I 3d and Pb4f decreases until they disappear for a C_{60} thickness higher than 5 nm. Note, that different to CFSYS, the information depth of XPS is limited to around 3-5 nm, thus information about the chemical composition of the interface is mainly obtained from the core level spectra of samples with $1-3 \,\mathrm{nm} \,\mathrm{C}_{60}$ thickness, while in the CFSYS spectra of $5-10 \,\mathrm{nm} \,\mathrm{C}_{60}$ samples occupied states from the interface and first monolayers are still visible (see Figure 6.14). Figure 6.1(c) shows that the C1s core level starts rapidly to rise, once C_{60} is deposited on the perovskite. As seen in chapter 5, the signal of the C 1s core level of bare perovskite is very low and thus in this scaling, compared to C_{60} containing samples, barely visible. In the F1s core level two components are visible for the "LiF" series, which can be attributed to fluorine–carbon (F–C) and fluorine–lithium (F-Li) bonds. Even though no fluorine is expected for the "no LiF" series, a substantial amount of fluorine-carbon bonds is actually observed for both "LiF" and also in a varying amount for "no LiF". Since C_{60} and LiF are both evaporated in the same processing chamber, this might result from cross-contamination during the evaporation of C_{60} and will be discussed in more detail later.

6.2.2 XPS core level modeling

The most prominent core levels have been fitted with individual models using the fitting software Fityk [56]. A linear background was assumed for all core levels, which is already subtracted in the shown spectra. In general, all absolute energetic positions were used as free fitting parameters in order to account for charging or SPV effects, and only relative constraints for individual components within one core level were set. Furthermore, for each individual component, corresponding to one chemical state, the FWHM was set the same throughout the whole C_{60} thickness series.

The F1s core level (Figure 6.1(a)) consists of two well separated individual components, one being attributed to F–C bonds at higher binding energies and one attributed to F–Li at lower binding energies [190, 191]. An energetic distance of 3.79 eV was found to separate both components. For the C1s core level (Figure 6.1(c)) five individual components were used to describe the total peak area. In general, the evaluation of the C1s core level is very demanding. Many species can potentially contribute (from the perovskite, the C_{60} , or surface contaminations) and their specific binding energies are often very close to each other. A detailed analysis should thus always take the core level of the respective element, which the bond is assigned to, into account. However, here the resolution it too low for an analysis of the N 1s and O 1s spectra and thus the assigned bonds cannot be confirmed by a correlation of the respective peak areas. For the evaluation further down, only the total C1s peak area is considered. The three most significant components are most likely attributed to C–C, C–N and C–O/C– F_x (from low to high binding energy). The components of C–O and C– F_x , where x can be 1-3 [191], cannot be resolved here and are thus combined in one peak. No significant appearance of the O1s core level was observed in the PES spectra. Additionally, a concomitant increase of the F–C bond in the F 1s core level with the $C-O/C-F_x$ component in the C 1s core level is found. Hence, most likely, the intensity of this component can predominantly be attributed to fluorine related bonds. The energetic distance of C–N and C–O/C– F_x relative to C–C is found to be $0.55 \,\mathrm{eV}$ and $1.78 \,\mathrm{eV}$, respectively. While the latter is in good agreement with values found in literature [191], the energetic distance between the two components of C–N and C–C in literature are often found to be slightly larger [156, 192]. Two broad features with rather low intensity are observed at around 287.5 eV and 290 eV, which can be attributed to further CF species [191, 193, 194].

I 3d and Pb 4f could be both fitted with one single transition (Figure 6.1(b) and (d)). Thus, especially no indication of metallic lead Pb^0 is observed.

For some samples not all detail spectra were acquired. In these cases, the survey spectrum in the specific region has been rescaled considering the different dwell time. These spectra are marked with an asterisk in Figure 6.1. Since this is only the case for core levels with no especially complex fitting model, they can be treated the same way as the results obtained by the more detailed spectra. However, a larger error needs to be

considered for the obtained fitting parameters.

6.2.3 Chemical composition of C₆₀ on CsMAFA

To evaluate chemical composition of the surface with increasing C_{60} thickness, in the following relative area ratios will be discussed and compared for both series "LiF" and "no LiF".

The growth and coverage of C_{60} on perovskite, represented by the Pb 4f core level can be evaluated with the area ratio of C 1s / Pb 4f (Figure 6.2(a)). The coverage of LiF on the perovskite can be investigated by the area ratio of the individual components of F 1s to Pb 4f (Figure 6.2(b)). As suggested by the appearance of a significant amount of fluorine in layers where none is expected, the contamination of the C_{60} by fluorine is investigated by the area ratio of the carbon related component of F 1s relative to the total area of C 1s (F–C in Figure 6.2(c)). Furthermore, both fluorine components enable to draw conclusions about the chemical bonding configuration of the LiF interlayer (Figure 6.2(c) and (d)). Using sensitivity factors for the specific measurement tool and core level would permit to evaluate atomic ratios for the individual elements. However, since reference samples with sufficiently well-known composition were not available, the sensitivity factors could not be determined and only the relative areas are evaluated here.

The area ratio of C 1s / Pb 4f (Figure 6.2(a)) increases exponentially from 0.05 (0.09) for bare perovskite to 1.9 (1.96) for $d(C_{60}) = 5 \text{ nm}$ for "no LiF" ("LiF"). For the very thinnest layers, a slightly higher area ratio of C 1s / Pb 4f for the LiF containing layer stack is observed. The exponential attenuation of the Pb 4f with the increasing coverage by C₆₀ can be described by the model function, which is shown in the graph. A more detailed discussion of the model function applied here, can be found in section 6.5.2 for a similar situation of the valence band/HOMO amplitude.

The observation that also for very thin layers, the area ratio is well described by the exponential fit, as expected for the attenuation of the Pb 4f signal by the C₆₀ overlayer indicates that indeed, also the coverage of very thin layers of C₆₀ is well reproducible. The slightly increased C 1s / Pb 4f area ratio for the LiF containing layer stack, can be a result of the additional 1 nm buffer layer, which further attenuates the intensity of photoelectrons originating from the perovskite in addition to the C₆₀. However, this effect is small and similar exponential growth parameters of the exponential function are found for "no LiF" and "LiF", respectively. In principle such an evaluation would also allow for the determination of the inelastic mean free path length, λ_{imfp} . Here, the high uncertainty of up to 50 % of the obtained λ_{imfp} suggests that more intermediate layer thickness steps or a higher number of samples would be needed to obtain a reliable result. Furthermore, the assumption of equal λ_{imfp} for the photoelectrons of both core levels is not valid, as they have different kinetic energies. In general, a similar behaviour for both series is found,

which justifies the direct comparison of the CFSYS spectra from the respective thin C_{60} layers with and without LiF.

In Figure 6.2(b) the area ratios of both components of the F 1s core level (F–C and F–Li) to Pb 4f are shown. The deposition of LiF between CsMAFA and C₆₀ leads to a significant appearance of the F–Li component in the "LiF" series. Note, that the 0 nm C₆₀ sample, shown here already has a 1 nm LiF layer deposited on top of the perovskite. The area ratio of F–Li / Pb 4f increases slightly from 0.75 for 1 nm LiF and no C₆₀ to 1.2 for 2 nm C₆₀ thickness and then decreases again to 0.68 for 5 nm C₆₀ thickness. The same area ratio for the "no LiF" layer stack stays at zero, independent of the C₆₀ layer thickness.

As the photoelectrons result from both materials, and if the F–Li bonds are only located in a defined thin layer, the area ratio should stay rather constant with increasing C_{60} layer thickness as both core levels get attenuated by the covering C_{60} overlayer. However, the photoelectrons originating from the Pb 4f and the F 1s core level core level have very different kinetic energies. As excitation source here Al- K_{α} was used with a photon energy of 1486.6 eV. For photoelectrons of the Pb 4f core level E_{kin} is thus roughly around 1430 eV and for the F 1s core level 860 eV. According to the universal curve, which describes the IMFP of electrons in dependence of their kinetic energy (see section 3.1.6) the photoelectrons of the Pb 4f have hence a longer IMFP, and get thus attenuated less by the C₆₀ cover layer than the photoelectrons from the F 1s core level. This would lead to a general decrease of the F–Li / Pb 4f area ratio with increasing C₆₀ thickness, while the opposite trend is observed for the thinnest C₆₀ layers. Another explanation could be a slightly different LiF thickness in between different samples, which were evaporated in different batches.

For the "no LiF" layer stacks, a general increase of the area ratio of F-C / Pb 4f is found from zero up to 0.53 for a C₆₀ thickness of 3 nm (Figure 6.2(b)). For 5 nm C₆₀ the area ratio decreases again to 0.14. As mentioned before, the values here are obtained by fitting the less precise survey spectra, which implies a significantly increased uncertainty when determining the area ratios. For several samples with identical layer stack, the area ratio of F-C / Pb 4f for "no LiF" was found to vary strongly in between different samples (not shown here), while at the same time the C₆₀ layer thickness was found to be similar by comparing the C1s / Pb 4f area ratio (Figure 6.2(a)). On the other hand, similar to the previously considered area ratio of C 1s to Pb 4f, for "LiF" also the area ratio of the F-C component in the F 1s core level and the Pb 4f area increases steadily with increasing C₆₀ layer thickness from zero at 0 nm C₆₀ to 0.8 at 5 nm C₆₀ (Figure 6.2(b)). However, a similar exponential increase of C 1s / Pb 4f and F-C / Pb 4f for "LiF" does not imply a homogeneous distribution of fluorine-carbon bonds in the C₆₀.

To evaluate the contamination with doping of fluorine in the C_{60} layer, in Figure 6.2(c)



Figure 6.2: Area ratios of the modeled XPS core level spectra versus the thickness of C_{60} on glass/ITO/MeO-2PACz/CsMAFA ("no LiF") and on glass/ITO/MeO-2PACz/CsMAFA/1 nm LiF ("LiF"). The spectra are shown in Figure 6.1. The individual panels show (a) the total peak area of C 1s with an exponential fit by the equation shown in the graph and discussed in the main text; (b) both components of F 1s (F–C and F–Li) relative to the peak area of Pb 4f; The individual components of the F 1s core level (c) F–C and (d) F–Li relative to the total peak area of C 1s.

the area ratio of F 1s–C / C 1s with increasing C₆₀ thickness up to 20 nm is monitored for both series "LiF" and "no LiF". All C₆₀ layers, independent of the deposition of the LiF interlayer, show the presence of fluorine. For "LiF" this follows a clear trend: After an initial increase of the F 1s–C / C 1s area ratio to a maximum of around 0.43 in the range of medium C₆₀ thickness up to 3-5 nm, the area ratio decreases again to a level of ≈ 0.2 up to 20 nm C₆₀ thickness. For "no LiF" shows in general a similar trend with initially increasing fluorine content up to an area ratio of 0.57 between 2-10 nm C₆₀ thickness and slightly lower fluorine content at 20 nm C₆₀ with an area ratio of 0.36. However, for "no LiF" there are substantial fluctuations in the considered area ratio, e.g. for the 5 nm C₆₀ thickness, where significantly less fluorine is found in the C₆₀.

The question arises how such high fluorine content in the "no LiF" series can be explained. The reason is probably that both materials, C_{60} and LiF, are evaporated in the same system. It is thus likely that the whole chamber is contaminated with fluorine and during each deposition an uncontrolled contamination of C_{60} with fluorine is present.

For the "no LiF" series, there are two different processes which might take place. First, the fluorine from the chamber walls might start to evaporate at the beginning of the evaporation process and after a certain time, the amount of available fluorine is reduced and thus the cross-contamination is also reduced. Second, the fluorine could already accumulate at the sample surface during the pumping before the evaporation or while preheating the C_{60} evaporation source and then diffuse into the C_{60} . Both would lead to an enhanced contamination close to the interface with a decreased contamination with increasing C_{60} thickness. As mentioned above, this process is entirely uncontrolled and thus large variations are expected. For the "LiF" series, in general a slightly lower amount of fluorine-carbon bonds are observed. Additionally, the deviation in between different samples and batches is significantly less compared to the "no LiF" series. For "LiF" two genuinely different mechanisms can lead to the appearance of F–C bonds, which should add up in the total core level area: the contamination during the evaporation process, same as for "no LiF", and potentially an additional contamination from dissociated LiF, where the fluorine could bond to carbon atoms instead. Surprisingly, the samples without LiF even show a higher F–C signal. Additional bonding of fluorine from dissociated LiF to carbon atoms can thus not be supported by this data. The more controlled behavior of the "LiF" series compared to the "no LiF" series can be well explained by the more welldefined chamber histories for different evaporation runs. The C_{60} is always evaporated directly after the thin LiF layer, without breaking the vacuum. For "no LiF" however, the chamber is at an undefined contaminated state before the deposition, which explains the variation from one evaporation process to another. Such contamination and variations in the composition might have a crucial influence on the work function and defect density. Since most of the devices in the lab contain C_{60} layers from this evaporator, this seems not to hinder the device efficiency, in general. However, as almost all layers contain fluorine contamination, a more detailed study with the present amount of samples is not possible with the available deposition tools. One possibility to investigate the effect of the fluorine contamination would e.g. be to use a different deposition technique for C_{60} , such as solution processing [195].

In Figure 6.2(d) the area ratio of the F–Li component of the F 1s core level relative to the C 1s core level is shown. For "no LiF" the area ratio stays close to zero. However, for 0 and 5 nm C₆₀ of the "no LiF" series, a very small amount of F–Li bonds appears. For the "LiF" series, a rapidly exponentially decreasing F–Li / C 1s area ratio from 8.5 for 1 nm LiF on CsMAFA with no C₆₀ on top to 0.35 for 5 nm C₆₀ and finally reaching zero for 20 nm C₆₀ is observed.

As the Li 1s core level is very hard to observe by XPS, due to its low excitation cross section, the observation of the F–Li bonds in the F1s core level assists to estimate the depth profile of lithium throughout the layer. The found rapid decrease indicates that the LiF itself stays at the interface and does not migrate far into the C_{60} . However, no statement about Li⁺ ions as a result of a potentially dissociated LiF can be made, as the resolution of the Li 1s core level spectra is too low. Considering both fluorine components in dependence of the C₆₀ thickness, the F–C bonds are observed for significantly higher C_{60} thickness, indicating that the fluorine itself can diffuse throughout the whole layer (or is "co-evaporated" during the deposition of C_{60}). The Li–F signal (thus LiF in its initial configuration) stays close to the interface. The signal of F–Li bonds in the F 1s core level in the "no LiF" series is mostly negligible, but some minor contributions do appear e.g. for $5 \,\mathrm{nm} \,\mathrm{C}_{60}$. Most likely besides the cross-contamination with fluorine also a minor contamination by LiF occurs during the deposition of C_{60} . However, these are preliminary results; to investigate the chemical effect of potentially additional doping by e.g. F⁻ as a results of dissociated LiF, XPS spectra acquired with a better resolution, especially for the Li 1s, C 1s and F 1s core levels is required.

The binding energies of the core levels shown in Figure 6.1 are given relative to the substrate Fermi level and thus might be shifted due to charging or surface photovoltage (SPV). In Figure 6.3, the energetic positions of the core levels are evaluated relative to each other, which excludes small charging effects. Upon the initial application of the first nm of C₆₀, the Pb 4f core levels already shift by 100-200 meV relative to C 1s. The energetic distance between Pb 4f and I 3d stays constant as also shown in the graph. Hence, the perovskite-related and the C₆₀-related core levels move apart from each other with increasing C₆₀ layer thickness. As the position of the C 1s for 0 nm C₆₀ is given by the carbon, contained in the perovskite itself (or surface contamination), the initial shift is an indication of a charge redistribution upon the deposition of another material (the C₆₀) on top of the perovskite. For increasing C₆₀ thickness, the relative peak position of Pb 4f



Figure 6.3: Shift of the core level binding energy of $Pb 4f_{5/2}$ $I \, 3d_{3/2}$ and upon the thickness variation of C_{60} on glass/ITO/MeO-2PACz/CsMAFA(/1nm LiF), labelled as "no LiF" ("LiF). The reference binding energy, the core level peak $E_0,$ is $_{\mathrm{the}}$ C1s (C–C position of component) and $Pb 4f_{5/2}$ core level, respectively, at $0 \,\mathrm{nm} \,\mathrm{C}_{60}$ thickness.

compared to C 1s increases. As it will become apparent in the following sections, upon the increase of C_{60} layer thickness, the charge carrier redistribution due to the forming contact changes and more charges are accumulated in the C_{60} . Those charges can thus lead to an increased shift between both core levels and a different band alignment for different C_{60} thicknesses. Note, that because of very different illumination conditions during the measurement, this shift cannot directly be compared to the valence band edge positions as they will be discussed further below. CsMAFA is a highly efficient photoabsorber; already a low photon flux from scattered background light can induce a significant photovoltage and the layer stack cannot be considered as in thermodynamic equilibrium. Furthermore, by the XPS measurement itself, the sample is illuminated with X-rays to excite the photoelectrons, which can itself lead to a quasi Fermi level splitting (QFLS) in the absorber. For the case of near-UV light this will be discussed in detail in section 6.4.1. However, here, entirely different illumination conditions do not allow to draw conclusions from the surface Fermi level measured by CFSYS (section 6.4.3) to the possible induced SPV in the XPS measurements as discussed here.

6.3 Density of states of C_{60} thin films

Here, the density of states of the C_{60} HOMO and in its band gap will be investigated by means of different UV-PES modes (He-UPS, NUPS and CFSYS). To that end, a C_{60} thin film with a thickness of 50 nm was evaporated directly on an ITO-coated glass substrate. Later on, in the next sections, the step-wise formation of the interface will be discussed by evaluating the density of states of both C_{60} thickness variation "no LiF" and "LiF". But first, the C_{60} itself will be considered.

6.3.1 Energetic positions of the HOMO density of states in C_{60}

In Figure 6.4 the obtained spectra of the C_{60} HOMO level, measured by He-UPS, NUPS and CFSYS are presented on a semi-logarithmic scale. The spectra are aligned to the con-


Figure 6.4: Photoelectron spectra of a 50 nm evaporated thin film of C_{60} on ITO-coated glass substrate. Comparison of different PES modes on a semilogarithmic scale: He-UPS with 21.2 eV, NUPS with 6.5 eV and CFSYS with $3.7 - 7.3 \,\mathrm{eV}$ excitation energy. The intensity of the He-UPS measurement (right scale) was rescaled to match the internal yield of NUPS and CF-SYS. The spectra are aligned to the Fermi level of the ITO, $E_{\rm F,ITO}$, which is contacted for the measurement.

tacted Fermi level of the substrate, $E_{\rm F,ITO}$, and thus not corrected for potential charging or SPV. The internal yield (NUPS and CFSYS) is compared to the photo electron count rate (intensity) as measured by means of He-UPS, where the count rate is scaled to match the internal yield of the HOMO peak at ~-2.5 eV.

While with He-UPS, the DOS can be measured throughout the whole HOMO region, NUPS and CFSYS only probe a narrow energy range down to around -2 eV binding energy with respect to $E_{\rm F,ITO}$, depending on the material work function. The SECO at ~-2 eV is a feature of NUPS, which provides information about the material work function, and is also required for selecting an appropriate final state kinetic energy in the CFSYS measurement. However, the photon energy of 6.5 eV is not sufficient to excite electrons from deep in the HOMO, just the very edge can be probed. For CFSYS the photon energy is varied up to $7.3 \,\mathrm{eV}$ and with this a slightly higher energy range of the HOMO can be traced. The photon flux of the applied Xenon gas pressure lamp for such high photon energies is comparably low (see Figure 3.7(b)) in section 3.1.5), but with the high DOS in the HOMO, the resulting photoelectron yield is still sufficient to trace the DOS of the HOMO down to a binding energy of $-2.5 \,\mathrm{eV}$. This also enables to quantify the HOMO edge position and its amplitude, as it will be discussed further down. Additionally, with the low noise floor the density of occupied gap states, D_{it} , can be traced up to the Fermi edge, which is visible at around 0 eV relative to the contacted ITO substrate's Fermi level, $E_{\rm F,ITO}$.

Two different energetic positions are usually considered for the evaluation of the C_{60} HOMO level [187, 196, 197]:

1. The HOMO edge (E_{HOMO}) which is obtained by the extrapolation of the linear part on the high energy side of the HOMO. As this is the highest electronic state with a substantial density of states, it is the one usually being used for determining the energy level alignment across heterojunctions;



Figure 6.5: PES spectra of glass/ITO/C₆₀(50 nm). The modeling of the C₆₀-HOMO level, measured by (a) He-UPS and (b) CFSYS, is shown. The maximum of HOMO (HOMO_{max}), modeled by three Gaussian distributions and the HOMO-edge ($E_{\rm HOMO}$), obtained by the intercept of a linear extrapolation of the HOMO and the background are indicated.

2. The maximum of the HOMO level DOS is mostly used to conveniently track e.g. band bending, since it is usually well visible in the He-UPS spectrum and here labeled as HOMO_{max}.

In Figure 6.5(a) and (b) those two positions are indicated in the spectrum of the C_{60} HOMO level, measured by a) He-UPS and b) CFSYS.

The HOMO-edge is found at -2.0 eV relative to $E_{\rm F,ITO}$ for both measurement methods and HOMO_{max} at an energetic distance of 0.52 eV and 0.53 eV towards lower energies for He-UPS and CFSYS, respectively. These similar values, obtained by both methods, ensure that $E_{\rm HOMO}$ evaluated from the CFSYS spectrum is indeed directly similar to results obtained by He-UPS, which is important for the sake of comparison to literature values where mostly He-UPS data is available.

Furthermore, the work function was obtained by a sigmoidial Boltzmann fit of the SECO, for both, NUPS and He-UPS. With the excitation energy of 6.5 eV a work function of 4.37 eV is obtained. This is slightly below the work function obtained by He-UPS with 4.53 eV. Bussolotti *et al.* investigated a 15 nm C₆₀ thin film on SiO₂ and found a similar HOMO-edge of 1.94 eV and work function of 4.51 eV by Xe-I UPS ($h\nu = 8.437 \text{ eV}$) [187]. The herein obtained values (with a similar photon energy) are thus in good agreement.

The HOMO level, measured by He-UPS has a slightly asymmetric shape, which could result from electron-phonon coupling [198] or structural disorder [199]. It can be modeled by three Gaussian distributions [187]. For the modeling, additionally a linear background is assumed and a fourth Gaussian peak is added to account for the energetically next lower feature. Sometimes also only the energetically highest of the individual components is evaluated in literature [187]. Even though the CFSYS measurement can only trace the high energy part of the HOMO level, it already shows the asymmetric DOS of the HOMO level and thus, to compare both methods, it is also modeled with three Gaussian distributions. Note, as there are no secondary electrons resulting from the measurement, the (low) background is not considered for CFSYS. Because of the limited energy range of the CFSYS spectrum, the energetic positions of the individual Gaussian distributions needed to be constrained to have the same FWHM and same relative energetic distance for both, He-UPS and CFSYS. The energetic position and peak area were used as free fitting parameters. From the sum spectrum of these three components, the maximum of the HOMO peak, HOMO_{max} is found at -2.52(10) eV and -2.53(10) eV for both He-UPS and CFSYS, respectively.

6.3.2 Defect states states in C₆₀ thin films

A significant sub band gap absorption in C_{60} thin films is widely observed by optical spectroscopy methods, such as optical absorption measurements [200], surface photovoltage measurements [201], photoluminescence or spectroscopic ellipsometry [202]. These methods all have in common, that optical transitions are measured, thus a quantity proportional to the convolution of HOMO and LUMO band tail states, whereas with PES the energetic distribution of the occupied states in the valence band/HOMO level can be accessed. In the past, C_{60} has been widely investigated by various PES methods [133, 203, 204]. Mostly the energetic positions, such as the HOMO level and the work function are investigated and less focus is put on the distribution of gap states. However, for the investigation of electrical interfaces, those gap states might act as charge traps and are of high importance, as they might crucially affect the electronic transport properties across the interface. If large amounts of gap states are found in the band gap of the C_{60} thin film, which are energetically higher than the ionization energy of CsMAFA, non-radiative trap assisted recombination with holes from the CsMAFA valence band can be enhanced. In consequence they might lead to worse surface passivation and thus losses especially in the $V_{\rm OC}$ of a solar cell device [125], see also the analogous discussion for the silicon heterojunction in section 2.2.4.

In Figure 6.6 the herein performed CFSYS measurement on 50 nm C_{60} thin film is compared to two high-sensitivity near UV-PES measurements by Bussolotti *et al.* [187] and Machida *et al.* [188]. The data has been redigitalized from the original publications and for the sake of comparison, the spectra have been aligned to E_{HOMO} . Furthermore, the CFSYS data as well as the data by Machida *et al.* has been scaled to match the DOS as obtained by Bussolotti *et al.* at E_{HOMO} . In both cited studies, the data was obtained by highly sensitive UPS measurements. Machida *et al.* deposited different thicknesses of C_{60} on rubrene and investigated the interface formation by low-energy UPS (LE-UPS) with 6.7 eV excitation energy. The spectrum shown here is taken from a C_{60} thin film with a thickness of 118 nm. The main advantage of the system used in their study is a



Figure 6.6: HOMO and band gap region of C₆₀ films measured by PES: CF-SYS on 50 nm C₆₀ on glass/ITO (own measurement), and redigitalized data of C₆₀ thin films by Bussolotti *et al.* [187] and Machida *et al.* [188]. All datasets are aligned to the HOMO edge E_{HOMO} and scaled to match the absolute DOS at E_{HOMO} as calculated by Bussolotti *et al.* [187].

high resolution with very low photon dose and thus small measurement induced damage on the sensitive organic layers. Bussolotti *et al.* investigated the density of gap states of a 15 nm thin film of C_{60} on SiO₂ with Xe-I (8.437 eV) UPS. Note, that there are some fundamental differences, when comparing LE-UPS measurements with CFSYS spectra, which are discussed in the methods section 3.1.5. Most importantly, the transition matrix element in general varies with the photon energy, which is neglected here, by directly comparing both measurement methods with each other.

All data sets show the clear signature of HOMO peak and a steadily decreasing density of gap states throughout the band gap up to $E_{\rm F}$. Assuming a constant matrix element, the density of states in units of eV⁻¹cm⁻³ can be estimated by aligning the herein measured data to the DOS as published by Bussolotti *et al.* [187], given in $eV^{-1}cm^{-3}$ and which they have obtained by a molecular packing density of $1.4 \cdot 10^{21}$ molecules cm⁻³ for the face centred cubic unit cell of C_{60} with a lattice parameter of 14.156 Å[205] and a procedure described by Sueyoshi et al. [206]. As seen in by CFSYS, the gapstate density, $D_{\rm it}$, decreases from $10^{20} \,\mathrm{eV^{-1} cm^{-3}}$ right above the HOMO-edge, by over two orders of magnitude down to $10^{18} \,\mathrm{eV^{-1} cm^{-3}}$ at the Fermi edge. In literature these states are considered as localized gap states, being located above the mobility edge [207]. In the general trend of decreasing $D_{\rm it}$ towards the Fermi level, one distinct defect band around $0.5\,{\rm eV}$ above the HOMO edge is observed. In the C_{60} film measured by Bussolotti *et al.*, a similar defect band around $0.7 \,\mathrm{eV}$ above E_{HOMO} is found. However, the DOS at this defect band for the herein investigated film is significantly enhanced by almost one order of magnitude. For the spectrum measured by Machida et al. it cannot be stated, whether a similar defect band is hidden behind the noise floor, but a substantial $D_{\rm it}$, exponentially decaying into the band gap can be observed. As the Fermi level in C_{60} is usually rather close to the LUMO level, it is likely, that the drop in DOS observed by Bussolotti et al. is not yet the Fermi edge, but the $D_{\rm it}$ decreases below the detection limit. This pronounced defect band with an excitation energy around $0.5 - 0.7 \,\mathrm{eV}$ below the fundamental band gap is also observed by optical measurements [200, 201]. With the additional knowledge from the CFSYS measurements shown here, the optical transition leading to this sub-band gap absorption energy can be assigned to electrons being excited from this state into the fundamental LUMO band.

6.4 Measurement induced surface photovoltage in near-UV PES measurements

For investigations by PES, it is essential to consider possible side effects induced by the electromagnetic radiation impinging on the sample. Besides the potential light induced degradation, which was already discussed in detail for CsMAFA for the various illumination conditions (section 5.4), the generation of a surface photovoltage (SPV) in photo active devices, such as solar cells, needs to be considered [175, 208]. In section 5.3.3 possible mechanisms, resulting in a shift of the spectra along the binding energy axis relative to the substrate Fermi level, $E_{\rm F,ITO}$, have been discussed.

In this chapter additionally C_{60} as an electron transporting layer is deposited on top of the perovskite. Thus, photogenerated holes can still be extracted at the hole selective back contact (ITO/MeO-2PACz/CsMAFA), where they recombine with electrons supplied via the electrical grounding of the ITO substrate. With the C_{60} present, additionally the electrons are extracted by the front contact (CsMAFA/ C_{60}). In Figure 6.7 the splitting of the quasi Fermi levels throughout a simplified solar cell like structure is sketched. The layer stack in the Figure only consists of an absorber, and a perfectly aligned hole transport layer (HTL) and electron transport layer (ETL). If the front contact is electrically separated from the back contact, the electrons accumulate in the C_{60} layer, which can result in a significantly larger SPV as compared to the situation without front contact layer. Note, that the illumination conditions are still the same as compared to bare perovskite, which should lead to a similar QFLS. The accumulation of electrons in the C_{60} then in turn results in a net voltage difference between the contacted $E_{\rm F,ITO}$ and the Fermi level of the electrons at the front surface, $E_{\rm F}^{*}$, which is here defined as SPV [173]. The actual magnitude of the SPV depends on the energy dependent absorption properties of the investigated material and the photon flux and the interface properties at the charge selective contacts. For nonphotoactive layer stacks, or those with very high surface recombination velocities (thus no possible charge accumulation at the surface) the SPV usually is negligible as generated charge carries recombine in very short time scales.

In a first step, here the quasi Fermi level splitting (QFLS) in the absorber will be estimated under simplified conditions. Second, the externally measured voltage (SPV = $E_{\rm F}^{*}$ - $E_{\rm F,ITO}$) will be investigated by comparing C₆₀ deposited directly on ITO vs. C₆₀ as the top layer of the full device stack (glass/ITO/MeO-2PACz/C₆₀). Last, the influence of the C₆₀ thickness on the observed SPV will be discussed.



Figure 6.7: Schematical solar cell device stack under near-UV illumination during the NUPS and CFSYS measurement. The illumination induces a quasi Fermi level splitting (QFLS), which leads to a voltage difference (surface photovoltage, SPV) between the contact on the stack's rear side, which defines the origin of the binding energy scale, and the surface Fermi level, $E_{\rm F}^* = E_{\rm F,n,front}$, of the electrons.

6.4.1 Estimation of quasi Fermi level splitting in CsMAFA induced by near-UV illumination

Here the QFLS, thus the energetic distance between the quasi Fermi level of the holes $(E_{\rm F,p,bulk})$ and the electrons $(E_{\rm F,n,bulk})$ under the specific illumination conditions during the NUPS and CFSYS measurement will be estimated. Note, that substantial assumptions are made for the calculation of the maximum QFLS. However, since the QFLS depends logarithmically on the generated charge carries it is rather insensitive towards slightly incorrect assumptions and the overall QFLS can still be considered as a reliable upper limit for the measured SPV.

Photons, which impinge on the sample's surface and are not reflected by the C_{60} are either transmitted or parasitically absorbed in the C_{60} depending on its absorption coefficient and thickness. In the perovskite the photons generate excess charge carriers, which leads to a splitting of the quasi Fermi levels. If the charge carriers do not recombine via some non-radiative mechanism, they eventually reach the carrier selective contacts, here being the hole-selective SAM at the bottom and the electron selective C_{60} at the top of the layer stack where they are selectively extracted. This is the basic working principle of each photovoltaic device. The impinging photon flux is monitored during the near-UV PES measurements. Hence, estimating the QFLS within a certain configuration provides information about the maximum illumination induced shift of the spectra that one can expect, and the difference between the observed SPV and the calculated QFLS contains information about the internal losses.

As not only the impinging, but also the reflected photon flux in dependence of the photon energy is measured during the CFSYS scan, the absorbed photon flux in dependence of the photon energy, $\Phi_0(E_{\rm Ph})$, in the sample is known. To calculate the photon flux per surface area, the spot size is estimated to be $(2 \times 5) \,\mathrm{mm^2}$. By assuming single photon absorption, no additional parasitic absorption due to e.g. interface defect states or thin film interference, and the UV-source being the only light source, the QFLS can be calculated by equation 6.1 [15], with $k_{\rm B}$, T and q being the Boltzmann constant, the



ab-Figure 6.8: (a)sorption coefficient of C_{60} and CsMAFA [211]. The colored crosses in panel (a) mark the photon energies for which the normalized photon flux is shown in (b) for C_{60} and (c) for CsMAFA, each vs. the depth in the respective film. The horizontal lines indicate the penetration depth of 1/e.

temperature and the elementary charge, respectively.

$$QFLS = \frac{k_B T}{q} \ln \left(\frac{\Phi_0 \left(E_{Ph} \right) \cdot \exp\left(-\alpha_{C_{60}} \left(E_{Ph} \right) \cdot d_{C_{60}} \right) \cdot PLQY \cdot q}{J_{0,rad}} \right)$$
(6.1)

The QFLS thus scales with the logarithm of all charges generated in the absorber relative to the dark saturation current, which is determined by the radiative thermal equilibrium current density, $J_{0,rad}$ and the photoluminescent quantum yield (PLQY) as $J_0 =$ $J_{0,rad}/PLQY$. $J_{0,rad}$ depends on the specific perovskite and is calculated by integrating the black body radiation multiplied with the absorptivity (obtained by EQE measurements) from zero to infinity [209]. For the herein used perovskite composition a $J_{0,\text{rad}}$ of $6 \cdot 10^{-21} \,\mathrm{Am^{-2}}$ is obtained [210]. Stolterfoht *et al.* obtained a similar dark saturation current for the same perovskite composition and similarly processed layers with $6.5(1.0) \cdot 10^{-21} \,\mathrm{Am^{-2}}$ [125]). As $J_{0,\mathrm{rad}}$ is dominated by the perovskite itself the small influence by the covering C_{60} is neglected here [125]. For estimating the contributing charges (numerator in the logarithm) first, one needs to consider the photon flux reaching the perovskite layer and thus calculate the parasitic absorption in the C_{60} top layer, which depends according to the Lambert-Beer law exponentially on the product of layer thickness, $d_{C_{60}}$ and energy dependent absorption coefficient, $\alpha_{C_{60}}(E_{\rm Ph})$. Both absorption coefficients of the perovskite and the C_{60} as investigated here are obtained by modeling the complex refractive index to spectroscopic ellipsometry measurements for a photon energy of up to 6 eV, which was performed by Alvaro Tejada and is shown in Figure 6.8(a) [211].

As α varies with the photon energy, the normalized photon flux shown for three exemplary values (3.7 eV, 4.5 eV and 5.9 eV) in Figure 6.8(b) and (c) for C₆₀ and CsMAFA, respectively. The characteristic penetration depth at 1/e for these photon energies varies from 20 to 40 nm for C₆₀ and is around 30 nm for CsMAFA.

Next, one needs to estimate the PLQY, thus the percentage of radiatively recombining charge carriers relative to all absorbed photons. The PLQY depends on the recombination dynamics of the charge carriers generated in the absorber material and especially the recombination at the interfaces. With the high energy photons used in the near-UV



Figure 6.9: (a) Calculated quasi Fermi level splitting (QFLS) in a CsMAFA absorber with a varying thickness of a C_{60} overlayer. The photon flux of the Xe-lamp, used for NUPS and CFSYS measurements, which reaches the perovskite layer is considered (hence taking parasitic absorption into account). A different PLQY is assumed for the CsMAFA with and without C_{60} . Furthermore, a detailed discussion of the calculation can be found in the main text. The colored arrows indicate the selected photon energies, for which in (b) the QFLS in the CsMAFA for varying thickness of the C_{60} top layer is shown. Note, that the plotted QFLS does start at $d(C_{60}) = 1 \text{ nm}$.

PES measurements, charge carriers are generated predominantly close to the front surface. As the interfaces have been found to significantly decrease the PLQY, this detrimental effect can be enhanced compared to illumination conditions of the AM1.5 spectrum, where photogeneration is more homogeneous throughout the film. For the herein investigated perovskite composition it was shown that the interface with C₆₀ decreases the PLQY from 1.4% for the bare perovskite by almost two orders of magnitude to around 0.038% [125]. To account for the surface near charge carrier generation, a factor of 0.1 is further estimated and considered for the PLQY under the present measurement conditions. In order to obtain more accurate results, the PLQY under the exact measurement illumination conditions could be measured. However, as the goal here is a rather rough estimation, a PLQY of $1.4 \cdot 10^{-3}$ and $3.8 \cdot 10^{-5}$ was used as approximation for bare perovskite and samples with C₆₀ top layer, respectively.

As discussed in the methods section 3.1.5, the photon flux provided by the Xe-lamp varies with the photon energy. In Figure 6.9(a), the estimated QFLS with the above mentioned considerations is shown for the bare perovskite and with different C₆₀ layer thicknesses and for the specific, energy dependent photon flux. In the bare perovskite a QFLS between 874 meV (at $E_{\rm Ph} = 5.9 \,\mathrm{eV}$) and 970 meV (at $E_{\rm Ph} = 3.7 \,\mathrm{eV}$) is estimated. Due to the lower PLQY, the estimated QFLS with C₆₀ is significantly lower and for e.g. 20 nm C₆₀ it varies from 751 meV (at $E_{\rm Ph} = 5.9 \,\mathrm{eV}$) to 862 meV (at $E_{\rm Ph} = 3.7 \,\mathrm{eV}$).

For the three selected photon energies indicated as colored arrows in 6.9(a), the max-

imum QFLS depending on the C₆₀ film thickness (from 1 nm to 60 nm) is shown in Figure 6.9(b). The QFLS linearly decreases with the layer thickness of C₆₀, e.g. for 4.5 eV from 845 meV with almost no parasitic absorption (1 nm C₆₀) to 832 meV for parasitic absorption in 20 nm C₆₀. The slope of the decrease depends again on $\alpha(\text{E}_{\text{Ph}})$.

In the case of perfect contacts, the QFLS is equal to the here obtained SPV. For measuring a CFSYS spectrum, the photon energy is varied and thus also the photon flux impinging on the sample varies throughout the measurement. Hence, the SPV in the sample might change while varying the photon energy for measuring the CFSYS spectrum, which can lead to a squeezed/stretched spectrum. With a work function of around $4.5 \,\mathrm{eV}$, photons with an energy of around $4.5 \,\mathrm{eV}$ excite the electrons close to the Fermi edge. For higher photon energy (probing the valence band region) a lower photon flux also leads to a lower QFLS as compared to the photons probing the Fermi edge. The extreme parts of the spectrum are thus stretched. As the valence band/HOMO edge is always obtained with roughly the same photon energy, compared in between different samples, the error due to varying illumination conditions is negligible. When comparing different energetic positions e.g. the Fermi edge and the valence band maximum of CsMAFA, which have an energetic distance of around 1.5 eV, a systematic overestimation of up to 60 meV might be needed to consider. These considerations show, how the obtained spectra need to be evaluated with great care and a detailed understanding of the underlying processes is required. The actual SPV can however deviate substantially from the induced QFLS, which will be discussed in more detail in the next sections.

6.4.2 Near UV-illumination induced SPV in C60 with/without absorber

After evaluating the maximum illumination induced voltage in the perovskite absorber by the QFLS, here the actually observed SPV as indicated in Figure 6.7, i.e. $E_{\rm F}^{*} - E_{\rm F,ITO}$, will be discussed.

Two different layer stacks are compared: i) a $50 \text{ nm } \text{C}_{60}$ thin film as also discussed in the previous section (glass/ITO/C₆₀(50 nm)), and ii) $20 \text{ nm } \text{C}_{60}$ in a full single junction solar cell like stack (glass/ITO/MeO-2PACz/CsMAFA/C₆₀(20 nm)), including the SAM MeO-2PACz as hole-selective contact and the CsMAFA as absorber.

In Figure 6.10 the spectra of the HOMO and band gap region of the two investigated layer stacks, i.e. glass/ITO/C₆₀ and glass/ITO/MeO-2PACz/CsMAFA/C₆₀ are compared a) measured with near-UV PES methods and b) measured with He-UPS. These spectra are shown relative to the contacted Fermi level, $E_{\rm F,ITO}$, i.e. on the binding energy scale. Hence, the shift of the modeled Fermi edge, $E_{\rm F}^{*}$, indicates the SPV.

For the near-UV based techniques, the bare C_{60} film on ITO is shown in orange (CF-SYS) and purple (NUPS) and the C_{60} layer deposited in the solar cell relevant layer stack is shown in dark yellow (CFSYS) and green (NUPS). For the solar cell-like device stack, the whole spectrum is found to be shifted by several hundreds of meV towards higher



Figure 6.10: Comparison of PES measurements of C_{60} with 50 nm thickness of glass/ITO and with 20 nm thickness on glass/ITO/HTL/CsMAFA/C₆₀, measured by (a) CFSYS and NUPS, and (b) He-UPS. The spectra are aligned to the ITO substrate Fermi level, $E_{F,ITO}$, contacted during the measurement and thus on conventional binding energy scale. The hole spectra, thus also the HOMO-edge, E_{HOMO} , shift due to a measurement induced surface photovoltage (SPV) when comparing both layer stacks.

energies. Two important energetic positions are indicated: $E_{\rm HOMO}$ and the surface Fermi level, $E_{\rm F}^{*}$, which was obtained by fitting a sigmoidial Boltzmann function to the observed Fermi edge as in section 5.3.2. For the ITO/C₆₀ layer stack $E_{\rm F}^{*}$ is found at -149 meV, thus slightly below $E_{\rm F,ITO}$, whereas for the solar cell like layer stack $E_{\rm F}^{*}$ is found 596 meV above $E_{\rm F,ITO}$. The total shift of 745 meV is observed similarly for $E_{\rm HOMO}$. The slightly negative value for the Fermi edge of ITO/C₆₀ can probably be attributed to charging, whereas the significant shift towards positive values is a result of the illumination induced QFLS.

For both layer stacks measured by He-UPS, and shown in Figure 6.10(b), an energetic shift of $\Delta E_{\text{HOMO}} = 1.13 \text{ eV}$ towards higher energies is observed for C₆₀ with the solar cell device stack underneath, as compared to C₆₀ on ITO. This is in the range of the QFLS reached at one sun illumination for a similar layer stack [125], and by far exceeds the SPV observed during near-UV measurements. However, since the high noise floor prohibits the direct observation of the DOS at the Fermi edge, it is not possible to give any reliable energetic positions relative to the relevant (surface) Fermi level. As E_{HOMO} for the ITO/C₆₀ sample measured by He-UPS is similar as found by CFSYS, no stronger charging than -145 meV needs to be expected for the ITO/C₆₀ sample measured by He-UPS. Hence, the observed shift is probably indeed due to a strong SPV of the order of more than 1 eV. Note, that for the near-UV measurements, the ionization gauge used to measure the pressure in the vacuum chamber has been turned off, to ensure as low background illumination as possible, while it has been left on for all He-UPS measurements, which could add some minor additional photon flux. However, the additional SPV is more likely to be attributed to the different measurement illumination conditions. For the high energy photons used in He-UPS, each photon might excite several charge carriers. However, as the illumination conditions of the helium gas discharge lamp are not investigated in more detail, a calculation as shown for the Xenon gas pressure lamp has not been performed. For the evaluation of the energetic positions, the undefined shift prohibits the systematic evaluation of the obtained He-UPS data.

Since the SPV shifts the whole DOS, including the core levels, it can also be investigated by evaluating the energetic shifts of the core levels observed by XPS. However, the illumination conditions during the XPS measurement are again different compared to He-UPS and near-UV PES. One option to circumvent this problem, when only He-UPS is available and the DOS at the Fermi edge is below the detection limit of the specific system, would be to compare energetic positions, e.g. the HOMO-edge or core levels, measured in the dark vs. measured with a *known* intensity of bias light, as presented e.g. by Hellmann *et al.* [175]. In their study the SPV for a closely related layer stack is found to be around 800 meV for 1 sun illumination, which fits well with the observations here. Additionally, to prevent the sample surface from charging an electron gun can help to refill a potentially charged sample surface with electrons. Another possible way to investigate the illumination induced SPV in He-UPS is to attenuate the impinging photon flux significantly and observe the variation in the energetic positions, such as in the valence band maximum [174].

Using the HOMO-edge, obtained for 50 nm C₆₀ on ITO and 20 nm C₆₀ in the full celllike stack (see Figure 6.10(a)) and the valence band edge of the perovskite, taken from chapter 5 (see Figure 5.4), we are able to draw the band alignment of both layer stacks under measurement conditions, as shown in Figure 6.11. Since the electron Fermi level at the front surface is directly visible with the Fermi edge, the energetic positions can be aligned with respect to $E_{\rm F}^*$. Taking this correction into account, the energetic positions found for both layer stacks match very well with $E_{\rm HOMO} = -1.86 \,\text{eV}$ and $E_{\rm HOMO} = -1.85 \,\text{eV}$, and a work function of 4.50 eV and 4.52 eV for C₆₀ on the device stack and on ITO, respectively. This yields an ionization energy of 6.36 eV, which is good agreement with literature [196, 212].

In Figure 6.11 the energetic positions of the two different C_{60} thin film samples are given relative to $E_{\rm F,ITO}$ with the indication of $E_{\rm F}^{*}$, where the SPV, as a result of the measurement illumination induced QFLS is also indicated. The work function and VBM of the ITO as well as the SAM (MeO-2PACz) are obtained from He-UPS (measurement not shown).

In this sketch no band bending is indicated, as especially at the buried interface of MeO-2PACz and spin-coated CsMAFA, it is not possible to investigate the actual alignment by



Figure 6.11: Energy level alignment of C_{60} on glass/ITO (left) and on glass/ITO/MeO-2PACz/CsMAFA (right), determined according to the (oversimplified) Anderson rule (see section 2.2.2). Here, neither band bending nor the formation of dipoles at the interfaces is considered. The vacuum level (E_{vac}) of CsMAFA and C_{60} is determined by NUPS, the CsMAFA valence band edge (E_V), and C_{60} HOMO-edge (E_{HOMO})) are measured by CFSYS. The measurement induced surface photovoltage (SPV) is indicated as the difference between the surface Fermi level, E_F^* and the substrate Fermi level, $E_{F,ITO}$. The energetic positions of ITO and MeO-2PACz are measured by He-UPS. A more detailed analysis of the CsMAFA/C₆₀ interface can be found in section 6.5.4, Figure 6.17.

conventional PES: With spin-coating, CsMAFA cannot be deposited in layers of several nm. Hence, the difference between the vacuum levels of MeO-2PACz and CsMAFA does not necessarily imply a strong dipole at this interface. Furthermore, the actual Fermi level position in the perovskite bulk is unknown. Even though, the Fermi level at the front surface is found close to the conduction band, the bulk might still be intrinsic. In the sketch here, a preliminary alignment of the CsMAFA/C₆₀ interface is shown with the values obtained from the separated layers, thus perovskite without C₆₀ on top and with a 20 nm thick C₆₀ film. Especially, the VBM relative to Fermi level at the interface can change significantly, once there is a contact layer deposited on top, due to charge transfer and changed band bending. Thus, the herein shown energetics need to be considered carefully, as they are always obtained from the free surface of each individual layer. In the next section, the formation of the CsMAFA/C₆₀ interface will be investigated in more detail in samples with a stepwise increased C₆₀ thickness.

6.4.3 Influence of the C_{60} thickness on surface photo voltage in PES

As discussed in the previous section for C_{60} in a full single junction perovskite solar cell, the illumination during the near-UV PES measurements induces a significant SPV of several hundreds of meV. Here, the influence of the C_{60} thickness as contact layer in the sample



Figure 6.12: Surface photovoltage (SPV), obtained by the shift of the surface Fermi edge, $E_{\rm F}^{*}$, relative to the Fermi level of the contact, $E_{\rm F,ITO}$ in the CFSYS spectra of samples with different layer thickness of C_{60} ($d_{C_{60}}$) on glass/ITO/MeO-2PACz/CsMAFA with and without 1 nm LiF interlayer. for The maximum QFLS the photon flux, $\Phi_{\rm Ph}$, of the Xe-lamp, used for the measurement of the CFSYS spectra, at $E_{\rm Ph} = 4.5 \, {\rm eV}$ as calculated in section 6.4.1 is also shown for C_{60} thickness between 1 and 20 nm.

series "no LiF" and "LiF" on the measured SPV is discussed. In Figure 6.12 the obtained SPV $(E_{\rm F}^* - E_{\rm F,ITO})$ with increasing C₆₀ thickness is shown. Both sample series with and without 1 nm LiF interlayer are compared. The calculated QFLS from section 6.4.1 with the photon flux of the Xe-lamp is also shown exemplary for a photon energy of 4.5 eV.

For the bare CsMAFA samples (black dots), $E_{\rm F}^{*}$ fluctuates quite substantially around $E_{\rm F,ITO}$, from -170 meV to + 134 meV (see chapter 5). For both series, "LiF" (blue triangles) and "no LiF" (brown triangles) already the first nm of C₆₀ leads to a significant charge separation with an SPV of around 400 meV. Up to $d_{\rm C_{60}} = 10$ nm the SPV increases to 679 meV and 622 meV for "no LiF" and "LiF", respectively. This corresponds to a difference compared to the calculated QFLS of 153 meV ("no LiF") and 210 meV ("LiF"). Up to $d_{\rm C_{60}} = 20$ nm the SPV decreases again to 596-668 meV (obtained for two different samples) for "no LiF" and 568 meV for "LiF".

The steep increase of SPV for low C_{60} thicknesses can be explained by the initial formation of the contact layer. The charges generated in the bulk of the perovskite cannot accumulate at the surface if no (or only few) states are present. With increasing C_{60} thickness, the charges can be extracted and accumulate in the C_{60} , leading to the observed SPV. A minimum thickness is needed to obtain a fully closed film and thus an efficient charge extraction and high selectivity. It has been shown that already very thin layers of C_{60} of only one nm can lead to high V_{oc} and FF in solar cells [213], which indicates, that even very thin layers can lead to an efficient charge extraction. This is in accordance with the substantial SPV observed here already for very thin C_{60} thickness. The slight decrease of the QFLS for thicker C_{60} might result from increasing parasitic absorption in the C_{60} , as the trend of the calculated QFLS suggests.

The deviation between the calculated QFLS and the actual observed maximum SPV

can be attributed to several reasons: i) The QFLS might be overestimated, as it was calculated under several assumptions. First, the PLQY is very likely to deviate from the assumed values and might even be smaller than used here, second, the illumination spot size is only estimated, which effects the normalized photon flux, and third the parasitic absorption in the C₆₀ was assumed without considering interface and thin film effects; ii) Internal losses in the device stack (series resistance in the layers and across interfaces or non-radiative recombination at interfaces) decrease the externally measured voltage difference; iii) Charging of the sample surfaces would shift of $E_{\rm F}^*$ to lower energies. However, $E_{\rm F}^*$ is reasonably well reproducible, whereas charging effects usually appear to a different extent in between separate samples; and iv) The small current flow, due to photoemitted electrons from the surface is neglected in the determination of the QFLS.

The SPV with LiF interlayer shows a very similar trend as compared to "no LiF" with SPV up to 600 meV. As the LiF with its high band gap is almost transparent for the used photon energies, no further parasitic absorption needs to be considered and thus a similar QFLS can be estimated. The SPV measured by PES can be understood analogous to the open circuit voltage of a solar cell, when assuming no voltage drop across the contacts. As solar cell devices with LiF buffer layer show a higher $V_{\rm OC}$ and less non-radiative surface recombination losses [14, 17], the deviation of the calculated QFLS and the measured SPV would rather be expected to decrease for LiF containing samples. However, without metallization, charges need to accumulate in the C₆₀, which can lead to an electric field at the CsMAFA/C₆₀ interface. Different to that, in a solar cell, with metal contact, they can flow into the metal and hence a different charge balance is expected at the interface.

In this section it became apparent, that the SPV during the PES measurements is mostly limited by the contact formation with the C_{60} and the available states, where the electrons can accumulate. By assuming loss-less interfaces at the contacts, the calculated QFLS for the respective photon flux should be equal to the observed SPV. In section 6.4.1 it was shown how the photon flux depends on the photon energy for the applied Xe-lamp, which directly affects the QFLS. As discussed, this would lead to a stretch of the CFSYS spectra. However, here it is found, that the SPV is dominated by the contact properties of the C_{60} . This is further supported by the observation, that a variation of the photon flux over several orders of magnitude did not significantly affect the observed SPV for a C_{60} thickness of 2 nm as shown in the appendix A.3.

In order to account for the observed SPV all spectra and energetic positions in the following will be given relative to the surface Fermi level, $E_{\rm F}^{*}$.

6.5 Energy level alignment at the $CsMAFA/C_{60}$ interface

Considering the discussion of the density of states of evaporated C_{60} in section 6.3.1 and 6.3.2, as well as the illumination induced shift of the front surface level in section 6.4.3, here the energy level alignment at the CsMAFA/C₆₀ interface will be investigated. This is based on the modeling of the CsMAFA valence band maximum in chapter 5. The therein presented polylogarithmic model is further adapted, in order to describe the evolution of the density of states upon the C₆₀ thickness variation. The respective XPS spectra have been discussed in section 6.2. In this section, the series "no LiF", thus a stepwise variation of the C₆₀ layer thickness from 1 nm to 20 nm on the layer stack of glass/ITO/MeO-2PACz/CsMAFA will be evaluated. The effect of the thin LiF interlayer on the energy level alignment will be considered thereafter, in section 6.6. First, the evolution of the density of states in the valence band and HOMO level will be discussed qualitatively. Afterwards, the models, applied to evaluate the energetic positions such as the HOMO-edge of C₆₀ and the valence band edge of perovskite will be introduced. This modeling enables to determine the energy level alignment at the interface and additionally to directly determine the offset between the perovskite valence band maximum and C₆₀ HOMO edge.

6.5.1 Evolution of density of states with increasing C_{60} thickness

In Figure 6.13 the internal yield of a) the SECO, measured by NUPS, and b) the internal yield in the valence band region up to the Fermi edge, measured by CFSYS is shown for the C₆₀ thickness variation from 0 nm (bare perovskite) to 20 nm C₆₀. The spectra are aligned to $E_{\rm F}^{*}$ and presented with an arbitrarily chosen offset of two orders of magnitude in the internal yield between the individual spectra.

The SECO, in the NUPS spectra is evaluated with a sigmoidial Boltzmann function and the edge position is indicated as a vertical line. The full CFSYS spectra are shown in Figure 6.13(b). The perovskite valence band maximum ($E_{V,PLog,High}$ from chapter 5) is obtained by applying the combined model which will be introduced in section 6.5.2 for all samples up to 5 nm C₆₀. The HOMO-edge was obtained for samples with 5 - 20 nm C₆₀ thickness, as will be discussed in section 6.5.3.

The density of states evolves gradually from bare perovskite towards the density of states of bare C_{60} , as introduced in the previous sections. With increasing C_{60} thickness, the photoelectrons originating from the perovskite get attenuated approximately exponentially, depending on the inelastic mean free path length (IMFP) and the thickness of the covering layer. The shape of the CFSYS spectra can be divided into three different C_{60} thickness ranges: i) For a layer thickness up to 2 nm the shape of the spectrum appears mostly perovskite-like and only the density of defects in the energy region between 0 and -1 eV slightly changes. The appearance of the C_{60} HOMO-peak at around -2.5 eV is barely visible for these thin C_{60} layers; ii) For an intermediate thickness of 3 - 5 nm the square-root behavior of the perovskite valence band edges is still visible, but simultaneously the DOS of the C_{60} HOMO at around -2.5 eV increases; and iii) For 10 nm and 20 nm the shape of the parabolic perovskite band edges is not visible anymore and the typical exponentially



Figure Near-6.13: UV PES of the spectra $\rm CsMAFA/C_{60}$ interface with increasing C_{60} thickness on top glass/ITO/MeOof 2PACz/CsMAFA. (a) NUPS measurement of the secondary electron cut-off (SECO) region. (b) CFSYS spectra with the position of the perovskite valence band maximum, $E_{\rm V,PLog,High}$ and C_{60} HOMO level position (see section 6.5.2). Furthermore, the C₆₀ HOMO-edge position, $E_{\rm HOMO}$ is indicated (see section 6.5.3). The spectra are aligned to the surface Fermi level, $E_{\rm F}^{*}$, and shown with offsets of two orders of magnitude in the internal yield. The energetic positions are given in units of eV.

decreasing density of gap states above the HOMO-edge starts to arise, from -1.8 to 0 eV. However, the gap states are enhanced for the $10 \text{ nm } C_{60}$, while for $20 \text{ nm } C_{60}$ the spectrum appears to be very similar to the obtained from of $50 \text{ nm } C_{60}$ on ITO (see also Figure 6.10).

6.5.2 Combined modeling of the density of states of CsMAFA and C₆₀

In chapter 5 (section 5.3.2), a model to describe the two highest valence band edges of the CsMAFA has been proposed and applied to the density of states of the bare perovskite spectra. Here, step by step C_{60} is deposited on top of the perovskite, which manifests in gradually changing spectra as shown in Figure 6.13. The photoelectrons of a CFSYS spectrum originate from depths of up to 5-10 nm. However, they are attenuated by the overlayers, which they have to pass on the path from their excitation origin to the sample surface (second step of the photoionization process, see also methods section 3.1.1). In the most simplistic picture, both the density of states of the CsMAFA valence band and the C_{60} HOMO are superimposed. However, additional contributions to the spectra, e.g. interface defect states can appear upon the formation of the interface. With the following model, the spectra, which contain information of the CsMAFA and the C_{60} as well as their interface can be described. Note, that this high information depth, and thereby the accessibility of buried films and interfaces, is a fundamental difference to He-UPS, where



Figure 6.14: Exemplary model fit of the density of occupied states, $N_{\rm OCC}$, to a CFSYS spectrum, obtained for a 5 nm C₆₀ thin film on ITO/MeO-2PACz/CsMAFA on (a) semi-logarithmic, (b) linear and (c) zoomed linear scale. The spectra are aligned to the surface Fermi level $E_{\rm F}^{*}$. The model consists of two parabolic band edges with an exponential band tail, representing the perovskite valence band edges (*VBM*, *PLog*, *Low* and *VBM*, *PLog*, *High*), a Gaussian distribution, representing the C₆₀ HOMO and three Gaussian distributions, accounting for the occupied states in the band gap. The $N_{\rm occ}$ is convolved with the system transfer function.

the information depth is around $0.5 - 1 \,\mathrm{nm}$ and spectra measured at samples with even thin $1 \,\mathrm{nm} \,\mathrm{C}_{60}$ thickness contain almost no information about the underlying CsMAFA.

Two different models have been applied depending on the C_{60} layer thickness.

- For a C_{60} layer thickness of ≥ 10 nm, the spectra were modeled with four Gaussian distributions, with the energetically lowest one representing the HOMO level of C_{60} and the others representing occupied gap states. The perovskite valence band edges are assumed to not significantly contribute to the overall measured DOS, as the IMFP of the photoelectrons is smaller than the C_{60} thickness.
- Up to $5 \text{ nm } C_{60}$ thickness, the perovskite valence band edges are still contributing significantly to the total DOS. Thus, a combined model for the perovskite valence band edges and the evolving C_{60} HOMO peak is needed. This model will be introduced in the following.

For the samples with a C_{60} layer thickness up to 5 nm, the model applied for bare perovskite is here further extended by a Gaussian distribution at around -2.5 eV with respect to E_F^* . Thus, the herein applied model combines the two parabolic band edges, representing the two highest valence band edges of the perovskite, the Gaussian shaped HOMO level, representing C_{60} and three Gaussian distributions, representing occupied states in the band gap. An exemplary fit for the sample with 5 nm C_{60} is shown in Figure 6.14 on a (a) semi-logarithmic, (b) linear and (c) more detailed linear scale.

In general, the aim was to use as few as possible restrictions on the fitting model. However, to obtain a physically reasonable fit, some constraints needed to be set: The energetic distance between $E_{\rm V,PLog,High}$ and the HOMO peak center was set to a range of 0.9-1.2 eV, the FWHM of the Gaussian peak representing C_{60} was limited to 0.45 eV and the three Gaussian distributions representing the gapstates D_{it} were energetically distributed throughout the band gap with the same FWHM for all three of them. Furthermore, both polylogarithmic functions were interconnected with constraints close to the fitting parameters, obtained for CsMAFA in the previous chapter (see also Figure 5.4): The ratio of both amplitudes was restricted to [6;8], the energetic distance of both band edges was allowed to vary between 0.36 and 0.42 eV. The tail parameter of the parabolic band edges was set to be the same for both. Because of the increasing D_{it} especially close to the band edges, it was restricted to a maximum of 50 meV.

For the polylogarithmic model fit to the neat perovskite layers in chapter 5, it was found that the measured DOS at lower energy than $E_{\rm V,PLog,Low}$ exceeded the modeled $N_{\rm occ}$. The approximation of these energetically lower transitions by a parabolic band edge might not be valid, as they consist of several valence bands, overlapping with each other. Hence, the data range, where the model for the neat perovskite was fitted to, was cut towards lower energies, covering only the range down to just below $E_{\rm V,PLog,Low}$. However, the HOMO level of the C₆₀ is located exactly in that energy range. Hence, for very thin C₆₀ layers, states from deeper CsMAFA valence bands superimpose with the states from the C₆₀ HOMO level. For the thickness variation of C₆₀, investigated here, this implies: At 0 nm C₆₀ thickness this Gaussian only consists of perovskite related states and has an amplitude of $A_{\rm Pero}$. With increasing C₆₀ thickness, this peak additionally contains the C₆₀ HOMO level and has an amplitude of $A_{\rm HOMO}$. The stepwise increasing thickness of C₆₀ on CsMAFA is schematically depicted in Figure 6.15(a). The estimated information depth of 10 nm is indicated with the shaded rectangles.

Without considering interface effects, such as enhanced defect densities, the measured internal yield in the valence band/HOMO part of the spectrum is approximately described by the superposition of the CsMAFA valence bands and the C₆₀ HOMO level. The ratio of the amplitude of this Gaussian peak and the amplitude of the highest modeled parabolic band edge ($E_{\rm V,PLog,High}$), a_0 , is shown in Figure 6.15(b) for increasing C₆₀ thickness.

Assuming a simple superposition of both densities of states, the amplitude of the Gaussian peak is given by equation 6.2.

$$A_{\rm Gauss} = A_{\rm HOMO} + A_{\rm Pero} \tag{6.2}$$

Simple layer

As mentioned above, the intensity of photoelectrons is exponentially attenuated with their increasing depth of origin. Assuming a homogeneous layer growth, the total PES signal is thus given by a constant factor and the integral over the depth in the sample, x, from zero to infinity over the exponential weighting of a constant C, with the inelastic mean



Figure 6.15: (a) Schematically indicated information depth (white rectangle) of CFSYS measurements at the interface of CsMAFA/C₆₀ for varying C₆₀ thickness. (b) C₆₀ HOMO peak amplitude relative to the amplitude of the highest perovskite valence band edge (*VBM*, *PLog*, *High*), $a_{0,PLog}$. Both amplitudes are obtained by the combined model, as described in the main text and shown in Figure 6.14.

free path length, λ_{imfp} , and the depth x as in equation 6.3.

$$A = C \cdot \int_0^\infty \exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right) \mathrm{d}x \tag{6.3}$$

Stack of two layers

If the same λ_{imfp} for both materials, C₆₀ and CsMAFA, is assumed, the contribution of the different layers can be estimated in dependence on the C₆₀ layer thickness, $d_{C_{60}}$.

The contribution of the perovskite to the total amplitude of the Gaussian, is assumed to be proportional to the modeled amplitude of the highest parabolic band edge, a_0 , with a factor of C_{Pero} . The PES signal from a_0 itself is exponentially attenuated as in equation 6.3. The density of states in the Gaussian that can be attributed to CsMAFA can thus be described as in equation 6.4, depending on the covering C₆₀ layer thickness $d_{C_{60}}$.

$$A_{\text{Pero}} = C_{\text{Pero}} \cdot a_0 = C_{\text{Pero}} \underbrace{C_0 \cdot \int_{d_{C_{60}}}^{\infty} \exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right) dx}_{(6.4)}$$

$$= C_{\text{Pero}} \underbrace{C_0 \cdot \lambda_{\text{imfp}} \cdot \exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right)}_{a_0}$$
(6.5)

For the C_{60} HOMO, the amplitude can be described by equation 6.6.

$$A_{\rm HOMO} = C'_{\rm HOMO} \cdot \int_0^{d_{C_{60}}} \exp\left(-\frac{d_{C_{60}}}{\lambda_{\rm imfp}}\right) dx \tag{6.6}$$

$$= C'_{\rm HOMO} \cdot \lambda_{\rm imfp} \cdot \left(1 - \exp\left(-\frac{d_{C_{60}}}{\lambda_{\rm imfp}}\right)\right)$$
(6.7)

Finally, the amplitude ratio, as shown in Figure 6.15(b), can be modeled by inserting equation 6.6 and 6.4 into equation 6.2. The C₆₀ thickness is assumed to be equal to the nominal layer thickness, which leaves C_{Pero} , C_{HOMO} and λ_{imfp} as free variables.

$$\Rightarrow \frac{A_{\text{Gauss}}}{a_0} = C_{\text{Pero}} + \underbrace{\frac{C'_{\text{HOMO}}}{C_0}}_{C_{\text{HOMO}}} \cdot \frac{\left(\exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right) - 1\right)}{\exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right)} \tag{6.8}$$

$$= C_{\text{Pero}} + C_{\text{HOMO}} \cdot \frac{\left(\exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right) - 1\right)}{\exp\left(-\frac{d_{C_{60}}}{\lambda_{\text{imfp}}}\right)}$$
(6.9)

Equation 6.9 was fitted to the ratio of the modeled $A_{\text{Gauss}}/a_{0,\text{PLog}}$ versus the C₆₀ layer thickness, shown in Figure 6.15(b). The obtained λ_{imfp} with 3.4 (4) nm is in good agreement with the 5-10 nm assumed as information depth for CFSYS, since up to a depth of around three times λ_{imfp} one can expect to observe a significant contribution of the photoelectrons to the PES signal.

6.5.3 HOMO-edge position of C_{60} with increasing thickness

Furthermore, to evaluate the HOMO-edge as discussed in section 6.3.1, E_{HOMO} was determined by the intercept of a linear extrapolation of the HOMO peak and a linear background. This modeling is additionally shown in the exemplary fitted spectrum in Figure 6.14.

In Figure 6.16 the CFSYS spectra as obtained for both series a) "no LiF" and b) "LiF" are presented on a linear scale. All spectra are aligned to the surface Fermi level $E_{\rm F}^{*}$ and an arbitrary offset is chosen for the internal yield. The determination of the HOMO-edge is shown for samples with 3 nm or higher C₆₀ layer thickness for both series. However, for 3 nm C₆₀, it is well visible that the fit relies on very few measurement points. Furthermore, the contribution of the perovskite valence bands still has a significant influence on the slope of the linear extrapolation. This is clearly visible by the large amount of occupied states above the linear fit. Hence, the HOMO-edge can only be reliably determined for a C₆₀ layer thickness above 5 nm. The same holds for the "LiF" series, which will be evaluated in section 6.6.



Figure 6.16: CFSYS specof tra C_{60} with varying thickness on glass/ITO/MeO-2PACz/CsMAFA (a) without and (b) with a 1nm LiF interlayer between CsMAFA and C_{60} on a linear scale. The spectra were aligned to the surface Fermi level, $E_{\rm F}^{*}$, and an arbitrary offset in the internal yield is chosen for different C_{60} thickness. The obtained energetic position of the HOMO-edge is shown in units of eV.

6.5.4 Energetic positions at the CsMAFA/C₆₀ interface

The energetic positions obtained as discussed in the previous sections, are summarized in Figure 6.17. All obtained energetic positions from the combined modeling, the work function, and the HOMO-edge are presented with respect to the surface Fermi level, $E_{\rm F}^{*}$. It is important to consider that each thickness step actually describes a different interface, where especially the charge transfer and thus the band bending might be different. Hence, Figure 6.17 shows the stepwise evolution of the interface and not depth profile of the perovskite/20 nm C₆₀ layer stack. These homo edge positions, as obtained here are further indicated as vertical lines in the full NUPS and CFSYS spectra in Figure 6.13(a) and (b).

The VBM for bare perovskite in the chapter 5 was found to vary between -1.37 eV and -1.50 eV. Here, one sample without C_{60} was chosen (sample 4, with $E_{V,PLog,High} =$ -1.37 eV), and was fitted again with the adjusted model, covering the DOS towards lower energies. With this $E_{V,PLog,High} = -1.36$ eV was obtained, and thus in good agreement with the position obtained without the additional Gaussian. Once C_{60} is deposited on top, the VBM of the perovskite is found to shift towards the Fermi level E_F^* by around 150 meV, as E_V is then found at -1.23 eV. Note, that sample 4 was the sample showing the energetically highest VBM among all CsMAFA samples investigated in chapter 5. Hence, compared to the samples with energetically lower VBM the shift towards the surface Fermi level is even larger. As discussed above, with C_{60} on top of the perovskite, the perovskite valence band maximum can be fitted up to 5 nm C_{60} . With the first nm of C_{60} , $E_{V,PLog,High}$ is found at -1.23 eV and with increasing C_{60} thickness, it decreases to -1.35 eV. With the band gap energy of the investigated perovskite composition being $E_g = 1.63$ eV, also the conduction



Figure 6.17: Energetic positions of the $CsMAFA/C_{60}$ interface with varying thickness of C_{60} and with respect to the surface Fermi level, $E_{\rm F}$ The work function, Φ , is obtained by NUPS. The valence band edge $(E_{\rm V})$ of the CsMAFA on glass/ITO/MeO-2PACz (black dots), the valence band edge of CsMAFA, obtained from samples with $1-5 \,\mathrm{nm} \,\mathrm{C}_{60}$ on the CsMAFA (blue crosses) and the C_{60} HOMO-edge (E_{HOMO}), obtained from samples with $5-20 \text{ nm } C_{60}$ (orange crosses) are shown and obtained by modeling CFSYS spectra as discussed in the main text. The thick lines indicate band positions that are calculated from the optical band gap of the perovskite and C_{60} .

band edge of the perovskite can be calculated and is indicated as thick, light blue line in Figure 6.17.

The variation of $E_{\rm V,PLog,High}$ with the C₆₀ thickness can be attributed to different charge balance between the perovskite and the contact layer, which can result in a different band bending and is well conceivable considering the changing SPV with varying C₆₀ layer thickness.

The work function for the bare perovskite layer is found to be 4.48 eV. For these relatively thin perovskite layers of several hundreds of nm, the work function can still be considered as strongly influenced by the substrate work function [150, 214, 215], since the Debye length is larger than the layer thickness [216].

For the first nm of C_{60} thickness the work function is slightly enhanced with 4.57 eV. For increasing C_{60} it gradually decreases to 4.5 eV within the first 3 nm and stays at that value up to 20 nm C_{60} . Thus, for the first nm, C_{60} is depleted. Note, that from PES it cannot be seen if this depletion persists close to the interface also for thicker C_{60} .

The HOMO-edge is found at -1.91 eV for 5 nm C₆₀ and stays within the uncertainty up to 20 nm, where 1.89 eV is obtained. Thus, an ionization energy of around 6.4 eV is obtained for the C₆₀, which is in good agreement with literature [187]. The HOMO-edge positions of C₆₀ vary substantially in between different studies, where values between -1.95 eV and -1.4 eV are found [187, 189, 196]. The herein obtained values for E_{HOMO} are thus among the energetically lower reported positions, which might be possible to explain by an unrecognized SPV in literature reports, where higher HOMO-edge positions are observed in full device stacks.

In general, the obtained energetic positions have several sources of uncertainty, e.g. the range of the fitted data, the fitting error itself, but also the "stretching" of the spectrum, due to varying photon flux. For the edge positions (SECO and Fermi edge), modeled by a sigmoidial Boltzmann function, an uncertainty of 50 meV was considered throughout the whole C_{60} thickness variation. For the VBM position of the perovskite obtained by the combined model as well as for the HOMO-edge, an uncertainty of 50 meV was considered. For the HOMO peak, the energetic position becomes more reliable with increasing C_{60} thickness. For a C_{60} thickness of up to 3 nm the peak position of the Gaussian is less defined, while the shape gets more pronounced and from 5 nm C_{60} thickness on. Thus 100 meV and 50 meV error are considered for a C_{60} thickness up to 3 nm and from 5-20 nm, respectively. As all energetic positions here are given relative to the fitted E_F^* the propagation of the error has been considered accordingly.

 C_{60} is applied as electron transporting layer, thus especially the energy level alignment of the CsMAFA conduction band and the C_{60} LUMO-edge is of interest. However, as by conventional PES only occupied states are accessible, the optical band gap needs to be considered carefully in order to obtain the LUMO-edge position. The optical absorption of C_{60} shows strong sub band gap absorption, which is consistent with the high density of gap states, observed by CFSYS. In the literature the range of reported band gap energies for C_{60} varies largely between 1.67 and 2.3 eV. In general the determined band gap energy depends on the experimental method, e.g. by a Tauc-plot of the absorption coefficient obtained from spectroscopic ellipsometry measurement data 1.67 eV is found [217] and by a combination of PES and inverse PES (IPES) up to 2.3 eV is reported [189]. However, even measured with the very same method, such as PES and IPES, substantially varying band gaps are obtained by Schulz *et al.* with $2.3 \,\text{eV}$ for C₆₀ on glass/ITO/NiO_x/MAPbI₃ [189], or Wolff *et al.*, who reported $1.73 \,\text{eV}$ for C₆₀ on glass/ITO/PTAA/MAPbI₃ [15]. These differences might be attributed to different SPV and thereby an unrecognized shift of the surface Fermi level due to either different measurement conditions or the different hole transporting layers. Furthermore, compared to PES the measurement conditions are very different in IPES, where the sample is not illuminated by photons, but electrons impinge on the sample. To combine both methods, IPES and PES, without considering the potentially different SPV in both experiments can thus be a large error source of the determined band gap energy. Here, the optical band gap of C_{60} was determined by a combination of spectroscopic ellipsometry and reflection and transmission measurements and is found to be 1.92 eV (see Appendix A.5 [211]). As the surface Fermi level is directly observable in CFSYS, the HOMO-edge can be directly evaluated with respect to the surface Fermi level and the position of the LUMO-edge can be determined by considering this optical band gap. The accordingly obtained LUMO-edge is indicated as orange line in Figure 6.17. The Fermi level is thus found to be very close/directly at the LUMO-edge, in accordance with the electron conducting behavior of C_{60} . Note, that the optical band gap in general deviates and is usually found to be smaller than the electrical (fundamental) band gap in organic semiconductors. The reason is the additional electron-hole pair binding energy of an excited (and not ionized) state in optical spectroscopy [218]. Hence, by using the

optical band gap energy, the LUMO-edge is potentially estimated too close to the Fermi level.

6.5.5 Determination of band offsets at the $CsMAFA/C_{60}$ interface

From the sample with an intermediate C_{60} thickness of 5 nm the offset between the perovskite valence band and the C_{60} HOMO-edge, ΔE_V , can be directly determined. Conventionally, heterojunction offsets are determined by considering the band edge positions obtained from the free surfaces of the individual materials and assuming the Anderson rule for the energy level alignment. However, at the interface, e.g. due to charge redistribution, interface states and thus Fermi level pinning the bands might align differently than expected by the energetic positions measured at the individual surfaces. Figure 6.17 shows the modeled band edge positions of CsMAFA and C₆₀. For the sample with 5 nm C₆₀ thickness, both, the C₆₀ HOMO-edge and the CsMAFA valence band maximum can be modeled. The fitted CFSYS spectrum is shown in Figure 6.14. From this ΔE_V can be directly determined.

 $\Delta E_{\rm V}$ between the highest modeled perovskite valence band edge $E_{\rm V,PLog,High}$ and $E_{\rm HOMO}$ of the C₆₀ is found to be 0.55 eV. With the band gap energy of the investigated perovskite composition being 1.63 eV and the optical band gap energy of C₆₀ of 1.92 eV, also the conduction band offset, $\Delta E_{\rm C}$ can be estimated to 0.26 eV. Hence, a type 2 heterojunction with a staggered gap is obtained.

The high valence band offset ensures an efficient hole blocking, while electrons can pass across the interface. However, the large "downwards" conduction band offset limits the open circuit voltage of the final device, which is in line with the observations by Stolterfoht *et al.* [125]. For a closely related layer stack with different hole transporting materials, they report that the perovskite/ETL interface clearly limits the obtained open circuit voltage of investigated solar cells. Note again, that the actual electrical conduction band offset could be somewhat smaller, as the optical and not the electrical band gap energy of C_{60} is considered here.

With MAPbI₃ as absorber on NiO_x (thus p-type) substrate, Schulz *et al.* found a slightly larger valence band offset to C₆₀ with 0.7 eV. Furthermore, they determined the conduction band offset by IPES to 0.1 eV [189], which is in good agreement to the herein obtained value, as they can directly refer to the electrical band gap energy of C₆₀. As discussed above, the here obtained energetic positions of E_{HOMO} for the C₆₀ are amongst the higher ones compared to literature, which might by due to unrecognised varying SPV in different studies. With the additional uncertainty about correctly evaluating the perovskite valence band edge as elaborated in chapter 5, also the estimated band offsets in literature need to be considered with care. E.g. Hellmann *et al.* found a valence band edge position of -1.43 eV below $E_{\rm F}$ for MAPbI₃ on NiO_x and a HOMO-edge of -1.51 eV for C₆₀ on top of this layer stack. Thus, they report a valence band offset of only 0.08 eV and by assuming

a significantly lower band gap energy for C_{60} (1.67 eV) a conduction band offset of 0.01 eV [175]. Especially, with the small valence band offset, a very poor hole blocking would result and thus no efficient carrier selectivity can be reached, which is contradictory to the good solar cell device performance, obtained for the same layer stack. The herein obtained results especially differ compared to literature in the edge position of the C_{60} HOMO, which is $\approx 0.4 \text{ eV}$ lower compared to Hellmann *et al.* [175]. Even though in their study, measurements under "dark" and "light" conditions are compared, an unrecognised SPV in the photoactive layer stack can still shift the surface Fermi level to higher energies and thus the HOMO-edge position might appear closer to the reference Fermi level.

6.6 Influence of LiF as interlayer at the $CsMAFA/C_{60}$ interface

Ultra-thin LiF layers of several Angstrom to nm thickness are often used in organic and perovskite based opto-electronic devices, such as solar cells or light emitting diodes (LED) for various purposes.

In organic devices, LiF has been most commonly used in combination with an aluminium cathode as LiF/Al double layer, leading to lower electron-injection barriers and thus lower operational voltages in LEDs [219, 220], and increased fill factor and open circuit voltages in organic solar cells [221]. A second very beneficial effect of LiF buffer layers in the double layer cathode is the improved device stability and protection against moisture [222, 223]. Because of the insulating nature of LiF, very thin layers are required, while the protection against environmental influences would benefit from thicker layers. Also nano-composites of C_{60} :LiF were investigated, and yielded well improved device stability [212].

Inspired by these findings for organic solar cells, similarly LiF/Al cathodes were applied in metal halide perovskite based solar cells and found to enhance the FF and open circuit voltage with e.g. the fullerene-derivate PCBM ([6,6]-phenyl-C₆₁-butyric acid methyl ester) as electron transport layer beneath [126], or more complex triple cathode buffer layers including PCBM/C₆₀/LiF layer stacks [224]. Especially, with the application of C₆₀ as electron transporting layer, LiF has been shown to form an ohmic contact to Al [225, 226], however not yielding an ohmic contact when being inserted e.g. between C₆₀ and Ag [227]. Among several Alkali-fluorides, LiF was found to uniquely lead to an ohmic contact as electron injection layer between C₆₀ and aluminium, as the size of the specific vapor phase monomers determines, whether they fit into the octahedral void of C₆₀ [228]. About the actual underlying mechanism of LiF as buffer layer underneath an Al-cathode several explanations have been discussed, as summarized by Quintero-Bermudez *et al.* [190]. With a combined experimental and theoretical study, they claim that the LiF might dissociate with the Li⁺ ions lowering the Schottky barrier height in the cathode and thus improving electron injection in LEDs and F^- ions increasing the electron density in the anode material and thus decreasing the barrier width.

Similar to thin tunnel oxide passivated silicon based solar cells (TOPCon) [229], different passivating buffer layers were tested for metal halide perovskite solar cells. In p-i-n devices e.g. polystyrene [222] or choline chloride [230] were demonstrated to passivate defects and thus lead to reduced non-radiative recombination at the electron selective interface. With ultra-thin LiF layers at the p-contact in combination with PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) in LEDs the device efficiency could similarly be increased by suppressing trap assisted recombination at the interface [231]. Furthermore, LiF has been investigated as an additive to mixed cation mixed halide perovskites and found to passivate defects at grain boundaries and interfaces to charge selective layers [232]. Applied as passivating tunneling layer LiF is an effective option to increasing the open circuit voltage by reducing non-radiative interface losses by around 35 meV for triple cation perovskite [14]. With this, high efficiency devices with improved open circuit voltage by around 50 meV [17] have been reported.

While LiF/Al as double cathode layer is well established, the positive effect of LiF as interlayer between metal halide perovskite and C_{60} on the device performance is not yet understood and an important question of ongoing research. Since the device performance stability deteriorates [17] with the implementation of this LiF interlayer, an understanding of the exact mechanisms can guide the search for other interlayers, which might lead to similarly beneficial effects, but do not enhance the degradation processes.

In this section, the influence of a thin 1 nm LiF interlayer on the valence band/HOMO density of states and energetic positions, such as the band edges and work function of the interface between CsMAFA and C_{60} will be investigated. To that end the two series, already described in the introduction of this chapter, with a variation of the C_{60} layer thickness from 1 nm to 20 nm on the layer stack of glass/ITO/MeO-2PACz/CsMAFA/ either with or without LiF interlayer between the CsMAFA and the C_{60} will be compared. The series with LiF interlayer is referred to as "LiF" and without interlayer as "no LiF".

6.6.1 Perovskite valence band maximum and C₆₀ HOMO-edge position with/without LiF interlayer

In order investigate the influence of LiF on this specific interface, the measured internal yield for the complete thickness variations of C_{60} for both series "no LiF" and "LiF" are directly compared in Figure 6.18 with (a) the SECO (measured by NUPS) and (b) the entire valence band spectra (measured by CFSYS). The data for the "no LiF" series is the same as shown in Figure 6.13 and again all spectra are aligned to the surface Fermi level, $E_{\rm F}^*$.

Qualitatively, the shape of the DOS in the valence band region is very similar, when



Figure 6.18: (a) NUPS CFSYS and (b) spectra of varying C_{60} thickness on glass/ITO/MeO-2PACz/CsMAFA with 1 nm LiF as interlayer ("LiF", full symbols and solid lines) and without ("no LiF", open symbols and dashed lines). The secondary electron cutoff (SECO), the perovskite maximum valence band $(E_{\rm V,PLog,High})$, and the C₆₀ HOMO-edge $(E_{\rm HOMO})$ are indicated. c) Internal vield from the measured CFSYS spectra subtracted by the modeled valence band edges of CsMAFA and the C_{60} HOMO.

comparing both layer stacks. However, for thin layers up to $3 \text{ nm } C_{60}$ the CFSYS spectra as well as the SECO are shifted towards lower energies. For the modeling of the "LiF" series, the same model as introduced in section 6.5.2 is used for a C₆₀ layer thickness of up to 5 nm. The spectra of samples with C₆₀ thickness of 10 and 20 nm are modeled without the polylogarithmic model for the perovskite valence band edges and thus only with the four Gaussian distributions, as described above for the "no LiF" series. The modeling of the HOMO-edge by a linear extrapolation for both series was already presented above in Figure 6.16(b). The obtained energetic positions (SECO, $E_{V,PLog,High}$ and E_{HOMO}) are shown in Figure 6.18(b) with dashed lines ("no LiF") and solid lines ("LiF").

Figure 6.18(c) shows the measured internal yield subtracted by the modeled perovskite band edges, $E_{\rm V,PLog,High}$ and $E_{\rm V,PLog,Low}$, as well as the Gaussian peak, representing the C₆₀ HOMO and energetically lower perovskite valence bands. Thus, it only includes the density of occupied states in the band gap, $D_{\rm it}$, up to the Fermi level, which are modeled by the three Gaussian distributions above the band edge and will be discussed in detail below in section 6.6.2.

The energetic positions of both series are summarized in Figure 6.19, where the work function and the perovskite and C_{60} band edges are shown in dependence of the C_{60} thickness. With the open symbols, the bare perovskite is compared to a sample with 1 nm LiF on perovskite, but without any C_{60} .

The work function of 1 nm LiF on perovskite without any C_{60} is already slightly decreased by 130 meV compared to the work function of the bare perovskite. Measured by He-UPS (and not corrected for any SPV!) a similar decrease of the work function of

130 meV is observed for this 1 nm LiF on CsMAFA, but not shown here. Note, as shown in Figure 6.12, the deposition of LiF already induces an SPV of almost 300 meV in CFSYS measurements and thus also in He-UPS a significant SPV (as discussed in section 6.4.2) is expected, which is however not considered here for the reported values, obtained by He-UPS. Furthermore, a thick (50 nm) LiF layer was deposited on CsMAFA and the obtained work function was found to be significantly decreased to 2.8 eV (He-UPS, not corrected for SPV). The higher work function of the thin LiF layer can be explained by a depletion of the thin layer, if deposited on the CsMAFA, which shows a significantly larger WF. The valence band edge of the thick LiF layer, also measured by He-UPS, was found to be at $-10.2 \,\mathrm{eV}$. Both positions obtained with respect to $E_{\mathrm{F,ITO}}$ yield an ionization energy of around 13 eV. With a LiF band gap of around 13.6 eV [233] even negative electron affinity could result [234]. For increasing thickness of LiF on Al, Shaheen et al. found a rapidly decreasing work function from $3.25 \,\mathrm{eV}$ for sub-nm thickness of LiF on Al down to $2.5 \,\mathrm{eV}$ for 13 nm LiF [235]. Thus the herein found decreased WF is in good agreement with values reported in literature. However, as the large band gap of the LiF makes the material almost transparent for the near-UV photons used for CFSYS and NUPS, the observation of the corresponding SECO is not easily possible with NUPS.

From Figure 6.19 it can further be observed that the work function for thin C₆₀ thickness up to 3 nm is decreased by around 150 meV from 4.55 eV for the "no LiF" series compared to 4.4 eV for the "LiF" series. This is accompanied by a 50 meV lower valence band edge in the perovskite for thin C₆₀ layers up to 3 nm for the "LiF" series compared to "no LiF". For "no LiF" the trend of the perovskite valence band edge, $E_{V,PLog,High}$, which can be evaluated with the thin layer of C₆₀ on top, and the work function of C₆₀ are very similar: both decrease concomitantly (dark green in Figure 6.19). For "LiF" however, the work function for thin layers of C₆₀ is following an opposite trend with increasing C₆₀ thickness as it increases from $\approx 4.4 \text{ eV}$ for 1-3 nm C₆₀ to 4.53 eV for 20 nm C₆₀ (light green in Figure 6.19).

The HOMO-edge of C_{60} is obtained for all samples with 5 nm or thicker C_{60} and found to stay around -1.9 eV for increasing C_{60} thickness, yielding an ionization energy of 6.4 eV for both series "no LiF" and "LiF". In Figure 6.19 additionally, the result of the 3 nm C_{60} layers is shown. As discussed above, the HOMO-edges for these thin layers are overestimated (thus found closer to the Fermi level than expected) as the spectra are influenced by the valence bands of the perovskite. Considering these HOMO-edges for the 3 nm C_{60} , an ionization energy of 6.3 eV would be obtained. However, if the material itself does not change, the ionization energy should not depend on the C_{60} thickness, which further supports that the 3 nm C_{60} samples cannot be used to determine the HOMO-edge by CFSYS. Note, that a hybridization of very thin layers and close to the interface could potentially indeed change the electrical configuration of the C_{60} close to the interface [236].

For $5 \text{ nm } C_{60}$ and thicker layers, the valence band maximum and HOMO-edge positions



Figure 6.19: Comparison of the energetic positions with respect to the surface Fermi level, $E_{\rm F}^*$, at the CsMAFA/C₆₀ interface with and without 1 nm LiF interlayer ("LiF" and "no LiF") for increasing C₆₀ thickness. The vacuum level (obtained by NUPS), $E_{\rm vac}$, the CsMAFA valence band maximum, $E_{\rm V}$, and the C₆₀ HOMOedge, $E_{\rm HOMO}$, (obtained by CF-SYS) are shown.

are similar for "LiF" and "no LiF". As already discussed for the CsMAFA/C₆₀ interface, the offset between the perovskite valence band and the C₆₀ HOMO-edge can be determined from the 5 nm C₆₀ sample. A slightly lower HOMO-edge of -1.94 eV for "LiF" compared to -1.91 eV for "no LiF" is obtained, which yields an offset of 0.58 eV for "LiF", whereas 0.55 eV for "no LiF" was obtained. However, this difference is statistically considering the uncertainty of the energy positions. Accordingly, the conduction band offset stays almost constant with 0.26 eV to 0.29 eV for "no LiF" and "LiF", respectively.

6.6.2 Influence of LiF at the $CsMAFA/C_{60}$ interface on the interface defect density

For evaluating the density of occupied gap states, on the one hand the spectra of the internal yield in the band gap, thus showing the distribution of the DOS over the binding energy (in Figure 6.18(c)), and on the other hand the integrated gap state density, obtained by integrating the area under the three Gaussian distributions included in the combined fitting model (in Figure 6.20) are considered. As already discussed for the modeling of the gap states in the bare perovskite in chapter 5, the number of Gaussian peaks used for fitting the DOS in the band gap is randomly chosen and thus no physical meaning is attached to that choice. The integrated area under these three Gaussian peaks (D1-D3) provides a measure of the gap state density at the forming interface per volume unit. While for the bare perovskite a normalization of the internal yield to volume units in cm⁻³ was made, for the gradually changing and superimposed spectra of CsMAFA and C₆₀, this is not straightforward. However, for each C₆₀ thickness, the integrated defect density and also the internal yield can be directly compared.

As observed from the full gap state spectra shown in Figure 6.18(c), for samples with a C_{60} thickness up to 5 nm the density of occupied gap states follows a similar shape



Figure 6.20: Integrated defect density, obtained by modeling three Gaussian distributions to the density of gap states of CFSYS spectra on CsMAFA(/LiF)/C₆₀ the interface with/without $1\,\mathrm{nm}$ LiFinterlayer ("LiF"/"no LiF") with varying C_{60} thickness.

and is rather flat between -1 eV and 0 eV (relative to the surface Fermi leve) without any distinct features (Figure 6.18(c)). The internal yield in the band gap of the bare perovskite is found to be around $2.8 \cdot 10^{-12} \,\mathrm{eV}^{-1}$ and stays similarly low for 1 nm LiF on CsMAFA (and thus without C_{60}). Between the Fermi edge and $-0.5 \,\text{eV}$ the internal yield is even slightly decreased for the "LiF" series. However, this is in the range of typical variations, as found for the defect density of the bare perovskite (see chapter 5). Once C_{60} is deposited on top, the defect density abruptly is increased for the "LiF" series: For a C_{60} layer thickness between 1 nm and 2 nm, the internal yield of the "LiF" series is roughly one order of magnitude higher as compared to "no LiF". For $3-5 \,\mathrm{nm} \,\mathrm{C}_{60}$ thickness, the internal yield in the band gap of the "LiF" samples is still slightly enhanced by a factor of 1.5. However, the difference between both series is much less pronounced. For the sample with $3 \text{ nm } C_{60}$ of the "no LiF" series an exceptional shape of the gap state density with a distinct peak at around $-1 \,\mathrm{eV}$ with respect to E_{F}^{*} is observed. A similar peak shape appeared for the neat perovskite sample, which has been stored in vacuum for 2 weeks, as discusses in the previous chapter in section 5.4.3 and shown in Figure 5.8(f). Even though the 3 nm sample has not been stored in vacuum for longer than the other samples here, it might be that this clear defect shape again is indicating a slightly degraded perovskite surface in that case, even before the deposition of the thin C_{60} layer. For higher C_{60} thickness beyond 5 nm, the shape of the density of gap states changes and is found to exponentially decay into the band gap for both "LiF" and "no LiF", as it was already observed above for thicker C_{60} layers. The highest defect density is obtained for a film thickness of 10 nm for both series, which is then again decreased for thicker films with $20 \,\mathrm{nm} \,\mathrm{C}_{60}$.

The sum of the three Gaussian distributions, shown in Figure 6.20, is a measure of the defect density per volume unit, and summarizes the observation made for the distribution of the occupied states in the band gap. For the "LiF" series the integrated gap state density is found to have a maximum for 1 nm C_{60} and then decreases again slightly up to 5 nm C_{60} .

For thin C_{60} layers of 1-2 nm the integrated gap state density of "no LiF" is around one order of magnitude below the one obtained for "LiF". As discussed above, for 3 nm C_{60} an additional defect peak is observed, and thus, the integrated defect density of "no LiF" appears to exceed the one obtained for "LiF". However, when considering the shape of the internal yield, an enhanced D1 is observed, which accounts for most of the integrated internal yield. As those states are potentially originating from the perovskite, here they lead to an overestimation of the defect density in the C_{60} . The actual measured internal yield up to the Fermi edge, shown in Figure 6.18(c), is similarly as for the other samples with up to 5 nm C₆₀ thickness, enhanced for "LiF" compared to "no LiF". Considering only the two energetically higher defect peaks (D2 and D3), the integrated defect density is enhanced roughly by a factor of two for "LiF" as compared to "no LiF". The areas of the individual defect peaks and their positions are further shown in detail in the Appendix in Figure A.4. With a C_{60} thickness of 5 nm, the integrated defect density is still enhanced for "LiF" as compared to "no LiF". However, also in the "no LiF" series, the defect density starts to increase. For thicker C_{60} thickness both series roughly yield the same integrated defect density.

To sum up, it can be stated that the defect density in the first monolayers of C_{60} up to 5 nm is significantly enhanced by the insertion of a thin 1 nm LiF interlayer at the CsMAFA/LiF/C₆₀ interface, especially in the first monolayers of C₆₀. As the defects start to clearly increase only once C₆₀ is deposited on the layer stack, they must be located in the very first nm of C₆₀, i.e. not in the perovskite.

6.6.3 Discussion of combined energy level alignment of the $CsMAFA/LiF/C_{60}$ interface

Combining the results of the previous sections 6.5 and 6.6 different conclusions about the formation of the CsMAFA/C₆₀ interface with the insertion of an ultra-thin LiF interlayer can be drawn.

In Figure 6.21 the energy level alignment for varying C_{60} thickness is shown: on the left side without LiF interlayer and on the right side with 1 nm LiF interlayer. The measured data (same as in Figure 6.19) is indicated as dots in the band line-up. Since only the front surface of the full layer stack is investigated, the energetic positions are here shown with respect to the surface Fermi level, which is directly obtained from the CFSYS spectra. The QFLS in the perovskite which leads to an SPV, and is induced by the illumination, required for the measurement, as discussed above, is hence not shown here.

Again, it is important to note that each C_{60} thickness can lead to a different charge balance at the interface. The drawn alignment can thus not be considered as a depth profile of the C_{60} , but each different C_{60} thickness has to be understood as an individual case. On the left side, it can be thus concluded that with 5 nm C_{60} the Fermi level in the perovskite (blue dots) is closer to the conduction band as compared to e.g. 1 nm C_{60} , due



Figure 6.21: Energy level alignment at CsMAFA(/1 nm LiF)/C₆₀ interface, obtained by detailed analysis of NUPS and CFSYS data and aligned at the surface Fermi level, $E_{\rm F}^*$. On the left side the CsMAFA/C₆₀ interface and on the right side the CsMAFA/LiF/C₆₀ interface is shown. All energies are given in units of eV. The energetic positions of the C₆₀ HOMO-edge, the perovskite VBM, the work function and the perovskite CBM (considering a band gap energy of 1.63 eV) are indicated as dots (blue for perovskite and orange for C₆₀). The optical band gaps of CsMAFA and C₆₀ are used for an estimation of the perovskite conduction band edge and the C₆₀ LUMO-edge.

to different charge redistribution. From measuring e.g. very thick C_{60} layers by PES, no detailed conclusions about the interface formation can be drawn, since only the surface is probed. This is a general problem of band alignments obtained by PES and visually presented as here, and can be highly misleading.

The measured and modeled energetic positions of the C_{60} are indicated as orange dots. The black lines are shown for an easier perception of the observed trend of the energetic positions. The valence band maximum which is indicated as black line at the perovskite band edges of is obtained by evaluating $E_{V,PLog,High}$ of the 1 nm C_{60} sample. Since the charge transfer across this interface is strongly changed upon the deposition of the electron accepting C_{60} , the valence band maximum of the "free" perovskite surface, does not describe the physical situation with a present C_{60} contact layer and is hence not used here. The trend of the perovskite band edge is obtained for up to 5 nm C_{60} and shown by the blue dots. A slight downwards band bending is drawn in the perovskite, implying a more intrinsic behavior in the bulk, can however not be measured with the surface sensitive PES methods. Since $E_{V,PLog,High}$ is found to be slightly lower for "LiF", also the indicated band bending is stronger here, assuming similar bulk properties of the perovskite.

Furthermore, the energy offsets between the perovskite conduction band and the C_{60} LUMO, and the perovskite valence band and the C_{60} HOMO are obtained from the 5 nm C_{60} samples to be respectively 0.26 eV and 0.55 eV for "no LiF", and 0.29 eV and 0.58 eV for "LiF". The "downwards" offset between the perovskite conduction band edge and C_{60} LUMO-edge is in line with the observation that the obtainable open circuit voltage of the actual device is limited by this interface: The potential energy of the electrons, once they are transferred to the C_{60} is lost to the lower lying LUMO compared to the conduction band. However, as mentioned above, the optical band gap is considered here, while the direct determination of the LUMO-edge by IPES would be the more reliable method. The energy offset as obtained here slightly exceeds the reported difference between QFLS with and without C_{60} , which is in the order of 100 meV [15]. However, if the QFLS is limited by the C_{60} LUMO-edge, the conduction band off-set should not exceed the loss in QFLS. Hence, a slightly lower conduction band offset would have been expected.

Considering a larger electrical than optical band gap energy of C_{60} , the herein found results still are in reasonable agreement with the observations in the full devices. Remarkably, the open circuit voltage in the device is increased with the insertion of the thin LiF layer, while the estimated LUMO-edge here is found lower for the "LiF" series, as compared to the "no LiF" case. Thus, either the conduction band offset does not dominate the limitation of the V_{OC} but, e.g. non-radiative recombination at the interface, or the electrical band gap is significantly larger than the optical band gap. If, e.g. 2.3 eV, as reported by Schulz *et al.* [189], are considered for the electrical band gap of C_{60} , the conduction band offset would have even a different sign and create a small barrier for the electron extraction of -120 meV for "no LiF" and a slightly reduced barrier of -90 meV for "LiF". This could then enable a higher device open circuit voltage with "LiF" by up to 30 meV, which is in the order of the observed V_{OC} enhancement for solar cells, which contain the thin LiF interlayer. With the potentially reduced extraction barrier also the FF could benefit.

As for C_{60} layers below 5 nm the HOMO-edge could not be obtained, here E_{HOMO} is estimated by assuming a constant ionization energy of C_{60} towards very thin layers. With this assumption, the band edges follow the trend of the work function. For "no LiF" the work function of the C_{60} traces quite well the trend of the perovskite valence band edge. Hence, the charge balance across the interface is consistent and constant band offsets are present at the interface for varying C_{60} thickness. Different to that for "LiF", the work function of C_{60} tends to decrease towards the interface, indicating an electron accumulation and a slight downwards band bending. However, the valence band position of the perovskite is found to show the opposite trend. This implies changing band offsets, which will be discussed below. The increased gap stated density in the C_{60} for "LiF" is indicated schematically by the small lines distributed all over the band gap, and which are especially enhanced for "LiF" close to the Fermi level and just below.

The influence of LiF on the interface formation can thus be described as follows:

First, the LiF has a significantly lower work function as compared to both neighboring materials, which leads to an electron accumulation at both sides of the film. This can be seen by the Fermi level being located closer to the perovskite conduction band and C_{60} LUMO-edge for the "LiF" series as compared to the "no LiF" series. Note, that besides the low work function of the LiF, fluorine ions might induce an additional ntype doping, either steaming from dissociated LiF, as suggested by Quintero-Bermudez et al. [190], or due to contamination with fluorine from the evaporation chamber. For devices however, with the very same layer stack as investigated here, it is found that only the direct deposition of LiF on the perovskite surface leads to the enhanced open circuit voltage, while e.g. depositing $1 \text{ nm } C_{60}$ and then the LiF/C₆₀ contact layer stack does not increase the open circuit voltage. A dissociation and diffusion or intermixing of Li⁺ and F^- ions can thus be excluded here. However, the C_{60} might indeed be doped by F^- ions, due to cross contamination during the evaporation process as observed here by means of XPS. For the "LiF" series, always LiF was evaporated just before the C_{60} . Therefore, an enhanced reservoir of fluorine ions might be present in the chamber, which could lead to an increased n-type doping, especially in the beginning of the C_{60} evaporation process. However, very low dopant concentration leading to increased charge carrier concentrations are below the detection limit of XPS measurements. Furthermore, for thicker LiF layer a largely decreased work function is observed as briefly discussed above. Experimentally, it is found that the improved open circuit voltage with LiF interlayer is only present, if the C_{60} is deposited directly after the LiF without breaking the vacuum. However, in order to measure the 1 nm LiF on CsMAFA by PES, the sample had to be transferred through inert atmosphere. In a device, this already would have prevented the benefits of the LiF. Notably, the work function is a surface property and thus highly depending on even minor changes at the surface. It might have already changed here, even though the measurement was started as quickly as possible after the deposition and the sample was transferred in inert atmosphere to the UHV system. The effect of the low work function of LiF could even be underestimated here. One possibility to circumvent this would be to evaporate the LiF in the very same vacuum system as the PES measurements are conducted in.

Second, the valence band offset of both interfaces, with and without LiF, deviates. On the one hand, ΔE_V is slightly increased in the "LiF" series compared to the "no LiF" series, which can enhance the hole blocking and thus lead to an improved selectivity. However, more importantly, considering C_{60} HOMO-edge position as estimated by assuming a constant ionization energy for all C_{60} thicknesses, the valence band offset is constant for "no LiF", while for "LiF" it increases for lower C_{60} thickness. Kotadiya *et al.* proposed an universal strategy of improving the hole injection in organic light emitting diodes by inserting a thin buffer layer, leading to an electrostatic decoupling of the energy bands of the materials forming the interface [237]. The only requirement for this interlayer was found to be a certain offset between the ionization energy of the charge transporting material and the buffer layer. A similar mechanism could take place here, as for very thin C_{60} layers, the Fermi level in the perovskite and C_{60} seem to independently align to the thin buffer layer of LiF, leading to a significantly increased valence band offset at the interface with the insertion of the thin LiF interlayer. Such a thin insulating buffer layer, in general, creates a barrier for the charge extraction. In Figure 6.21 it is well visible that the electrons, generated in the CsMAFA, need to either surpass this barrier, which however is very high, or rather tunnel through the thin layer of around 1 nm. Similarly, holes could tunnel through the layer into defect states in the band gap of the C_{60} .

In literature it has been reported for very similar perovskite compositions that the main beneficial effect of the LiF interlayer is the suppression of non-radiative interface recombination of the photo-generated charge carriers, thus enhanced interface passivation [14, 231, 238]. For some buffer layers, such as choline chloride, also a chemical passivation of defects in the perovskites was suggested [230], and further fluorine ions have been reported to passivate perovskite by e.g. substitution of halide vacancies or forming chemical bonds to the organic cation and halide anions, which prevents them from moving in the perovskite crystal and thus also enhance both, the passivation and device stability [238, 239]. A chemical passivation of defect states in the perovskite can however not be supported with the herein presented results: The defect density for the bare perovskite with and without 1 nm LiF on top is found to be very similar. Considering the CFSYS spectra very close to the Fermi edge, only a slightly decreased gap state density could be suggested (see Figure 6.18(c)). This deviation of the gap state density is in the range of

typical sample-to-sample variations of the bare perovskite, which might also be influenced by the UV illumination from the measurement, as found in the previous chapter. Thus, even if there was indeed a chemical passivation of this perovskite composition, it might not be possible to detect with the here available spectroscopy methods.

In contrast to that, the enhanced defect density in the C_{60} and especially close to the interface should actually be detrimental to the device performance, especially the open circuit voltage. However, the opposite effect is observed. Thus, it appears that the improved hole blocking and reduced hole concentration at the interface overcompensates the increased density of trap states.

Overall, the increased electron density at the interface for "LiF" compared to a slightly depleted interface for "no LiF" can indeed lead to a better electron transfer due to higher conductivity across the interface, while the larger valence band offset improved the hole blocking and the reduced hole concentration leads to less non-radiative recombination activity, despite enhanced defect densities in the C_{60} .

6.7 Chapter summary

In this chapter the electronic structure of C_{60} and the energy level alignment between C_{60} thin films and the mixed cation mixed halide perovskite CsMAFA has been investigated. Additionally, the influence of a 1 nm LiF interlayer between the perovskite and the C_{60} on the energy level alignment at this interface was investigated. Such LiF interlayers are known to reduce the non-radiative recombination and increase the open circuit voltage of solar cell devices based on a similar layer stack as investigated here [14, 17].

Two sample series with varying C_{60} thickness in the layer stack of glass/ITO/MeO-2PACz/CsMAFA/(1 nm LiF)/C₆₀ have been investigated.

By means of XPS it was found that all C_{60} layers, independent of the presence of an LiF interlayer, can contain a substantial amount of fluorine. Without LiF interlayer, the relative amount of the contamination did not follow any predictable trend. With the LiF interlayer, however fluorine was observed in an enhanced amount in the first monolayers of C_{60} . This was attributed to the controlled chamber condition with the precedent LiF evaporation in the very same evaporation chamber.

In the near-UV PES spectra of layer stacks containing the perovskite absorber and C_{60} as electron transporting layer, a substantial offset of the surface Fermi level relative to the back contact Fermi level was observed. This shift could be quantified by directly observing and modeling the Fermi edge in the CFSYS spectra and was found to reach up to 679 meV. The quasi Fermi level splitting, induced by the photon flux, required for the CFSYS measurement was estimated to be in the order of 750-900 meV. Thus, the observed shift can reasonably be attributed to a strong surface photovoltage, separating
the front surface Fermi level from the one contacted by the ITO substrate at the back contact. With directly observing the Fermi edge of the electrons at the C_{60} surface, for the first time, the modeled energetic values, obtained for the C_{60} and the interface energy level alignment could be corrected by this sample-specific SPV.

The large information depth of near-UV CFSYS measurements is a specific advantage, which allows for the investigation of buried interfaces. For thin C_{60} layers the density of states of the perovskite bottom layer and the C_{60} top layer superimpose in the measured CFSYS spectra. To account for this in our fit model, the polylogarithmic model for the two highest perovskite valence band edges, which has been elaborated in the previous chapter, here was further expanded by an additional Gaussian distribution, representing the HOMO of the C_{60} . From a sample with 5 nm C_{60} on perovskite the band offset between the perovskite valence band maximum and the C_{60} HOMO-edge could directly be evaluated and modeled in one spectrum for the first time. It was found to be 0.55 eV. With the band gap of the investigated perovskite composition of 1.63 eV and an optical band gap of 1.92 eV for C_{60} , the energy offset between the perovskite conduction band minimum and the C_{60} LUMO is thus estimated to 0.26 eV.

Furthermore, the effect of a thin LiF interlayer between the CsMAFA and the C_{60} on the energy level alignment in the CsMAFA/LiF/C₆₀ layer stack was investigated. It could be shown that the LiF, due to its low work function, leads to an increased electron concentration close to the interface, on both sides of the interface. This can lead to an improved electron transport across the interface due to a higher conductivity for the electrons. The gap state density in the C₆₀ layer close to the interface is found to be significantly enhanced by the insertion of the thin LiF layer. However, as at the same time the hole concentration at the interface is reduced, less holes will recombine at the interface defects. Considering the reduced non-radiative recombination found in cells with LiF interlayer, it appears that this effect overcompensates the detrimental effect of additional defect states. Additionally, in the case with the thin LiF interlayer, the offset at the interface between the perovskite valence band maximum and the C₆₀ HOMO-edge is found vary depending on the C₆₀ thickness. This improves the hole blocking and could be a sign of an electrostatic decoupling of both materials by the LiF buffer layer.

The herein obtained results for the working mechanism of the LiF interlayer can be only a part of the complete picture. As discussed above, the herein investigated properties of the LiF interlayer suffer in compatibility to the actual device situation from the vacuum break in between the deposition of the LiF and the PES measurements. Hence, the direct deposition of LiF and C₆₀ in the same UHV system as the PES measurements are conducted in, could exclude the influence of the exposure to inert atmosphere. Furthermore, there are several other options for forming such a buffer layer with similar properties (e.g. NaF, CsF, KCl, or KF), which however are not found to improve the device's V_{OC} [210]. It would hence help to clarify further the beneficial effect of LiF, if a similar investigation

CHAPTER 6. ELECTRONIC PROPERTIES OF THE CSMAFA/C $_{60}$ INTERFACE

on the energy level alignment would be performed with one of these alternative interlayers.

Chapter 7

Conclusion and Outlook

Understanding the energetics of interfaces between charge carrier selective contacts and photovoltaic absorbers in solar cells is essential to the optimization of charge carrier extraction and recombination and thus the open circuit voltage and fill factor of such devices. In this thesis, two interfaces, each between a photovoltaic absorber and a charge carrier selective contact, relevant for state-of-the-art silicon or perovskite solar cells, were studied in detail: First, a metal oxide based hole selective contact for crystalline silicon was investigated as an alternative to p-doped amorphous silicon, which is conventionally applied in silicon heterojunction solar cells. Second, an important contribution to the open question of the exact energetic position of the valence band maximum (VBM) of metal halide perovskites was made by a detailed study using near-UV photoelectron spectroscopy (PES). The precise determination of the perovskites valence band maximum subsequently enabled the investigation of the energy level alignment and defect density at the interface of a mixed cation mixed halide perovskite towards the fullerene C_{60} , which is used as the standard electron transport layer in recent p-i-n perovskite solar cells.

Conventional PES, such as He-UPS and XPS were used to analyse these interfaces and the chemical composition of the films in the heterojunctions. For UPS and XPS measurements, the incident photon energy is kept constant (and given by the respective illumination source), and the intensity of the excited photoelectrons at different kinetic energies is measured. In this thesis, however, the focus is on a different PES variant, namely constant final state yield spectroscopy (CFSYS), which was explored for the investigation of metal halide perovskite (HaP) related interfaces. For CFSYS, the photoelectron yield at one final state, thus one set kinetic energy, is measured, while the incident photon energy is varied. Here, a Xenon gas pressure lamp with a broad emission spectrum from 4-7 eV photon energy, combined with a double grating monochromator was used. With this, the density of states in the valence band region and band gap of the considered semiconductors could be traced over a high dynamic range of up to 7 orders of magnitude, which allowed for the probing of very low defect densities. With the high energetic resolution and a large probing depth of up to 5-10 nm also buried interfaces can be investigated.

In the first experimental part, chapter 4, mixed indium tungsten oxide (IWO_x) thin films were investigated regarding their suitability as hole selective contact for silicon hererojunction (SHJ) solar cells. For maintaining a sufficiently high band bending in the n-doped c-Si, it was established previously that an indium oxide content in the mixture below 25% is required. By means of CFSYS it could be shown that the defect density of pure tungsten oxide in the band gap and close to the Fermi level is very low and thus potentially hinders an efficient recombination based contact between the c-Si valence band and the IWO_x conduction band. A significant defect peak appeared in the mixed oxide layers with < 20% InO_x-content, which could potentially improve the trap-assisted recombination, needed at this contact. Furthermore, the optoelectronic properties of IWO_x upon high temperature annealing up to 700°C have been studied. The crystallization temperature for an InO_x-content above 50 % was found at $T_{\rm C} \approx 200 - 250^{\circ}$ C and below 50 % InO_x -content at $T_C \approx 400-600^{\circ}C$. An estimate for the parasitic absorption loss, assuming a layer thickness of 10 nm and front side application in a SHJ solar cell, was modelled from reflection and transmission spectra. The as-deposited tungsten oxide rich layer as well as all mixed oxide layers above an annealing temperature of 200°C showed very low parasitic absorption with losses below $0.5 \,\mathrm{mA \, cm^{-2}}$. However, the low conductivity of the mixed oxide layers could not be improved significantly, neither by increasing the InO_x -content nor by the annealing procedure. They remained either below or just above the measurement limit of 10⁻⁶ Scm⁻¹. For the pure tungsten oxide, the conductivity was found to be slightly increased for annealing temperatures above $T_{\rm C}$ to $1.6 \cdot 10^{-4} \, {\rm Scm}^{-1}$. Consequently, applied as hole selective contact in SHJ solar cells and thereby replacing the p-type a-Si, very low fill factors and severe S-shaped IV-characteristics were observed, pointing to strong charge carrier extraction barriers. The most promising IWO_x composition was found for an InO_x -content of 16%, yielding cells with a power conversion efficiency of 13.3% and a rather poor fill factor of only 59%.

In the second experimental part, a detailed investigation of the energy level alignment between the widely applied triple cation perovskite $Cs_{0.05} (MA_{0.17}FA_{0.83})_{0.95} Pb (I_{0.83}Br_{0.17})_3$ (CsMAFA) and the fullerene C₆₀ was investigated. First, in chapter 5, the density of states (DOS) in the valence band and the occupied defect states in the band gap of the perovskite were investigated by means of CFSYS. While in literature the determination of the VBM is usually based on an arbitrary cut-off of the valence band edge by the noise floor of conventional He-UPS spectra, the low detection limit of CFSYS enabled the observation the actual VBM including an exponential band tail, decaying over two order of magnitude. The two highest valence band edges, potentially resulting from two different k-vectors, could be distinguished using an advanced DOS model, which was adapted from optical spectroscopy (work of A. Tejada [211]). The model describes a parabolic band edge and an exponential band tail (as a result of structural and/or dynamic disorder) in one single equation, and is based on a polylogarithmic function. Furthermore, by observing the Fermi edge in the CFSYS spectra, charging and/or surface photovoltage effects (induced by the illumination required for the measurement) could be quantified. With this the highest VBM was found at an average position (obtained by four samples) of $-1.43 \,\mathrm{eV}$ with respect to the directly observed surface Fermi level. A second transition, probably related to a different k-vector, was found 0.38 eV below the highest one. Further, the effect of different illumination and environmental conditions on the density of occupied defect states in the band gap, $D_{\rm it}$, was quantified. By assuming a constant dipole matrix element, the internal yield, measured by CFSYS, is directly proportional to the DOS in units of eV⁻¹cm⁻³. The CFSYS spectra could hence be normalized to a calculated density of states at the VBM for the closely related MAPbI₃, by making use of density functional theory calculations taken from literature. The UV-illumination during the measurement already initially increased the density of defect states, to around $D_{\rm it} = 1.1 \cdot 10^{17} \, {\rm cm}^{-3}$. Almost no additional damage was observed by the irradiation during the He-UPS measurement. However, 3 h of X-ray illumination were found to severely smear out the valence band structure and increase the defect density to $D_{\rm it} = 3.9 \cdot 10^{18} \,{\rm cm}^{-3}$. Short exposure to air led to a similarly high $D_{\rm it}$ of $6.1 \cdot 10^{17} \, {\rm cm}^{-3}$, and long sample storage of 2 weeks under vacuum to the appearance of a distinct localized defect peak around 0.38 eV above the highest modelled valence band edge.

Based on the modelling of the CsMAFA VBM, the energy level alignment of the $CsMAFA/C_{60}$ interface was investigated in chapter 6. To that end, samples with different C_{60} thickness on a perovskite single junction solar cell-like layer stack, thus including a self assembled monolayer as hole selective contact, were studied by means of XPS, NUPS (UPS with $h\nu = 6.5 \text{ eV}$), and CFSYS. The measurement induced surface photovoltage (SPV) in the layer stack could directly be quantified from the high sensitivity CFSYS spectra by measuring the shift of the surface Fermi edge with respect to the Fermi level of the contacted ITO substrate. With increasing C_{60} thickness, the SPV increased up to 679 meV. The energy level alignment was corrected for this measurement induced artefact. In the CFSYS spectrum of a sample with $5 \text{ nm } C_{60}$ thickness, both, the perovskite VBM and the C_{60} HOMO-edge were modelled. Using this model, the valence band offset between those energy levels was determined to be $0.55 \,\mathrm{eV}$. With an optical band gap of C_{60} of $1.92 \,\mathrm{eV}$ the LUMO-edge is estimated at 260 meV below the perovskite conduction band edge. Such a band line-up would limit the open circuit voltage, consistent with what is observed for devices. Last, the influence of a 1 nm LiF interlayer between the CsMAFA and the C₆₀ on the energy level alignment and interface defect density was investigated. The work function of the 1 nm LiF layer on CsMAFA is found to be 200 meV below the one of the free CsMAFA surface. By assuming a constant ionization energy of the C_{60} and modelling the buried perovskite valence band edge in CFSYS spectra, the C_{60} HOMO-edge and the perovskite VBM could be measured and evaluated up to 5 nm C_{60} thickness. For the LiF-containing interface, both positions were found to decrease with respect to the surface Fermi level, indicating a reduced hole concentration at both sides of the interface, when compared to the case without LiF. Additionally, for the LiF-containing interface, the valence band offset was found to increase towards the interface, potentially due to electrostatic decoupling of both layers. No significant chemical passivation of the defects in the perovskite could be observed in the spectra. On the other hand, the defect density in the C_{60} was significantly enhanced when introducing the LiF interlayer. This would actually increase the non-radiative recombination at the interface, while however the opposite is experimentally observed for devices. Thus, the reduced hole concentration in combination with the increased valence band offset with LiF interlayer overcompensates the increased defect density in the first monolayers of C_{60} .

<u>OUTLOOK</u>

Further device optimization of the complex layer stacks of silicon/perovskite tandem solar cells will potentially lead to increased PCE records in the coming years [240]. One key challenge will then be to not only enhance the PCE, but to improve the device stability of the perovskite top-cell. The interfaces between the perovskite absorber and charge carrier selective contact layers play a crucial role for both key challenges. The device long term stability of perovskite based solar cells can be enhanced by tuning charge carrier selective contacts e.g. by the insertion of diffusion barriers or chemical/electrical passivation of defects. Such layers can also help to enhance the device open circuit voltage and the fill factor (and hence the PCE), through improved passivation and energy level alignment, and thus better selectivity.

A crucial point for monolithic silicon/perovskite tandem solar cells is the optimization of the recombination junction, interconnecting both individual cells [241, 242]. At this junction, several charge carrier selective contact layers are stacked on top of each other and their energy level alignment, including e.g. band offsets, determine the charge carrier transport in between both sub-cells. By detailed near-UV PES studies, possible loss-mechanisms could be pin-pointed and thereby guide the search for even more suitable contact layers. This thesis could demonstrate with the example of one CsMAFA composition and C_{60} as electron selective layer that near-UV PES is indeed a powerful tool, to investigate such interfaces.

There are four main subject areas regarding perovskite solar cells, in which CFSYS can be very useful for answering open research questions about the energy level alignment and defect formation at semiconductor interfaces:

- The characteristically low density of states at the *valence band maximum* of HaPs is right at the detection limit of conventional He-UPS measurements, but well detectable with CFSYS. In future research and for a more detailed investigation of the influence of the chemical composition on the valence band maximum and the exponential band tail, e.g. additives or different perovskites compositions should be considered. The interpretation of the results would further benefit from a comparison to DFT calculations for the specific HaP under investigation, while experimentally, ARPES measurements could clarify the valence band structure in comparison to the angle-integrated CFSYS spectrum.
- In p-i-n HaP based devices, the electron selective contact, often realized by fullerenes, still limits the open circuit voltage and the fill factor, which creates the need for alternatives. With its high information depth, near-UV CFSYS can assist to determine the *energy level alignment* at heterojunction interfaces. Specifically, the valence band

offset at the interfaces can be determined directly. Furthermore, CFSYS is ideal for the investigation of thin interlayers – as shown here for the example of LiF – and their influence on the energy level alignment. While e.g. LiF increases the device open circuit voltage, it is also known to deteriorate the device stability. CFSYS could assist in the search for new and more stable interlayers.

- Since for PES, there is always the need for illumination by photons and metal halide perovskites are excellent photoaborbers, even a very low photon flux can induce a quasi Fermi level splitting and thus potentially an SPV, making the measurement of device relevant layer stacks challenging. The Fermi level position and valence band maximum in HaPs is still far from being consistently determined in the research community. The high sensitivity of CFSYS however can enable to directly observe the surface Fermi level and relate the VBM to it. With this, the actual *measurement induced surface photovoltage* (SPV) can be quantified, without relying on the indirect way of observing the valence band shift between low and high photon flux ("dark" and "light") PES measurements.
- The detrimental effect of *defects* in the absorber bulk material, at surfaces, and interfaces on the device performance of solar cells is well known. With the low detection limit, defect states in the band gap can be directly investigated. Here it needs to be considered that the UV-light used for the measurement might itself enhance the defect density, as found for the perovskite composition, which was investigated in this thesis. However, first experiments already show promising results with less defect generation on Pb-Sn based perovskites. The PES-based research on such defects with sufficiently low detection limit has just recently started [128, 153, 154] and further systematic studies on the electronic structure, e.g. depending on the PbI₂ content, or a variation of additives could lead to a better understanding of the defect formation dynamics in HaPs.

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Appendix A

Appendix

A.1 List of publications

- <u>D. Menzel</u>, M. Mews, B. Rech and L. Korte.
 Electronic structure of indium-tungsten-oxide alloys and their energy band alignment at the heterojunction to crystalline silicon.
 Applied Physics Letters 112(1), 011602 (2018).
 DOI: 10.1063/1.5010278
- <u>D. Menzel</u> and L. Korte.

Evolution of Optical, Electrical, and Structural Properties of Indium Tungsten Oxide upon High Temperature Annealing. *Physica Status Solidi (A)* 217(18), 2000165 (2020).

DOI: 10.1002/pssa.202000165

A. Al-Ashouri, E. Köhnen, B. Li, A. Magomedov, H. Hempel, P. Caprioglio, J. A. Márquez, A. Belen Morales Vilches, E. Kasparavicius, J. A. Smith, N. Phung, <u>D. Menzel</u>, M. Grischek, L. Kegelmann, D. Skroblin, C. Gollwitzer, T. Malinauskas, M. Jošt, G. Matič, B. Rech, R. Schlatmann, M. Topič, L. Korte, A. Abate, B. Stannowski, D. Neher, M. Stolterfoht, T. Unold, V. Getautis and S. Albrecht. Monolithic perovskite/silicon tandem solar cell with 29% efficiency by enhanced hole extraction. *Science* 370(6522), 1300-1309 (2020).

DOI:10.1126/science.abd4016

Contribution of Dorothee Menzel: Photoelectron spectroscopy measurements of selfassembled monolayers and perovskite absorber.

• I. Levine, A. Al-Ashouri, A. Musiienko, H. Hempel, A. Magamedov, A. Drevilkauskaite,

V. Getautis, <u>D. Menzel</u>, K. Hinrichs, T. Unold, S. Albrecht and T. Dittrich.

Charge transfer rates and electron trapping at buried interfaces of perovskite solar cells.

Joule 5(11), 2915-2933 (2021).

DOI:10.1016/j.joule.2021.07.016

Contribution of Dorothee Menzel: X-Ray photoelectron spectroscopy measurements and analyzing the coverage of different self-assembled monolayers on indium tin oxide.

• <u>D. Menzel</u>, A. Tejada, A. Al-Ashouri, I. Levine, J. A. Guerra, B. Rech, S. Albrecht and L. Korte.

Revisiting the Determination of the Valence Band Maximum and Defect Formation in Halide Perovskites for Solar Cells: Insights from Highly Sensitive Near-UV Photoemission Spectroscopy.

ACS Applied Materials & Interfaces 13 (36), 43540-43553 (2021). DOI: 10.1021/acsami.1c10171





Figure A.1: Modelled density of states of the valence band region for four different, but nominally identically processed CsMAFA layers, which are further discussed in chapter 5.

Sample	$D_{\rm it}$ [rel. to a_0]					$E_{\rm Di} - E_{\rm V, Plog, High} [eV]$			
	D1	D2	D3	Sum	D1	D2	D3		
1	$1.1 \cdot 10^{-4}$	$3.0 \cdot 10^{-5}$	$1.1 \cdot 10^{-5}$	$1.5 \cdot 10^{-4}$	0.42	0.87	1.24		
2	$1.6 \cdot 10^{-4}$	$1.6 \cdot 10^{-5}$	$7.3 \cdot 10^{-6}$	$1.8 \cdot 10^{-4}$	0.34	0.86	1.33		
3	$3.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$3.8 \cdot 10^{-4}$	0.32	0.89	1.32		
4	$9.2 \cdot 10^{-5}$	$3.0 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$	0.41	0.91	1.26		

Table A.1: Obtained fitting parameters for the Gaussian peaks in the combined model for four different, but nominally identically processed CsMAFA layers. The energetic position of the Gaussian distributions, E_{Di} is given relative to the energetically higher modelled valence band edge $E_{\text{V,PLog,High}}$. The area under the individual defect peaks is given relative to the amplitude scaling parameter, a_0 , of $E_{\text{V,PLog,High}}$.



Figure A.2: Modelled density of states of the valence band region of CsMAFA for different sample histories, as they are further in chapter 5: after NUPS (15 min near-UV illumination at 6.5 eV), after He-UPS (He-I illumination, 40 min) and XPS (Al-K α X-Ray illumination, 3 h), after two weeks of storage in ultra-high vacuum and a short (<10 min) exposure to ambient air.

Sample		$D_{\rm it}$ [rel. to a_0]				$E_{\rm Di}$ - $E_{\rm V,Plog,High}$ [eV]		
		D1	D2	D3	Sum	D1	D2	D3
2	After NUPS meas.,	$1.6{ m x}10^{-4}$	$1.6 \cdot 10^{-5}$	$7.3 \cdot 10^{-6}$	$1.8 \cdot 10^{-4}$	0.34	0.86	1.33
	initial CFSYS scan							
2	Second CFSYS scan	$4.2 \cdot 10^{-4}$	$2.8 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	$4.6 \cdot 10^{-4}$	0.17	0.86	1.43
3	After NUPS meas.	$3.1 \cdot 10^{-4}$	$5.5 \cdot 10^{-5}$	$1.4 \cdot 10^{-5}$	$3.8 \cdot 10^{-4}$	0.32	0.89	1.32
3	After He-UPS meas.	$2.2 \cdot 10^{-4}$	$7.6 \cdot 10^{-5}$	$1.0 \cdot 10^{-5}$	$3.0 \cdot 10^{-4}$	0.46	1.06	1.61
3	After XPS meas.	$3.8 \cdot 10^{-3}$	$2.5 \cdot 10^{-3}$	$1.4 \cdot 10^{-3}$	$7.7 \cdot 10^{-3}$	0.76	1.16	1.49
-	10 min. air exp.	$7.4 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$	$1.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$	0.40	0.90	1.32
-	Vacuum storage	$2.0 \cdot 10^{-3}$	$1.4 \cdot 10^{-4}$	$5.4 \cdot 10^{-5}$	$2.2{\cdot}10^{-3}$	0.38	0.94	1.21

Table A.2: Obtained fitting parameters for the Gaussian peaks in the combined model for different sample histories, as they are further in chapter 5: after NUPS (15 min near-UV illumination at 6.5 eV), after He-UPS (He-I illumination, 40 min) and XPS (Al-K α X-Ray illumination, 3 h), after two weeks of storage in ultra-high vacuum and a short ($\approx 10 \text{ min}$) exposure to ambient air

A.3 Influence of the photon flux on the SPV during the near-UV PES measurements for full device stack



Figure A.3: CFSYS measurement with variation of the monochromator slit width from 0.2 mm to 4 mm on a layer stack of glass/ITO/MeO-2PACz/CsMAFA/C₆₀. The full spectra are shown in panel (a) and the measured photon flux during each CFSYS scan is shown in penal (b).
A.4 Modelling parameters of the density of occupied defect states with increasing C_{60} thickness



Figure A.4: Defect density, obtained by modelling three Gaussian distributions (a) D1, (b) D2, (c) D3) to the density of gap states of CFSYS spectra on the CsMAFA(/1 nm LiF)/C₆₀ interface with varying C₆₀ thickness. (d) Energetic position of the modelled Gaussian Distributions relative to the surface Fermi level E_F^* .

A.5 Determination of the optical band gap of C_{60}

A 50 nm thick evaporated C_{60} film on a quartz-glass substrate was used to determine the optical band gap energy of C_{60} . The samples were prepared by Amran Al-Ashouri and Manuel Piot. Transmission, reflection, and backreflection measurements were carried out with the assistance of Danbi Yoo. The data evaluation and modelling of the band gap energy was performed by Alvaro Tejada [211].

The complex refractive index of the 50 nm C_{60} thin film was obtained by a combination of spectroscopic ellipsometry measurements in the wavelength range from 190 nm - 950 nm at three different angles (50°, 60°, 70°), transmittance and reflection data, according to the procedure described by Tejada *et al.* [98] and the obtained *nk*-data is shown in Figure A.5.



Figure A.5: Refractive index n and extinction coefficient k obtained from a combination of spectroscopic ellipsometry and reflection and transmission measurements, as in ref. [98]. The figure is contributed by Alvaro Tejada [211].

The absorption coefficient was calculated from the extinction coefficient and modelled by equation A.1 according to Tejada and co-workers [98]. The modelled data is shown in Figure A.6 on a semi-logarithmic scale with the red dots indicating the fitted data range. The obtained modelling parameters are summarized in Table A.3. A band gap energy for C_{60} of 1.92 (1) is thus assumed for the estimation of the LUMO-edge and the conduction band offset in chapter 6.

$$\alpha(h\nu) = -\frac{1}{2}\frac{\alpha_0}{h\nu}\sqrt{\frac{\pi}{\beta}}\mathrm{Li}_{1/2}\left(-\exp\left(\beta(h\nu - E_{\mathrm{G}})\right)\right)$$
(A.1)



Figure A.6: Modelling of the absorption coefficient of C_{60} by a band fluctuation model as in equation A.1 according to the procedure, described in [98], performed by Alvaro Tejada [211] to obtain the optical band gap energy. The same data is shown on a linear (top left), semilogarithmic (top right) and Tauc-type (bottom) scale. The red dots indicate the data fitting range. The figures are contributed by Alvaro Tejada [211]

	Estimate	Standard Error	Confidence Interval
$\alpha_0 [\mathrm{cm}^{-1}]$	68213.5	5355.53	$\{57615.1, 78812.\}$
$\beta \ [eV^{-1}]$	18.2	0.9	$\{16.4, 19.9\}$
$E_{\rm G} \left[{\rm eV} \right]$	1.92	0.01	$\{1.90, 1.94\}$

Table A.3: Obtained modelling parameters by the band fluctuation model of evaporated C_{60} thin film.

A.6 Abbreviations and symbols

α	absorption coefficient		
a_0	amplitude scaling parameter of polylogarithm model-function		
χ	electron affinity		
C_{In}	indium oxide fraction in indium tungsten oxide mixture		
Cps	counts per second		
D(E)	density of states		
D_{it}	density of occupied defect states at the surface of a sample or at the		
	interface between two materials		
$\Delta E_{\rm V}, \Delta E_{\rm C}$	valence and conduction band offset		
$E_{\rm B}$	binding energy		
$E_{\rm C}$	conduction band minimum		
$E_{\rm F}$	Fermi level		
E_{F}^{*}	measured Fermi level at the sample surface		
$E_{\mathrm{F,p}}, E_{\mathrm{F,n}}$	quasi Fermi level of holes and electrons		
$E_{\rm G}$	band gap energy		
$E_{\rm HOMO}$	HOMO edge		
$E_{\rm kin}$	kinetic energy		
$E_{\rm ph}$	photon energy		
$\dot{E_{\mathrm{t}}}$	exponential tail slope parameter of polylogarithmic model-function		
$E_{\rm SECO}$	edge position of the secondary electron cut-off		
$E_{\rm V}$	valence band maximum		
$E_{\rm V,Lin}, E_{\rm V,Log}$	valence band edge, obtained by linear extrapolation on linear and semi-		
, , , , ,	logarithmic scale		
$E_{\rm V,PLog}$	valence band edge, obtained by modelling with polylogarithmic function		
$E_{\rm vac}$	vacuum level		
f(E)	Fermi-Dirac distribution		
FF	fill factor		
Φ	work function		
$\Phi_{ m ph}$	photon flux		
h	Planck's constant		
\hbar	reduced Planck's constant		
h u	photon energy		
$I_{\rm SC}$	short circuit current		
IE	ionization potential		
$j_{ m SC,loss}$	estimate for loss in short current density by parasitic absorption		
k	wave vector		
$\lambda_{ m IMFP}$	inelastic mean free path length		
$m_{ m e}^*,m_{ m h}^*$	effective mass of electrons (e) and holes (h)		
$N_{\rm occ.}$	density of occupied states		
$N_{\rm unocc.}$	density of unoccupied states		
$N_{\rm C,V}$	effective density of states in the conduction and valence band		
S	index of interface behaviour		
$S_{ m F}$	XPS sensitivity factor		
Т	temperature		
$T_{\rm C}$	crystallization temperature		

$Y_{ m int}$	internal photoelectron yield	
$Y_{\rm ext}$	external photoelectron yield	
$V_{\rm OC}$	open circuit voltage	
a-Si	amorphous silicon	
ARPES	angle-resolved photoelectron spectroscopy	
c-Si	crystalline silicon	
CB	conduction band	
CBM	conduction band minimum	
CFSYS	constant final state yield spectroscopy	
CNL	charge neutrality level	
CsMAFA	Cs0.05(MA0.17FA0.83)0.95(PbI0.83Br0.17)3	
DFT	density functional theory	
DOS	density of states	
ESC	electron selective contact	
ETL	electron transporting material	
FA	formamidinium $CH_2(NH_2)_2^+$	
FWHM	full width at half maximum	
HaP	halide perovskite	
He-UPS	ultra-violet photoelectron spectroscopy with He-I excitation	
HOMO	highest occupied molecular orbital	
HSC	hole selective contact	
HTL	hole transporting material	
IMFP	inelastic mean free path length	
ITO	indium tin oxide	
IWO	mixed indium tungsten oxide	
LiF	lithium fluoride	
	lowest unoccupied molecular orbital	
MAPhla	methylammonium lead iodide. CH_NH_PhI_	
MeO_2PACz	[2-(3.6-dimethoxy-9H-carbazol-0-yl)ethyl] phosphonic acid	
MPP	maximum power point	
NUPS	ultra-violet photoelectron spectroscopy with 6.5 eV excitation energy	
PCE	nower conversion efficiency	
PES	photoelectron spectroscopy	
PLOY	photoluminescence quantum vield	
PV	photovoltaics	
OFLS	quasi Fermi level solitting	
SAM	self assembled monolayer	
SC	semiconductor	
SECO	secondary electron cut off	
SECO	scanning electron microscony	
SHI	silicon hotorojunction solar coll	
SDV	surface photovoltage	
TCO	transparent conductive oxide	
IW	ultra violot	
UV	ultra violet photoelectron spectroscopy	
ULD Ho HDC	ultra violet photoelectron spectroscopy	
116-01 0	unra-violet photoelectron spectroscopy with ne-r excitation	

APPENDIX A. APPENDIX

VB	valence band
VBM	valence band maximum
WF	work function
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Appendix B

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