

Tuning the Electronic Properties of Molybdenum Dichalcogenides via Heterostructuring and Defect Engineering

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Eric Juriatti
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Dekan:

Prof. Dr. Thilo Stehle

1. Berichterstatter:

Prof. Dr. Marcus Scheele

2. Berichterstatter:

Prof. Dr. Frank Schreiber

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Zusammenfassung

In dieser Dissertation werden die vielseitigen Möglichkeiten zur gezielten Modifizierung der elektronischen Eigenschaften von Molybdändichalcogeniden (MoS_2 , MoSe_2) durch die Variation der Anzahl ihrer Lagen, das Einführen von Defekten und die Bildung von Heterostrukturen mit Elektrodenmaterialien wie Gold, Kupfer oder Titan und den Übergangsmetallphthalocyaninen Cobalt(II)-phthalocyanin (CoPc) und Cobalt(II)-hexadecafluorphthalocyanin (CoPcF_{16}) untersucht. Das Ziel dieser Arbeit ist ein besseres Verständnis dieser Heterostrukturen und ihrer Optimierung für den Einsatz in Halbleiter-Bauteilen für optoelektronische Anwendungen, beispielsweise als Photodetektoren oder Feldeffekttransistoren.

Zur Untersuchung der elektronischen Eigenschaften dieser neuen Heterostrukturen dient eine Kombination aus ausgewählten Formen der (Röntgen- und Ultraviolett-) Photoelektronenspektroskopie (PES) und Röntgenabsorptionsspektroskopie (XAS). Durch winkelaufgelöste PES (ARPES) kann die Bandstruktur an der Grenzfläche der Halbleitermaterialien visualisiert werden. Mittels Photoemissionselektronenmikroskopie (PEEM) können auch kleine Strukturen, wie die untersuchten MoS_2 -Monolagen, in Mikrometerskala aufgelöst werden.

In der ersten Publikation, welche diese kumulative Dissertation beinhaltet, wird untersucht, welche Auswirkungen das Verdampfen der Elektrodenmaterialien Au, Cu und Ti und das anschließende Ausheizen dieser gebildeten Heterostrukturen auf die elektronischen Eigenschaften des verwendeten Molybdändisulfids haben. Während Titan die Oberfläche stark verzerrt, sorgen die edleren Metalle Au und Cu für eine n-Dotierung der MoS_2 -Oberfläche, welche auch nach dem Ausheizen auf 250 °C bestehen bleibt. Jedoch wird beobachtet, dass Kupferatome unter die Oberfläche migrieren, während Goldatome teilweise an der Oberfläche verbleiben, was über die Wechselwirkung zum Cobalt-Atom des CoPcF_{16} nachgewiesen werden konnte.

Die zweite Publikation widmet sich den Eigenschaften der Grenzflächen zwischen MoS_2 und CoPc bzw. CoPcF_{16} in Abhängigkeit der Anzahl der MoS_2 -Lagen der untersuchten Mikrostrukturen. Für eine Struktur mit einer großen Anzahl an Lagen, auch *bulk* genannt, wird eine flachliegende Geometrie der organischen Moleküle auf dem MoS_2 erkannt. Wird die Zahl der MoS_2 -Schichten hin zu Monolagen verringert, zeigt sich hingegen eine verkippte Geometrie der Cobalt-phthalocyanine auf dem

anorganischen Halbleiter. Diese Erkenntnis ist entscheidend beim Design von Heterostrukturen, da die Orientierung der Phthalocyanine maßgeblich festlegt ob und wie die Systeme miteinander interagieren können.

Eine detaillierte Untersuchung zu den Möglichkeiten der defektkontrollierten Dotierung von MoS₂ durch Bombardierung mit Argon- und Neon-Ionen und den Möglichkeiten einer Heilung der entstandenen Defekte durch CoPcF₁₆ wird in der dritten Publikation beschrieben. Es zeigt sich, dass durch den Beschuss mit Argon-Ionen unterschiedlicher Dosis immer eine p-dotierte Oberfläche erzeugt wird, während der Beschuss mit Ne-Ionen zu einer n-Dotierung in der obersten Schicht führt. Die elektronischen Eigenschaften dieser Oberfläche können trotz des hohen Grades der Defekte durch die Bildung einer Grenzfläche mit CoPcF₁₆ weiter verändert werden.

Nachdem bereits vielseitige Erfahrungen bezüglich den Heterostrukturen des MoS₂ gemacht wurden, fokussieren sich die weiteren Ergebnisse dieser Arbeit auf die Grenzfläche zwischen MoSe₂ und CoPc(F₁₆). Während keine starken Wechselwirkungen zwischen MoSe₂ und CoPc erkennbar sind, zeigt sich eine Ausbildung von Grenzflächenzuständen unter Ladungstransfer zum Cobalt-Atom des CoPcF₁₆ für die MoSe₂/CoPcF₁₆-Grenzfläche. Dies ist besonders stark ausgeprägt, bei n-dotiertem MoSe₂ zu beobachten.

Somit zeigt diese Arbeit, eine Vielzahl von Möglichkeiten auf, wie die elektronischen Eigenschaften von Übergangsmetalldichalcogeniden, angepasst werden können um sie für spätere Anwendungen als Halbleiter-Bauteile zu optimieren.

Abstract

In this thesis, the various possibilities to modify and specifically tune the electronic properties of molybdenum dichalcogenides (MoS_2 , MoSe_2) by varying the number of its layers, the introduction of surface defects and the formation of heterostructures with electrode materials like gold, copper or titanium and the transition metal phthalocyanines cobalt(II) phthalocyanine and cobalt(II) hexadecafluorophthalocyanine are examined. The object of this work is a more profound understanding of these heterostructures and their optimization to utilize them as semiconducting devices for optoelectronic applications such as photodetectors or field-effect transistors.

To investigate the electronic properties of these novel heterostructures a combination of selected types of (X-ray and ultraviolet) photoemission spectroscopy (PES) and X-ray absorption spectroscopy (XAS) are used. By angle-resolved PES (ARPES) the band structure at the interface of the semiconductors can be mapped, via photoemission electron spectroscopy (PEEM) very small flakes on a micrometer scale, like the investigated MoS_2 monolayers, can be resolved.

In the first publication of this cumulative thesis, the effects of depositing the electrode materials Au, Cu and Ti and their subsequent annealing on MoS_2 are discussed. While titanium leads to a strong distortion of the surface, the more noble metals Au and Cu lead to n-type doping of the MoS_2 surface which prevails even after annealing to 250 °C. However, a migration of copper atoms below the surface is observed while gold atoms partially remain on the surface which was verified by the charge transfer towards the Co atom of the CoPcF_{16} molecule.

The second publication is dedicated to the properties of the interfaces between MoS_2 and CoPc or CoPcF_{16} depending on the number of MoS_2 layers of the investigated structures. For the bulk structure a flat-lying geometry of the organic molecules on the MoS_2 plane is observed. If the number of MoS_2 layers is decreased down to single layers, a slightly tilted geometry of the cobalt phthalocyanines on the inorganic semiconductor was found. This discovery is crucial for the design of heterostructures since the orientation of the phthalocyanines is a deciding factor for possible interactions between the two systems.

A detailed examination on the opportunities of defect-controlled doping of MoS_2 by Ar- and Ne-ion bombardment and the possibilities of healing of the formed defects by CoPcF_{16} is discussed in the third publication. The results show that after sputtering with different doses of argon ions, always a p-type doped surface is formed while sputtering with neon ions leads to an n-type doping in the top layer. Despite the high degree of defects, the electronic properties of these surfaces can be tuned by the interface formation with CoPcF_{16} .

After achieving broad experiences on the heterostructures of MoS_2 , further results focus on the interface between MoSe_2 and $\text{CoPc}(\text{F}_{16})$. While no strong interactions between MoSe_2 and CoPc were observed, the emergence of interface states under charge transfer towards the cobalt atom of CoPcF_{16} was found for the $\text{MoSe}_2/\text{CoPcF}_{16}$ interface. This is most prominent for n-doped MoSe_2 .

Thus, this work shows a variety of possibilities on how to tune the electronic properties of transition metal dichalcogenides to optimize them for later applications in semiconducting devices.

Table of Contents

Zusammenfassung	I
Abstract	III
1. Introduction	1
1.1 Motivation	1
1.2 Objectives	2
1.3 Outlines	2
2. Theoretical Fundamentals and Methodology	5
2.1 Transition metal dichalcogenides for application in semiconducting devices	5
2.1.1 Structural properties of TMDCs	5
2.1.2 Electronic properties of TMDCs	7
2.1.3 Fabrication of TMDC monolayers	8
2.1.4 Integrating TMDCs in semiconducting devices	9
2.2 Cobalt phthalocyanines	11
2.3 Tuning the electronic structure of semiconductors	13
2.3.1 Introduction of defects by sputtering	13
2.3.2 The transition metal dichalcogenide/metal interface	15
2.3.3 Heterostructuring transition metal dichalcogenides with organic molecules	18
2.4 Measurement techniques and set-ups	21
2.4.1 X-ray photoemission spectroscopy	22
2.4.2 Ultraviolet photoemission spectroscopy	27
2.4.3 Angle-resolved photoemission spectroscopy	29
2.4.4 Photoemission electron microscopy	31
2.4.5 X-ray absorption spectroscopy	33
3. Publications	39
3.1 Effects of Annealing on Electrode/MoS ₂ Interfaces Studied by Photoelectron Spectroscopy	39

Table of Contents

3.1.1	Abstract	42
3.1.2	Introduction	42
3.1.3	Experimental Section	43
3.1.4	Results and discussion	45
3.1.5	Conclusion	53
3.2	Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes	54
3.2.1	Abstract	56
3.2.2	Introduction	56
3.2.3	Methods	58
3.2.4	Results and Discussion	60
3.2.5	Conclusion	69
3.3	Tuning the electronic properties of defect-rich MoS ₂	70
3.3.1	Abstract	72
3.3.2	Introduction	72
3.3.3	Experimental section	73
3.3.4	Results and Discussion	75
3.3.5	Conclusion	85
4.	Non-peer-reviewed Results	87
4.1	Interfaces between Cobalt Phthalocyanines and MoSe ₂ : Conditions for charge transfer and the Nature of Gap States	87
4.1.1	Abstract	89
4.1.2	Introduction	89
4.1.3	Experimental section	91
4.1.4	Results and Discussion	93
4.1.5	Conclusion	102
5.	Outlook	103
5.1	Future works on the MoSe ₂ /CoPcF ₁₆ interface	103

5.2	Effects of metal contacts and sputtering on the electronic structure of further TMDCs	104
5.3	Expanding the research to further TMDCs and TMPcs	105
5.4	Roll-to-roll TMDCs	107
6.	Summary & Conclusion	110
7.	Appendix.....	113
7.1	Supporting information: Effects of Annealing on Electrode/MoS ₂ interfaces Studied by Photoelectron spectroscopy	113
7.2	Supporting information: Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes 125	
7.3	Supporting information: Tuning the electronic properties of defect-rich MoS ₂ 130	
7.4	Supporting Information: Interfaces between Cobalt Phthalocyanines and MoSe ₂ : Conditions for charge transfer and the Nature of Gap States	147
	Bibliography.....	165
	List of Abbreviations and Symbols.....	193
	List of Figures & Tables	197
	List of Publications and Scientific contributions	206
	Declaration of Contribution	209
	Acknowledgements	211

1. Introduction

1.1 Motivation

In our digitalized world, the quest for faster and faster semiconducting materials is ubiquitous e.g. to fabricate photodetectors, which can process incoming data from optical fibers into electrical signals as efficiently as possible, or manufacturing more efficient field-effect transistors (FETs).^{1,2} Even though silicon proved itself as a comparatively fast and reliable material,³ its physical limitations like the short channel effect do not allow much further miniaturization below gate lengths of approximately 10 nm.^{4,5} In 1965, Gordon Moore proposed that the number of transistors on microchips doubles every two years.⁶ In order to satisfy Moore's law, 2D Materials came into the spotlight.⁵ The discovery of graphene in 2004 brought a huge emphasis on the investigation of these layered materials.^{2,7} While graphene also has semiconducting properties, the absence of a band gap makes it not suitable for the desired applications.⁸ In contrast, transition metal dichalcogenides (TMDCs) like molybdenum disulfide (MoS_2) and molybdenum diselenide (MoSe_2) exhibit semiconducting properties with band gaps in the optical and near-infrared regime, depending on their chemical composition and especially the number of layers in the transition from bulk to monolayer.⁹ In previous studies, these TMDCs already proved their potential as being promising semiconductors for extremely fast and highly responsive devices.^{10–12}

Electronic properties of TMDCs, like the position of the Fermi level in the band gap, are tunable by external factors.^{13–15} With both intrinsic and extrinsically induced defects, doping of the TMDC can be achieved.^{16–19} In addition, the formation of heterostructures can induce doping as well.^{14,20–22} These heterostructures already arise by contacting the semiconductors with electrode materials like gold.^{21,23,24} The resulting TMDC/metal interfaces have a distinct electronic structure which influences the nature of the device, a fact that is often neglected and therefore not studied sufficiently.²¹ In addition, heterostructuring with organic molecules has proven to be a suitable technique to alter the electronic properties of TMDCs. Interfacial interactions can lead to defect healing at the interface and therefore improve its photoconductive properties.^{25,26}

In previous studies, transition-metal phthalocyanines (TMPcs) like (perfluorinated) cobalt(II) phthalocyanine have proved themselves to be interesting molecules due to their structural and electronical superiority. These organic semiconductors initially attracted interest as materials for organic photovoltaics, but during the last years increasing attention was given on the use for heterostructured TMDC photodetectors.^{20,22,27} Beneficial for their application is their easy accessibility as commercially available organic molecules, their thermal durability, which allows evaporation at high temperatures of 400 °C, and their stability at atmospheric conditions.^{28,29}

1.2 Objectives

To implement the TMDCs into technical devices, further understanding and alteration of the electronic properties are necessary. This work serves to get a deeper understanding into the electronic structure of TMDCs and especially its tunability. MoS₂ and MoSe₂ are chosen as the best-studied representatives of the group of TMDCs and due to the commercial availability of large-area synthetic single crystals (up to 2 × 1 cm) and a uniform plane surface (especially for MoS₂) which allows a full cleaving of the upper layers to ensure perfectly clean surfaces in every experiment. The findings of this thesis can be implemented for future device fabrication to achieve the ideal electronic properties leading to the best suited structures in application.

1.3 Outlines

In this work, the tunability of the electronic structure of the TMDCs MoS₂ and MoSe₂ is discussed in three publications and one additional unpublished result.

To understand the foundations of the performed work, Chapter 2 '*Theoretical Fundamentals and Methodology*' gives insight into the materials used and their properties. Afterwards the possibilities of changing the electronic structure are explained and the expected effects on the TMDCs are depicted with a special emphasis on the current state of research. Furthermore, the utilized techniques of spectroscopy to measure the systems of interest are introduced.

In Chapter 3 '*Publications*' the manuscripts which were published and/or submitted are presented.

The first publication '*Effects of Annealing on Electrode/MoS₂ Interfaces Studied by XPS*' in 3.1 discusses how the electrode materials change the electronic structure of the TMDCs and how annealing affects these. In this study, typical electrode materials (Au, Cu, Ti) are compared. Organic CoPcF₁₆ is used as a probe to detect metal atoms at the surface using the charge transfer between metal atoms and the Co(II) center atom of the molecule.

The second publication '*Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes*', presented in 3.2, revolves around the orientation of Co(II) phthalocyanines on MoS₂ flakes in dependence on the number of layers of the TMDC. The small structures on a micrometer scale were resolved using photoemission electron microscopy (PEEM) and further investigated by X-ray absorption spectroscopy (XAS). For effective interactions between the molecule and the substrate, the geometry of the interface is of great importance since it dictates which molecular orbitals are overlapping with the orbitals provided by the TMDC substrate.

The third publication in 3.3 '*Tuning the electronic properties of defect-rich MoS₂*' investigates the influence of gentle noble gas ion sputtering on the electronic structure of MoS₂ substrates and the question whether further tunability by heterostructuring with CoPcF₁₆ is possible. It can be shown that by sputtering p- and n-type doped MoS₂ can be yielded, and further tuning is possible to some extent. Additionally, a charge transfer from the sputtered MoS₂ to the Co atom of the CoPcF₁₆ molecule was found.

In Chapter 4, '*Non-peer-reviewed Results*', the work focused on '*Interfaces between Cobalt Phthalocyanines and MoSe₂: Conditions for charge transfer and the Nature of Gap States*'. In this work the heterostructure between MoSe₂ and the TMPcs CoPc and CoPcF₁₆ are investigated. While no interaction between the TMDC and the non-fluorinated TMPc was observed, the MoSe₂/CoPcF₁₆ interface exhibits the formation of interface states accompanied by a charge transfer of electrons from the substrate towards the Co atom of the organic molecule which also affects the photoluminescence of the molecule. For n-type doped MoSe₂ this effect is even more pronounced.

In Chapter 5, '*Outlook*' perspectives for extended studies are given. Since the MoSe₂/CoPcF₁₆ interface discussed in Chapter 4 proved itself to be an especially interesting heterostructure, ideas for continuous research are given in 5.1. To achieve

deeper understanding about the TMDC/metal interface, the work shown in 3.1 could be expanded to the other TMDCs. Feasible approaches are discussed in 5.2. Chapter 5.3 discusses the huge variety of possible TMDC/TMPc heterointerfaces and which combinations that have yet to be investigated are promising in terms of their energetic alignment. In Chapter 5.4 a new technique for fabricating large-scale polycrystalline TMDC films is introduced which might link the mostly macroscopic experiments of this thesis to miniaturized device fabrication.

In Chapter 6, '*Summary & Conclusion*', the results of the publications of this thesis are summarized and concluded. This chapter also gives an overall conclusion on the initial question on how the electronic properties of molybdenum dichalcogenides can be tuned and highlights the significance of this thesis for future device fabrication.

Chapter 7 '*Appendix*' includes the supporting information of the publications discussed in Chapter 3 and the Unpublished Results in Chapter 4 to provide additional insights into the experiments conducted.

2. Theoretical Fundamentals and Methodology

This chapter serves to give insights into the properties and electronic structure of the transition metal dichalcogenides and organic molecules used, and their possible applications in photodetection which have already been studied in previous literature. Furthermore, the behavior and benefits of heterostructures to tune the electronic properties of possible devices are eluded. Since intrinsic defects and therefore intrinsic doping play a huge role in the properties of TMDCs, this work serves to give further understanding on controlling and manipulating these aspects while retaining the conductive properties of the used materials. Concluding, the methods used to study the TMDCs, and the fabricated interfaces are explained.

2.1 Transition metal dichalcogenides for application in semiconducting devices

Before discussing the benefits of heterostructures it is pivotal to understand the structure and electronics of the used molybdenum dichalcogenides. This chapter serves to show why TMDCs are seen by many as one of the most promising candidates for novel semiconducting devices. It is also eluded which obstacles are still preventing these raw materials from being used in widespread application.

2.1.1 Structural properties of TMDCs

Since the discovery of graphene in 2004 by Novoselov et al.⁷ TMDCs found a rapidly increasing interest as they share a similar layered structure.³⁰ In all cases, TMDCs have the chemical formula of MX_2 with M being a transition metal and X a chalcogen atom. Even though there is a large number of metals that form these TMDCs, the two metals of group VI (Mo, W) are of special interest since they form semiconductors exhibiting a band gap in the optical and near infrared range with the chalcogen atoms S, Se, Te (only semiconducting as MoTe_2).³⁰ This thesis focusses on the molybdenum dichalcogenides MoS_2 and MoSe_2 and therefore, those are discussed primarily in this chapter. For the transition metal dichalcogenides, three different phases are known which are characterized by their lattice symmetry (H: hexagonal, T: tetragonal, R: rhombohedral) and the number of layers in one unit cell. In nature, the semiconducting 2H-phase and the 3R-phase are observed.³¹ In addition, a metallic 1T'-phase can be

synthesized.³² The 2H-phase discussed in this work is always regarded as the thermodynamically stable phase, while the others are considered metastable.

The bulk 2H-MoS₂ (2H-MoSe₂), depicted in Figure 2.1, is built of individual layers of MoS₂ (MoSe₂) sheets in which the Mo atoms are sandwiched between the sulfur (selenium) atoms. The distance between Mo and sulfur (selenium) atoms is 2.41 Å (2.54 Å), with a single layer thickness of 3.17 Å (3.34 Å).^{33,34}

While the atoms inside of one layer experience strong covalent bonding, the different layers stacked on top of each other are solely bound by van-der-Waals-interactions. This allows the exfoliation of bulk TMDCs down to single layers which will be described in 2.1.3.

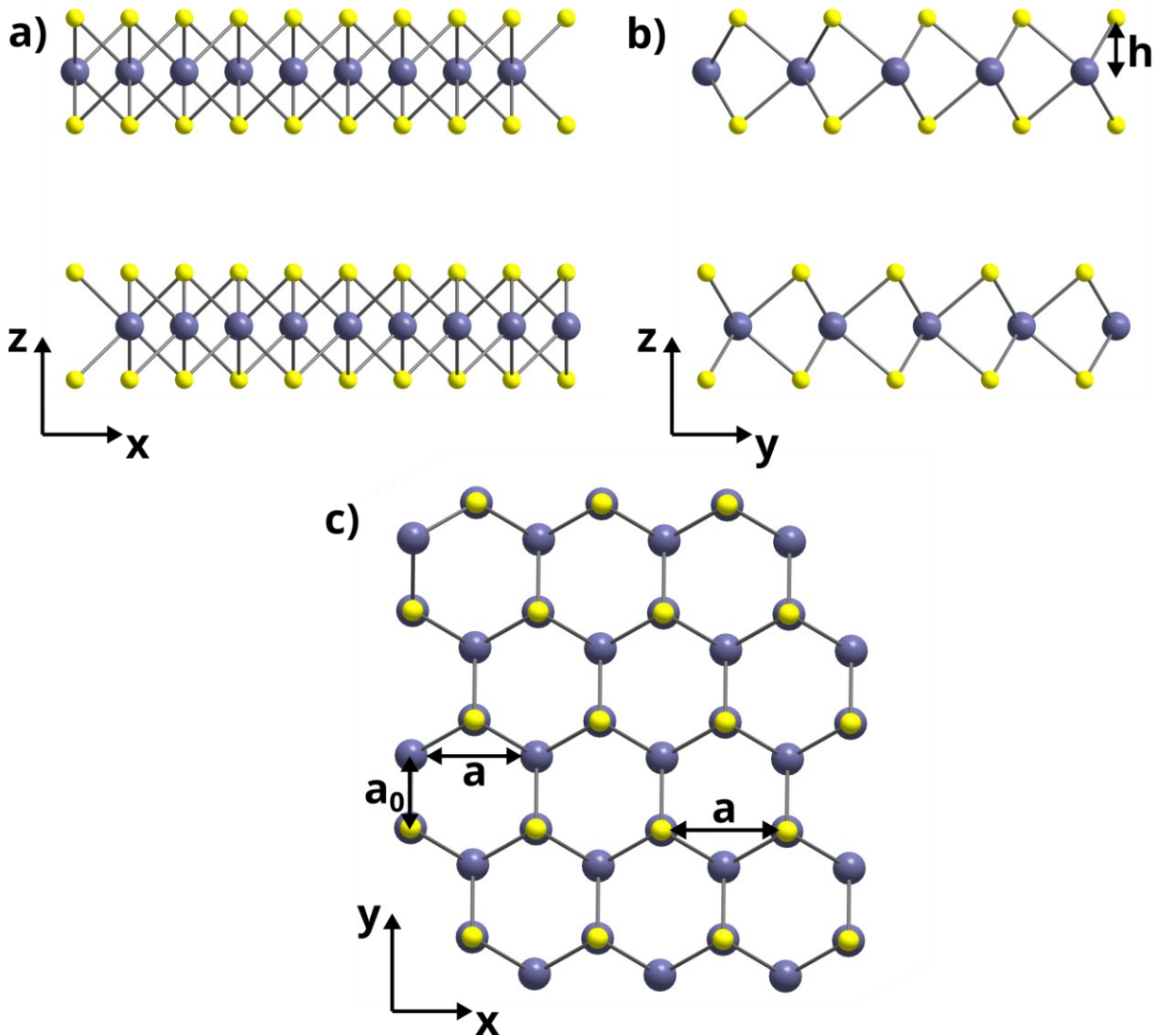


Figure 2.1: Structure of 2H-TMDCs from a) y perspective, b) x perspective with the height between the sulfur plane and the molybdenum plane $h=1.58$ Å for MoS₂ (MoSe₂:

$h=1.67 \text{ \AA}$) and c) z-perspective with added lattice parameter $a= 3.16 \text{ \AA}$ (MoSe₂: $a= 3.29 \text{ \AA}$ ³⁵) and the Mo-S distance $a_0=\sqrt{\frac{a^2}{3}+h^2}=2.41 \text{ \AA}$ (MoSe₂: $a_0=2.54 \text{ \AA}$).^{33,34}

2.1.2 Electronic properties of TMDCs

As previously discussed, the semiconducting properties of TMDCs are of special interest. The molybdenum dichalcogenides MoS₂ and MoSe₂ exhibit indirect band gaps of 1.23 eV (1008 nm) and 1.09 eV (1137 nm) in the near infrared.³⁶

To understand the nature of the electronic structure of TMDCs, the coordination and the number of d-electrons must be considered. For the group VI TMDCs like MoS₂ or MoSe₂, the trigonal prismatic D_{3h} structure, paired with the two valence electrons in Mo⁴⁺ atoms leads to a splitting of the d bands with a filled d_{z²} orbital as shown in Figure 2.2.

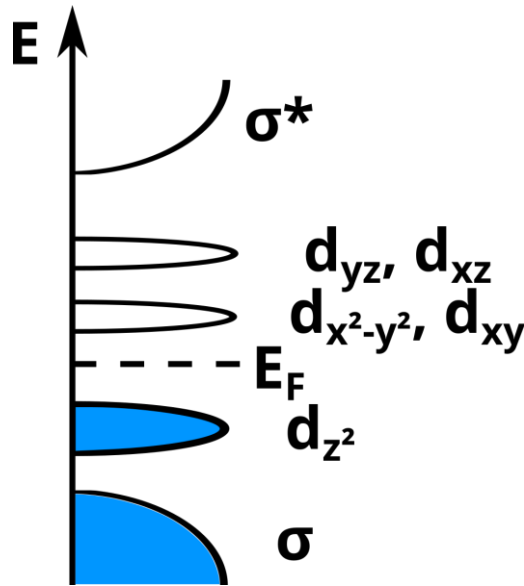


Figure 2.2: Occupation of molecular orbitals in 2H-TMDCs. Own representation based on Kolobov et al.³⁰

By reduction of its layer numbers from bulk down to monolayers, the TMDCs become a direct band gap semiconductor with a band gap in the optical spectrum of 1.88 eV (659 nm) for MoS₂ and 1.57 eV (790 nm) for MoSe₂.³⁷

To illustrate the transitions with the lowest energies for bulk and single layer MoS₂ and MoSe₂, the hexagonal structure in reciprocal space must be considered as depicted in Figure 2.3a. The most important points of high symmetry shown in Figure 2.3a are Γ as the center of the hexagonal lattice, K at the edge of the hexagon and M in the center

between Γ and its neighboring Γ . In addition, the low-symmetry Q-point is described as a point on the straight line between Γ and K. For the bulk MoS₂ in Figure 2.3b (as well as bulk MoSe₂) the transition with the lowest energy lies between the Γ -point and this Q-point. For monolayers (Figure 2.3c) a direct band gap transition at the K-point is observed.³⁸

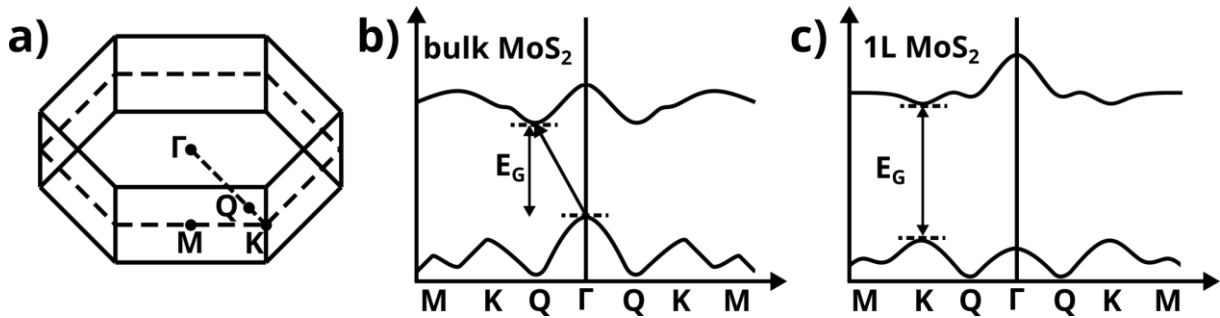


Figure 2.3: a) Hexagonal reciprocal lattice of MoS₂ and the schematic band structure of b) bulk MoS₂ and c) single layer MoS₂. The symmetry and transitions for MoSe₂ are comparable. Own schematical representation based on the publication by Roldan et al.^{30,38}

2.1.3 Fabrication of TMDC monolayers

To obtain single layer sheets of TMDCs like MoS₂, two main types of methods are typically used. The top-down approach starts with bulk MoS₂ which is then exfoliated, while in the bottom-up approach the single layer is grown individually e.g., by chemical vapor deposition (CVD).³⁰ It is important to note that the resulting structure is heavily influenced by its method of fabrication. When compared to CVD grown flakes, the exfoliated monolayers exhibit a more homogenous surface, possibly due to less strain and a higher carrier density which potentially makes this fabrication method more suited for optoelectronic devices.^{30,39}

Due to these benefits, only exfoliated MoS₂ monolayer flakes were investigated in this thesis. Mechanical exfoliation allows a simple, yet very efficient method to fabricate MoS₂ monolayers as shown in Figure 2.4: Using commercially available scotch tape, the top layers of bulk MoS₂ can be removed as shown in Figure 2.4a. After several steps of exfoliation (Figure 2.4b), the number of layers of the TMDC on the scotch tape is gradually reduced to yield single layer flakes. The MoS₂ flakes can then be pressed onto a polydimethylsiloxane (PDMS) stamp (Figure 2.4c) and transferred further to a substrate of choice (e.g. silicon wafers) as shown in Figure 2.4d.²⁷

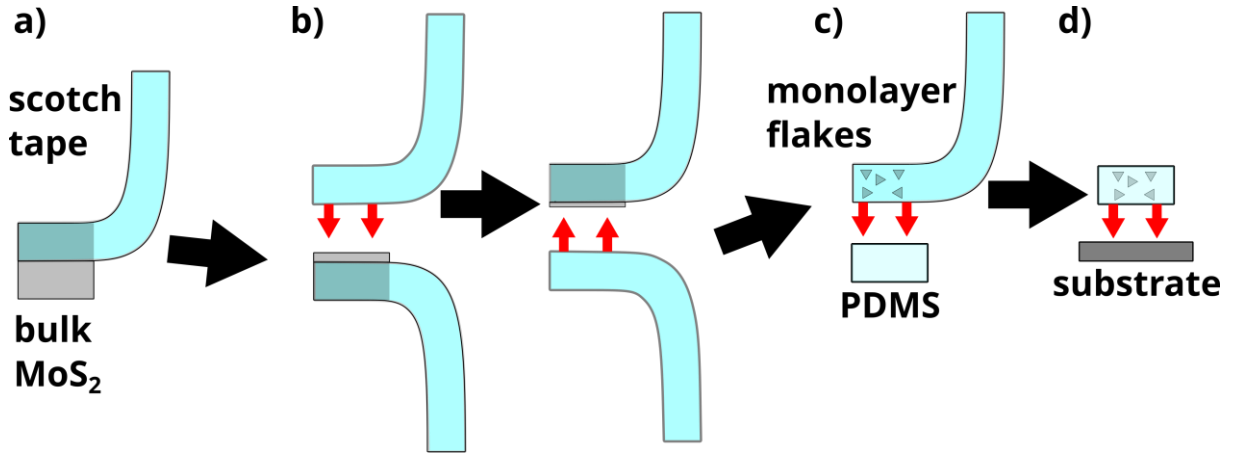


Figure 2.4: Standard procedure for mechanical exfoliation (scotch tape method): a) Removal of top layers of the TMDC from bulk MoS_2 , b) repeated stripping down to monolayer flakes with scotch tape, c) transfer to PDMS stamp and d) stamping of Monolayer flakes onto the desired substrate.

2.1.4 Integrating TMDCs in semiconducting devices

Due to their favorable properties in terms of strong excitonic binding energies, high extinction coefficients and large carrier mobilities, TMDCs emerged as a highly promising candidate for future optoelectronic devices like photodetectors.^{40–42} To classify how well-suited a material for photodetection truly is, several parameters must be taken into account with ideal target performance numbers: a high responsivity (electrical output per optical input) $>1\text{A/W}$, short response times with electrical bandwidths in the GHz regime, a small footprint of a few μm^2 and a relatively low dark current which can get as low as a couple of nA.^{43,44} For monolayer TMDC photodetectors, the direct band gap transition is typically associated with larger extinction coefficients and faster recombination times of the charge carriers which would make them best-suited in terms of responsivity and speed which is reflected by their low intrinsic response time (the lifetime of charge carriers from exciton dissociation to photocurrent generation) of e.g. 10 ps for MoTe_2 at a thickness of 4 nm.^{10,45} However, the true signal processing time of a photodetector is determined by its extrinsic response time which is defined by the materials rise and fall time (time for the output signal to increase from 10 % to 90 % and vice versa). For TMDC devices this time is typically governed by the RC time as the product of the capacitance and the resistance of the given device. This time also includes the carrier injection time and the electrode material transfer time as part of the contact resistance.¹⁰ When

comparing the extrinsic response times of MoS₂ monolayers with its respective multilayer counterpart, it can be seen that the multilayers typically yield around 1000-times faster devices as the device speed suffers from surface trap states which are better screened for bulk-like materials.⁴⁶ In contrast, the extrinsic response time of WSe₂ flakes seems to be less affected by its layer number offering switching speeds in the low nanosecond regime in each case with a rise time of 8 ns for bulk WSe₂ and 29 ns for bilayer WSe₂.⁴⁷ The responsivity of these ultrafast pure TMDC materials typically reaches from 10^{-3} – 10^{-1} A/W.^{11,47} These findings show that, while the fabrication of relatively fast and somewhat responsive TMDC photodetectors is possible, further improvements are necessary to truly fulfill the desired requirements in photodetection. To further decrease the extrinsic response time, a feasible approach lies in reducing the contact resistance between the electrode and the TMDC. Typically, the TMDC is contacted by photolithography of the electrode metal onto the surface. However, the hot metal atoms create a defect-rich metal/TMDC interface accompanied by Fermi-level pinning which decreases the photoconductive properties of the material.^{48–50} In a novel approach, introduced by Geladari et al.⁵¹ the laser-induced printing of gold electrodes from a precursor gold nanocluster on TMDCs was described. In a recent study by Roberts et al.⁵² the authors were able to fabricate a WSe₂ photodetector with an electrical bandwidth up to 250 MHz and a maximum responsivity of about 1 A/W using this technique. Another strategy that might allow a reduction of the extrinsic response time is mitigating the defects at the TMDC surface as those lead to undesired trap states for charge carriers.¹⁰ A promising approach to heal those defects might be the formation of van der Waals heterostructures by the deposition of organic molecules like transition metal phthalocyanines which will be discussed further in Chapter 2.3.3.

2.2 Cobalt phthalocyanines

In this work the interfaces between TMDC based substrates and cobalt(II) phthalocyanines are studied. These organic semiconductors belong to the group of transition metal phthalocyanines (TMPcs) which are of major interest in various technological applications due to many beneficial properties like their superior stability against water/oxygen and thermal stress, indicated by their sublimation temperatures $>400\text{ }^{\circ}\text{C}$ or their chemical versatility.^{28,29} In electronic devices these semiconductors can be used as active layers in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photovoltaics (OPVs) or organic spintronic devices.^{53–58} Their planar chemical structure, depicted in Figure 2.5, makes them especially suited for the formation of heterointerfaces e.g. with TMDCs.^{20,22,27}

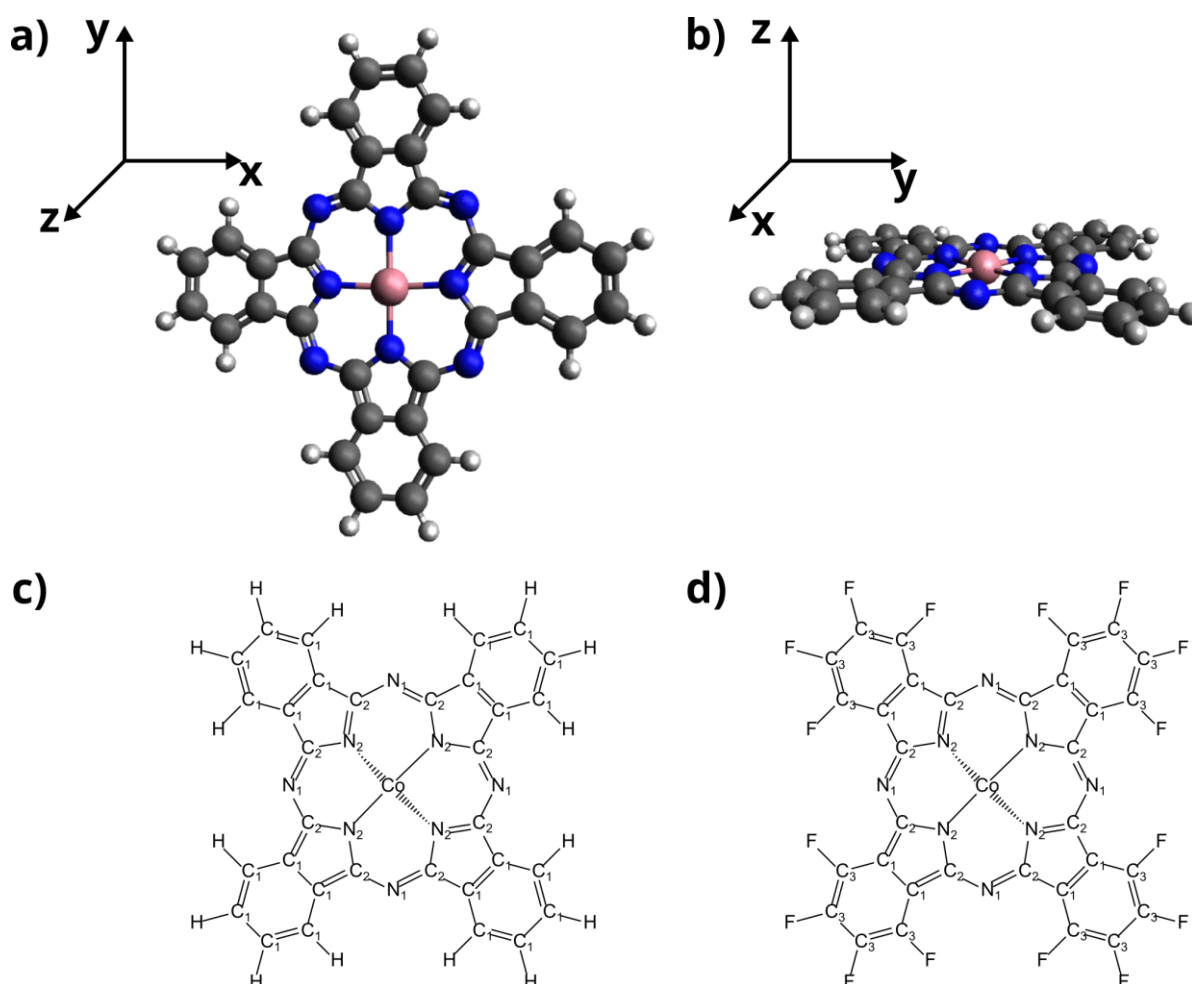


Figure 2.5: Chemical structure of transition metal phthalocyanines. a) ball-and-stick model of CoPc viewed in the z-direction, b) ball-and-stick model of CoPc viewed in the xy-direction, c) chemical formula of CoPc and d) chemical formula of CoPcF₁₆. C₁ represents carbon atoms bond to other carbon (C-C) or hydrogen (C-H) atoms, C₂

represents carbon atoms bond to nitrogen atoms (C-N) and C₃ represents carbon atoms bond to fluorine atoms (C-F). Bridging Nitrogen atoms are labeled as N₁ and Nitrogen atoms bond/coordinated to the cobalt atom are labeled as N₂.

TMPcs consist of a heteroaromatic, π -conjugated ring system, containing carbon and nitrogen atoms and a central metal atom in the oxidation state +II. The bond between the ring system and the metal has a significant covalent nature.⁵⁹ In addition, it is possible to substitute the terminal hydrogen atoms by halides like fluorine to change the electronic properties (especially the ionization potential) of the molecule while keeping the overall structure intact. By using different central metal atoms like Fe, Cu, Co, Ni, Zn, Mn and more, the electronic structure can be tuned further.²⁸ In a study by Grobosch et al.⁶⁰, it was shown how the metal atom influences the electronic properties of the TMPc. By utilizing electron energy-loss spectroscopy and photoelectron spectroscopy, it was shown that the HOMO and LUMO are largely defined by the 3d orbitals of the central metal atom for MnPc and FePc while ZnPc, CuPc and NiPc are more influenced by the ligand orbitals. CoPc is described as an intermediate case where the electronic structure at the Fermi level is heavily influenced by both, the 3d orbitals of the metal and the orbitals of the ligand.⁶⁰

Since this work focusses on the fully fluorinated (CoPcF₁₆) and non-fluorinated cobalt(II) phthalocyanines (CoPc), the Co(II) center is of special interest. Its single occupied d_{z²} orbital leads to distinctive magnetic (magnetic moment of 1.01 μ_B ⁶¹) and electronic properties characterized by a close proximity of ground and first excited state, strong influence of Coulomb and exchange interactions and spin-orbit coupling.⁶² The out-of-plane geometry of the d_{z²} orbital, which is mostly involved in charge transfer processes,⁶³ makes the molecule also well suited for interactions with substrates like the used TMDCs. The fluorination of the CoPc molecule leads to an increased ionization potential from around 4.9 eV for CoPc to 6.15 eV for CoPcF₁₆ which can lead to different total charge transfers between various substrates and the molecules.⁶⁴

2.3 Tuning the electronic structure of semiconductors

To further engineer the electronic properties of TMDCs like MoS₂ and MoSe₂, doping of the semiconductors is a feasible approach. The term doping typically refers to either the introduction of foreign atoms or the removal of atoms of the lattice resulting in a change of the position of the Fermi level in the band gap. To achieve this, various techniques are well-studied. By thermal annealing or noble gas sputtering, surface defects can be generated by creating vacancies.¹⁶ In addition, heterostructuring with metals or organic molecules is known as another possibility to change the electronic structure at the newly formed interfaces.^{20–23}

As mentioned before, the TMDCs used in this thesis offer another unique way to tune their electronic properties by changing the number of layers of the semiconductor from bulk down to single layers e.g. via exfoliation. This leads for example to changes in the band gap and the ionization potential as discussed in Chapter 2.1.^{65,66} These structures can then again be further tuned by e.g. heterostructuring with TMPcs.²⁷

2.3.1 Introduction of defects by sputtering

In order to change the electronic structure of the transition metal dichalcogenides of interest, the selective introduction of surface defects is discussed. In general, various defects are observed for TMDCs like MoS₂. Point defects found intrinsically in MoS₂ are: the sulfur vacancies V_S , V_{S_2} as well as the Mo_S , Mo_{S_2} , Mo_{2S_2} and $Mo_S Mo_S$ defects where sulfur atoms are replaced by molybdenum atoms.⁶⁷ Figure 2.6 depicts the most common defects observed, which are monosulfur vacancies (V_S) and the antisite Mo_{S_2} defects where one Mo atom is substituting two sulfur atoms.⁶⁸

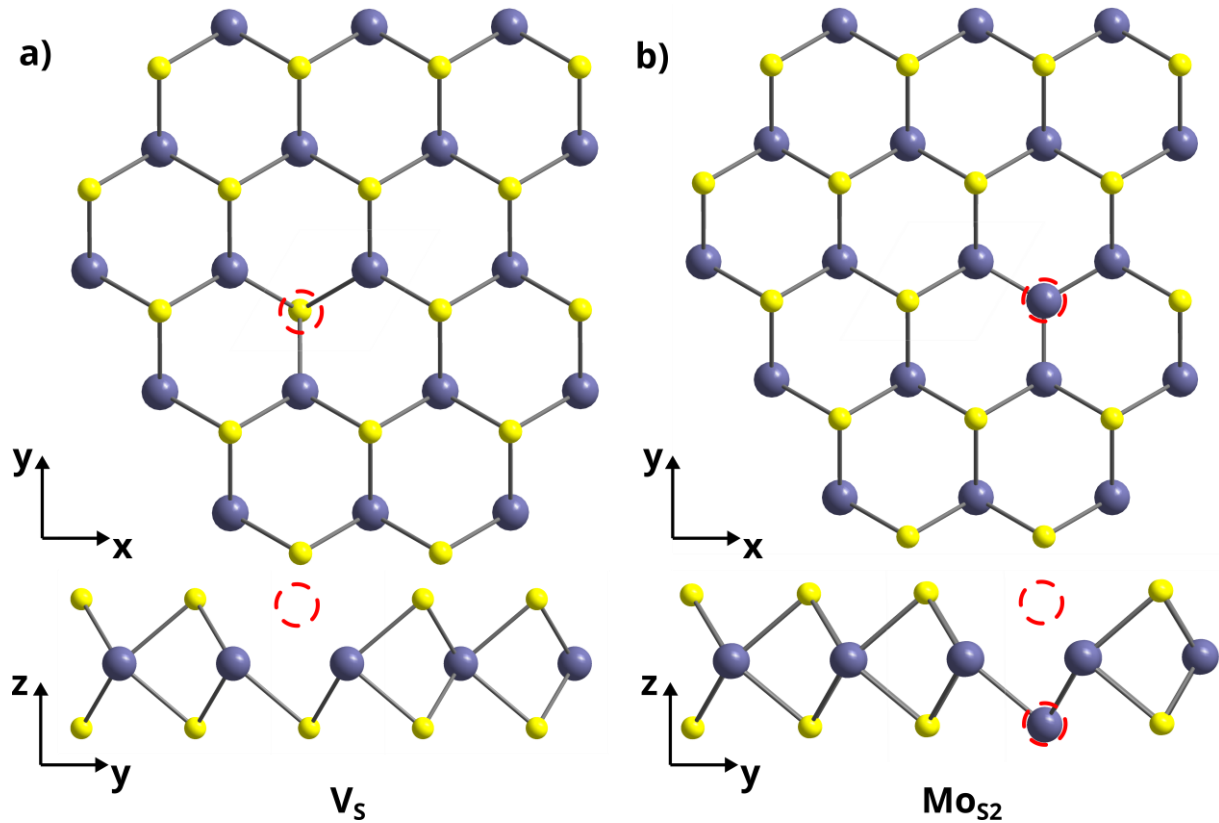


Figure 2.6: Most common vacancies in MoS₂: a) depicts V_s highlighted by the red dotted line, b) depicts the MoS₂ defect with the missing two sulfur atoms highlighted by the red dotted line.

Using scanning tunneling microscopy (STM), Lu et al.¹⁶ claim that by sputtering at very low energies (50 eV Ar⁺), mostly single top layer sulfur atoms are removed, creating monosulfur vacancies. At higher energies (100 eV Ar⁺) the topmost and second tri-layer of MoS₂ can be removed. Even higher energies (500 eV Ar⁺) lead to the formation of granulated nanostructures which may affect the chemical, electronic and optical properties of MoS₂.¹⁶ Both, Lince et al.^{69,70} and Santoni et al.⁷¹ report that the bombardment with Ar⁺ or Ne⁺ ions lead to the formation of metallic molybdenum structures while the remaining sulfur atoms seems to be unaffected.

According to McDonnell et al.,¹⁸ Scanning tunneling spectroscopy (STS) and X-ray photoemission spectroscopy (XPS) measurements of exfoliated MoS₂ show that the intrinsic defects can dominate the metal/MoS₂ contact resistance providing a low Schottky barrier independent of the metal contact. In addition, defects can locally induce both n-type and p-type doping.¹⁸

In general, the changes in electronic structure of defects are not easily predictable. In a previous work by Yang et al.¹⁷ lower concentrations of monosulfur vacancies in MoS₂ are associated with electron accepting behavior resulting in p-type doping. Higher concentrations, which can be achieved by sputtering with e.g. Ne⁺, are typically associated with n-type doping.^{17,70}

2.3.2 The transition metal dichalcogenide/metal interface

By depositing a second material like metals or organic molecules onto the TMDC substrate, heterostructures are created. It is important to discuss the electronic structure and effects that take place at these interfaces.

In the first step, the semiconductor-metal interface will be discussed: Without contact, the energy levels of the vacuum level E_{vac} of the metal and the semiconductor align. In contrast, when a metal and a semiconductor come in contact, their Fermi levels must align according to Anderson's rule.⁷² Since the work functions of these materials are typically different, a charge flow is observed at the interface which leads to an energy barrier called the Schottky barrier that causes the valence band (VB) and the conduction band (CB) of the semiconductor to bend. This barrier controls the charge flow and the capacity behavior of the heterostructure.

According to the Schottky-Mott rule, described by equation 2.1, the Schottky barrier height ϕ_B of the metal semiconductor contact (under ideal conditions) only depends on the work function of the metal ϕ_M and the electron affinity of the semiconductor χ_{SC} as the difference in energy between the conduction band minimum (CBM) and the vacuum level.^{73,74}

$$\phi_B = \phi_M - \chi_{\text{SC}} \quad (2.1)$$

These barriers exist for both electron and hole injection and are therefore labeled accordingly as ϕ_B^e and ϕ_B^h . In practice, deviations from this ideal behavior must be considered. The Schottky-Mott rule does not account for possible interface states, interfacial dipoles or chemical reactions at the interface. Figure 2.7 gives a schematic representation of the formation of metal-semiconductor interfaces resulting in band bending and the formation of interface states (IF).

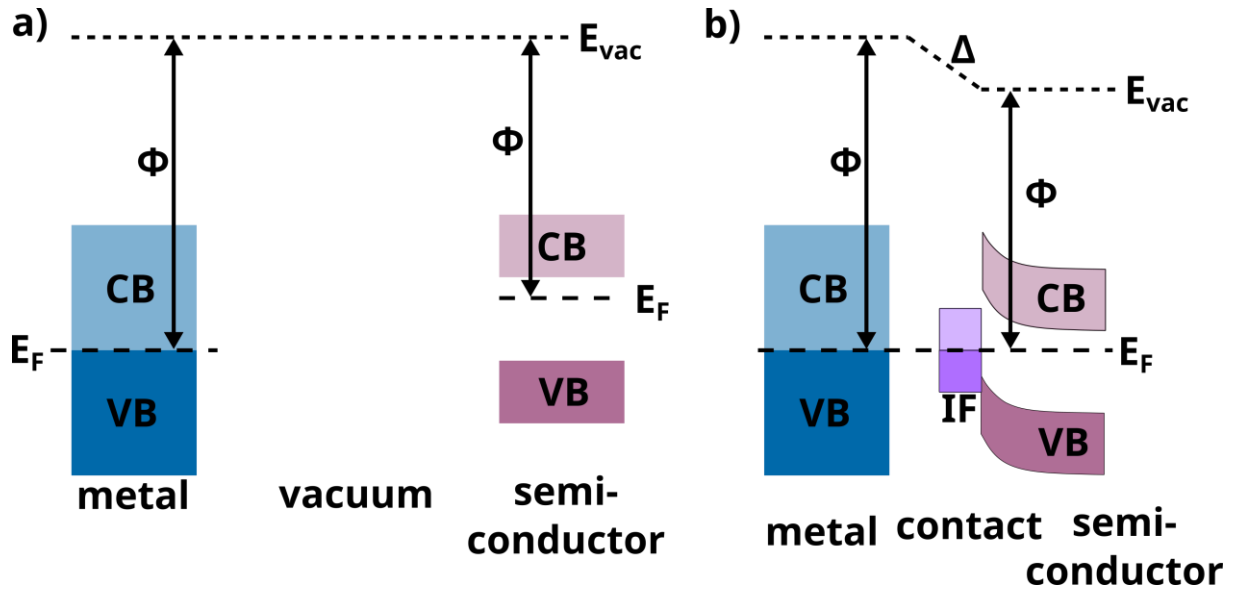


Figure 2.7: Electronic structure of a semiconductor substrate and a metal a) without contact and b) in contact under formation of an interface state (IF) and an interface dipole Δ and the resulting band bending.

According to the Schottky-Mott rule one would expect the tunability of the Schottky barrier height by using electrode materials with different work functions. However, it is observed that on many occasions ϕ_B^e barely changes for different ϕ_M . This effect is attributed to Fermi level pinning at gap states.^{75,76}

To characterize the strength of Fermi level pinning, the pinning factor S can be considered via equation 2.2:

$$S = \frac{\Delta\phi_B^e}{\Delta\phi_M} \quad \text{and} \quad S = \frac{\Delta\phi_B^h}{\Delta\phi_M} \quad (2.2)$$

With $\Delta\phi_B^e/\Delta\phi_B^h$ as changes in the Schottky barrier height for electrons and holes respectively for a given change of the work function $\Delta\phi_M$. Small values of S indicate a strong Fermi level pinning.⁷⁷

In previous reports, the dominant reason for strong Fermi level pinning was given as ground state charge transfers involving sulfur vacancy induced gap states. More recent studies emphasize the importance of defect creation as a consequence of the evaporation of the metal electrodes onto the semiconductor and showed that by a gentler transfer of the electrode material, Fermi level pinning can mostly be prevented.⁷⁷

For 2D materials, the Schottky-Mott rule was expanded by Park et al.⁷⁷ considering changes of the dielectric constant ϵ_r due to dielectric screening with a subsequent renormalization of the electronic structure of monolayer TMDCs (bandgap, electron affinity, ionization energy) which would also influence the Schottky barrier height. In this work they could also investigate the contribution of the work function of the semiconductor to the Schottky barrier height. It is reported that for substrates with work functions below 4.5 eV strong Fermi level pinning occurs with a reduction of the ionization energy (IE) and χ due to band gap renormalization, while for work functions of more than 4.5 eV vacuum level alignment is observed with different S values for holes and electrons. In addition, surface defects created by the deposition of metal electrodes change the strong dependence of the Schottky barrier height from the work function of the metal.

When fabricating semiconductor devices based on materials like MoS₂, the interface between the TMDC and the contact metal must be investigated further since aspects like the contact resistance behavior, which can heavily influence properties like drain current, photoresponse and charge carrier mobility, are not fundamentally understood and the manufacturing of desirable low resistance Ohmic contacts is not achieved yet.²³ In a study by Das et al.⁷⁸ it is described that Fermi level pinning close to the conduction band of MoS₂ strongly affects the MoS₂/metal interface, and contact metals with low work functions like scandium or titanium are best-suited to form contacts with high carrier injection and low contact resistance as they form extremely low Schottky barriers of 0.03 and 0.05 eV. Considering the band alignment of high work function metals like Au and monolayer MoS₂, the formation of interface dipoles is expected. Gong et al.⁷⁹ describe the formation of gap states at the MoS₂/Au interface under a change in work function of the MoS₂ substrate leading to Fermi level pinning. The nature of various bulk MoS₂/metal contacts was investigated by Smyth et al.²³ for Au, Ir, Cr and Sc. After deposition of the noble gold atoms both, the MoS₂ and Au metal, did not show any reaction independent of the presence of small amounts of oxygen. Instead, n-type doping at the MoS₂ surface was observed. The less noble Ir, Cr and Sc react at the interface under the formation of metallic molybdenum (Cr, Sc) and contact metal sulfides (Ir, Cr, Sc) which heavily affects the behavior at the interface. In a subsequent study by McDonnell et al.²⁴ the reaction at the MoS₂/Ti interface was discussed as titanium is frequently used as adhesion layer for electrodes. The study shows that the deposition of Ti can lead to a complex interface of metallic Mo, Mo_xS_y,

and Ti_xS_y which dictates the behavior at the interface and leads to relatively high contact resistance. These examples show how complex the TMDC/metal interfaces can be depending on the contact metal used and how drastically they may affect the properties of devices containing such interfaces. This highlights why extended work in this field is valuable when designing new TMDC-based devices.

2.3.3 Heterostructuring transition metal dichalcogenides with organic molecules

In the second step the interfaces between the semiconducting TMDCs and the semiconducting organic TMPs are discussed: According to Anderson's rule the energy diagrams of semiconductor-semiconductor interfaces are constructed by aligning the vacuum levels of the two materials similar to metal/semiconducting interfaces. The conduction band offset ΔE_c and valence band offset ΔE_v are then calculated using the electron affinities of the inorganic semiconductor (SC) χ_{SC} and the organic molecule (O) χ_{O} and the bandgaps $E_{\text{g(SC)}}$ and $E_{\text{g(O)}}$ of the materials by equation 2.3.

$$\Delta E_c = \chi_{\text{SC}} - \chi_{\text{O}} = \Delta E_v - (E_{\text{g(SC)}} - E_{\text{g(O)}}) \quad (2.3)$$

Considering Anderson's rule, the different possible band-edge lineups in semiconducting interfaces can be discussed. A distinction between Type I (straddling), Type II (staggered) and Type III (broken gap) is depicted in Figure 2.8.^{72,80}

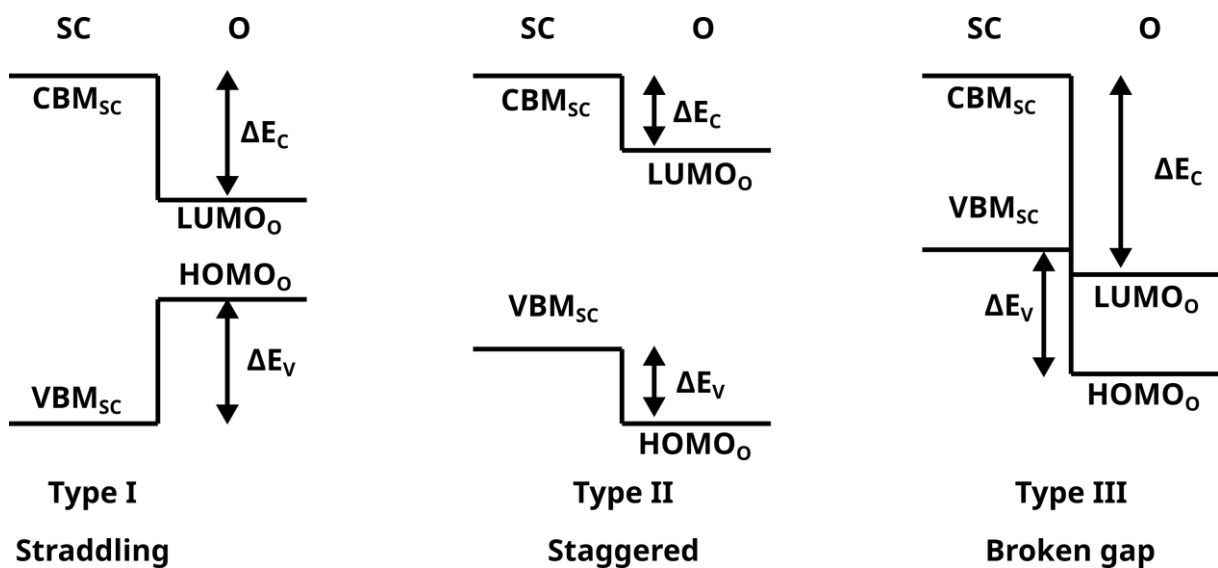


Figure 2.8: Different types of semiconductor-organic band gap lineups. For Type I Straddling, the HOMO-LUMO gap of the organic molecule lies in between the band

gap of the semiconductor. In the case of Type II, Staggered interface, the HOMO and LUMO of the organic molecule both lie below or above the respective bands of the semiconductor. For the Type III, Broken gap, both the HOMO and LUMO of the organic molecule lie below the VBM or above the CBM of the semiconductor. Own representation based on the publication by Xu et al.⁸⁰

For semiconducting devices, large conduction band offsets lead to an electron barrier which leads to a strong electron confinement on the material with the lower conduction band minimum. In contrast, at an interface with small ΔE_c charge transfers can happen more easily. In the same way large valence band offsets lead to a strong hole confinement while small ΔE_v allows the holes to leak across the interfaces. Therefore, smaller offsets are typically attributed to higher current flow and easier injection of charge carriers.⁸¹

In Figure 2.9, the energy level alignment (ELA) of a semiconductor-organic semiconductor interface is depicted.

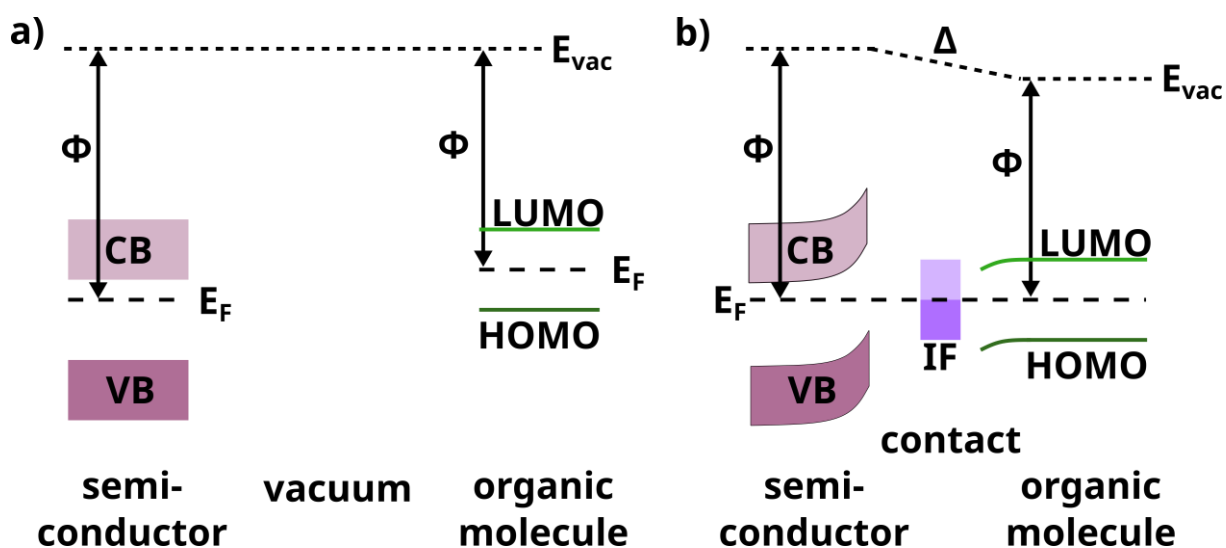


Figure 2.9: Electronic structure of a semiconductor substrate and an organic molecule a) without contact and b) in contact under formation of an interface state (IF), an interface dipole Δ and band bending. Own representation based on Ishii et al.⁸²

Heterostructuring TMDCs with organic molecules proved itself as a valuable approach to modify its electronic properties. Especially since the 2D TMDCs are known to contain many defects as discussed in 2.3.1, which affect the performance in electronic and photonic applications due to limited charge mobility. The absence of dangling bonds at the TMDC surface allows the formation of weakly interacting van der Waals

organic/TMDC heterostructures. By charge transfers across the interface electrostatic interactions occur, mostly for strong donor or acceptor molecules.²⁵ For example, via photoemission spectroscopy Song et al.⁸³ demonstrated p-doping of single layer WSe₂ by heterostructuring with the electron accepting fullerene C₆₀F₄₈. Additionally, in a study by Zheng et al.⁸⁴ it was shown that the organic molecule perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) forms interfaces with single layer WSe₂ that exhibit strong screening of the HOMO-LUMO gap of the molecule by 1.0 eV proving the capability of TMDCs to allow electronic interactions in organic-inorganic devices. The comprehensive study by Mouri et al.⁸⁵ showed how p-type doping of MoS₂ via 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and n-type doping via nicotinamide adenine dinucleotide (NADH) allowed tuning of the photoluminescence (PL) of the TMDC. The p-type doping with the TCNQ molecule led to a drastic increase in the PL intensity which was attributed to the switching of the recombination of negative trions to the recombination of excitons while for the n-type doped MoS₂/NADH interface a suppression in exciton PL intensity was observed due to the injection of excess electrons.

By these selected examples the potential of TMDC/organic molecule interfaces could already been shown. Therefore, the interest in expanding these findings to other heterointerfaces has increased. Since strong interactions involving integer charge transfers lead to an undesired localization of the charge, the TMPc/TMDC interfaces are desired as those molecules are typically found to be weakly interacting.²⁰ Pak et al.^{86,87} were able to demonstrate that the functionalization of MoS₂ with CuPc leads to an improved performance in photodetection with lower photoswitching decay times which was attributed to the transfer of charge carriers from CuPc to MoS₂. Inspired by these findings, many more TMDC/TMPc heterostructures like the MoS₂/FePc(F₄, F₁₆), MoS₂/CoPc(F₁₆) or the WSe₂/CoPcF₁₆ interfaces have been investigated which underlines the significance of future works in this field.^{20,22,88}

2.4 Measurement techniques and set-ups

To investigate the electronic properties of the TMDCs and interfaces of interest it is pivotal to utilize appropriate techniques of spectroscopy. Photoemission spectroscopy (PES) allows a highly surface sensitive analysis of the electronic structure, with information depths down to 2–10 monolayers. Experiments using the techniques below were conducted at three different facilities: the home laboratory offers a monochromatized Al K α source ($h\nu = 1486.6$ eV) and a He discharge lamp with He I ($h\nu = 21.2$) and He II ($h\nu = 40.8$ eV) excitation to measure XPS and ultraviolet photoemission spectroscopy (UPS). Using synchrotron radiation (schematically depicted in Figure 2.10) at the *Karlsruhe research accelerator* (KARA) and *Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung* (BESSY II), additional experiments in terms of angle-resolved photoemission spectroscopy (ARPES), photoemission electron microscopy (PEEM, only at KARA) and X-ray absorption spectroscopy (XAS) can be performed which allow mapping of the band structure, microresolution of monolayer flakes and further insights in the electronic structure and the orientation of the investigated structures.

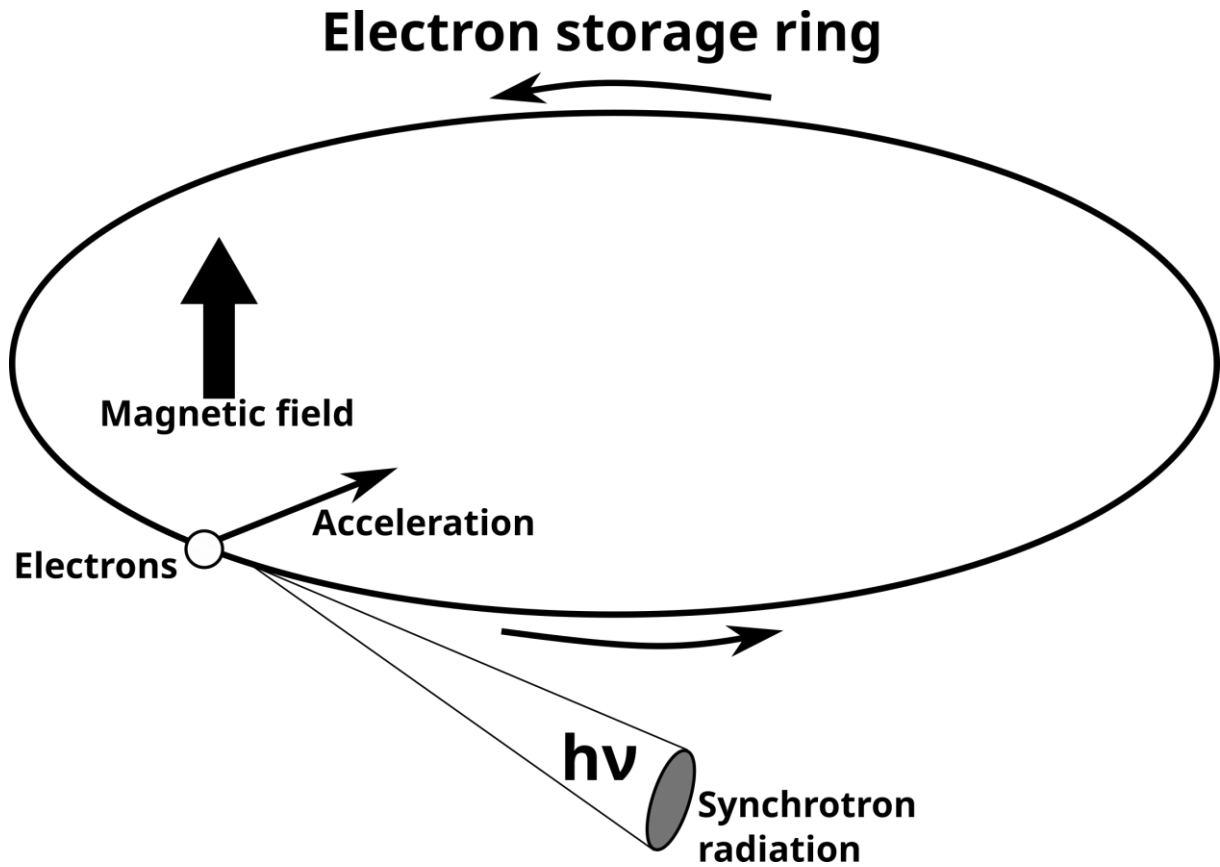


Figure 2.10: Formation of synchrotron radiation at an electron storage ring. The electrons, which have been accelerated to relativistic velocities by a linear accelerator or booster, are injected into the storage ring where they interact with a magnetic field to keep their circular trajectory under emission of synchrotron radiation as depicted.

2.4.1 X-ray photoemission spectroscopy

After Albert Einstein was awarded the Nobel prize in 1921 for the explanation of the photoelectric effect, Kai Siegbahn developed a novel technique for the investigation of solid matter in the 1950s which was later called XPS. The irradiation by X-rays leads to the emission of photoelectrons if the excitation energy of the incoming light ($h\nu$) is sufficient to overcome the binding energy (E_B). The analyzer can detect the incoming photoelectrons in dependence of their kinetic energy (E_{kin}) according to the fundamental equation of XPS (eq. 2.4):

$$E_{kin} = h\nu - E_B - \phi_S \quad (2.4)$$

With ϕ_S as the work function of the spectrometer which is the minimum energy a previously emitted photoelectron in the spectrometer needs to traverse from its Fermi level to the vacuum level.⁸⁹

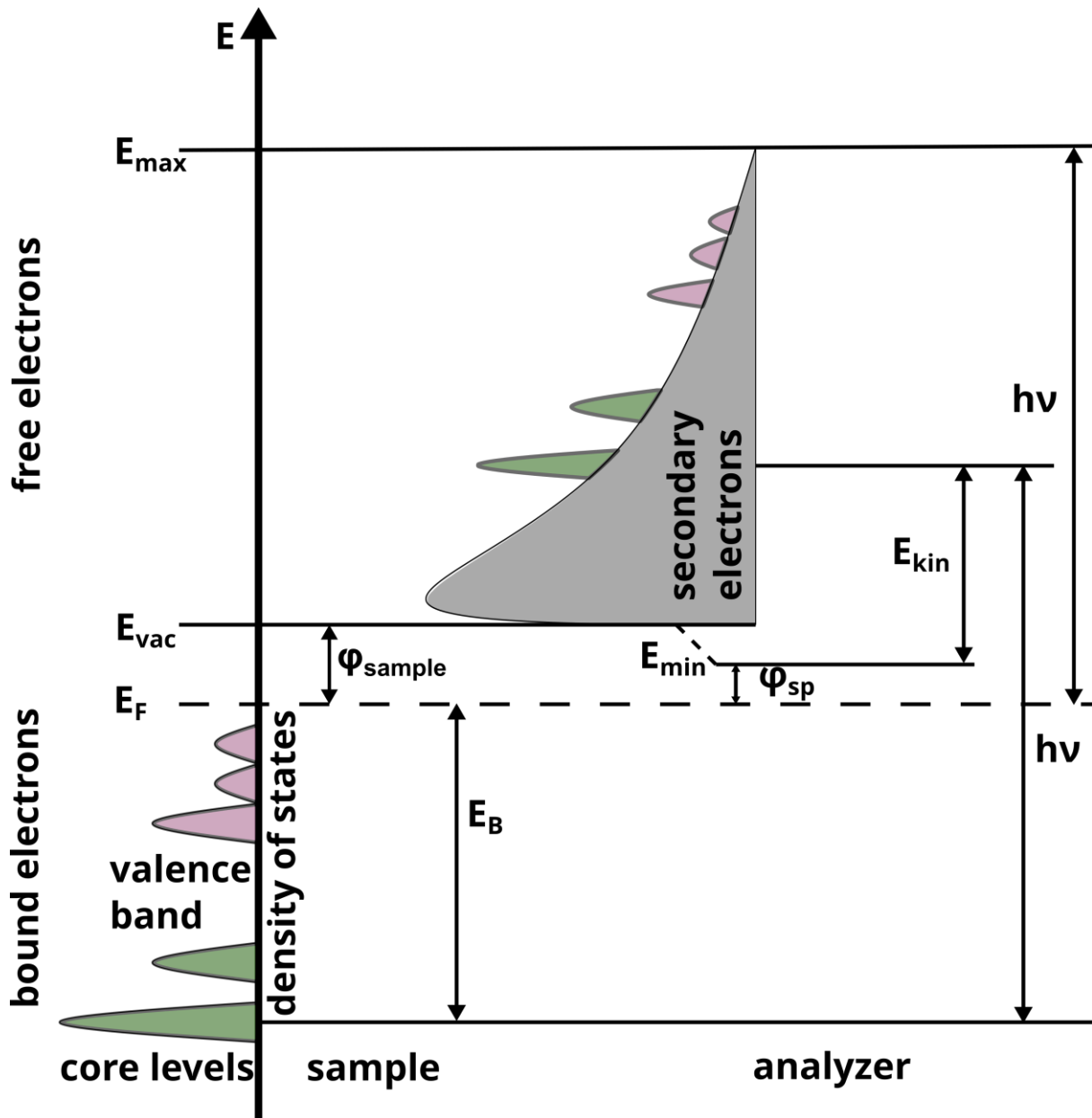


Figure 2.11 :Photoionization and detection of photoelectrons at the sample and the analyzer. Own representation based on Henzler et al.⁹⁰

To fully grasp the photoemission process, the three-step model is introduced:

In the first step, the photoelectron is created by the photoexcitation, via the incident X-rays, of an electron inside the material. In the second step, the photoelectron travels to the surface of the sample where it is then emitted to the vacuum in the third step.⁹¹

The photoemission intensity is then given as a function of the kinetic energy of the photoelectron in vacuum and the photon energy $h\nu$.

To interpret core level spectra a brief explanation about the most important characteristics of yielded spectra is given:

1. Chemical shift

In core level spectroscopy, differences in kinetic energy of detected photoelectrons can be observed due to the dependence of the binding energy of a particular electronic state on its chemical environment. According to the Koopmann theorem, the emission of an electron does not affect the remaining atomic/molecular orbitals and therefore the measured binding energy is equal to the orbital energy $-\epsilon_i$ of the initial state i . During photoemission the system with N electrons (initial state) is transformed to a system with $N-1$ electrons and a hole (final state). Since the hole is shielded by the remaining $N-1$ electrons, the observed binding energies are smaller than $-\epsilon_i$ which is expressed by the dynamic relaxation energy R_D .

The chemical shift ΔE_B as the difference in binding energy between the examined sample and a reference sample (e.g. doped vs. undoped sample, lower oxidized vs higher oxidized sample) can be separated in an initial state contribution and a final state contribution. The initial state is decisively affected by the potential effect. Due to different chemical environments, the electron distribution in the sample is changed. Assuming point charges, the Pauling charge q_p of a central atom A can be calculated as:

$$q_p(A) = \frac{q}{e} + \sum_B \delta(AB_i) \quad (2.5)$$

With the formal charge $\frac{q}{e}$ and the ionicity $\delta(AB_i)$ calculated with the electronegativities χ_A and χ_B for the central atom and its neighbors B :⁹⁰

$$\delta(AB_i) = 1 - e^{-0.25(\chi_A - \chi_B)^2} \quad (2.6)$$

2. Spin-orbit splitting

For all orbitals with a quantum number $l > 0$, doublets are observed in the core level spectra. The interaction between the spin and the angular momentum of the electron leads to a spin-orbit-coupling quantified by the quantum number $j = l + s$. For $s = \pm \frac{1}{2}$ the spin-orbit splitting and the population of states $(2j+1)$, which governs the intensity ratio observed in the spectra, can be calculated for the different orbitals as shown in Table 2.1.

Table 2.1: Spin-orbit splitting and density of states for p,d and f orbitals.

Orbital	$j = l + s$	Population of states ($2j+1$)
p ($l=1$)	$\frac{3}{2}; \frac{1}{2}$	4:2
d ($l=2$)	$\frac{5}{2}; \frac{3}{2}$	6:4
f ($l=3$)	$\frac{7}{2}; \frac{5}{2}$	4:3

Additionally, if an atom contains unpaired spins (e.g. Co^{2+}), spin-spin coupling between the electronic spin of the emitted photoelectron and the unpaired electron can be observed. This leads to a more complex multiplet structure.⁹²

3. Satellite peaks and surface plasmons

During photoemission, the photoelectron can excite another electron under the loss of energy. The detected photoelectron is then observed at slightly lower kinetic energy (or higher binding energy) as a satellite. If the secondary electron is excited to a higher orbital, it is called a shake-up satellite, if it is also emitted, it is referred to as a shake-off satellite.

In addition, the emitted photoelectron can also interact with surface plasmons (quantized electron oscillation) which leads to an additional loss in kinetic energy. These peaks are typically called loss signals.⁸⁹

Calculation of film thicknesses

By comparing core level intensities of the photoemission peaks of overlayer and substrate signals, layer thicknesses can be calculated by determining the inelastic mean free path of the detected photoelectrons.

Firstly, the attenuation of the substrate signal must be considered via equation 2.7:

$$I_S = I_{0,S} \exp\left(\frac{-d}{\lambda_S \cdot \cos(\theta)}\right) \quad (2.7)$$

With I_S as the intensity of the attenuated substrate signal, $I_{0,S}$ as the intensity of the substrate signal without attenuation, d the layer thickness, λ_S the inelastic mean free path (IMFP) of the photoelectron of the substrate signal and θ as the angle between sample and analyzer. For higher layer thicknesses, an increasing signal of the overlayer is expected according to (2.8):

$$I_D = I_{\infty,D} \left(1 - \exp\left(\frac{-d}{\lambda_D \cdot \cos(\theta)}\right)\right) \quad (2.8)$$

With I_D as the intensity of the overlayer signal, $I_{\infty,D}$ as the intensity of an infinitely thick overlayer and λ_D the IMFP of the photoelectron derived from the overlayer.

Since $I_{0,S}$ and $I_{\infty,D}$ can typically not be measured directly, the ratio between them can be replaced with the ratio between the respective sensitivity factors for the substrate s_S and the overlayer s_D .

$$\frac{I_D s_S}{I_S s_D} = \frac{1 - \exp\left(\frac{-d}{\lambda_D \cdot \cos(\theta)}\right)}{\exp\left(\frac{-d}{\lambda_S \cdot \cos(\theta)}\right)} \quad (2.9)$$

Assuming $\lambda_D \approx \lambda_S \equiv \lambda$ the equation can be simplified further as:

$$d = \lambda \cos(\theta) \cdot \ln\left(1 + \frac{I_D s_S}{I_S s_D}\right) \quad (2.10)$$

In a final step the number of emitters per volume must be taken into consideration since not all atoms from substrate and overlayer molecules are of the same species.

$$d = \lambda \cos(\theta) \cdot \ln\left(1 + \frac{I_D s_S \left(\frac{\rho x}{M}\right)_S}{I_S s_D \left(\frac{\rho x}{M}\right)_D}\right) \quad (2.11)$$

where ρ is the density, x the stoichiometry number (number of atoms in the chemical formula) and M the molar mass.⁹³

According to Seah and Dench⁹⁴ the IMFP for atomic (metal), and organic (phthalocyanine) overlayers can be calculated by the following equations:

$$\lambda_m = \frac{538}{E^2} + 0.41\sqrt{aE_{kin}} \quad \text{for atoms} \quad (2.12)$$

$$\text{and} \quad \lambda_d = \frac{49}{E^2} + 0.11\sqrt{E_{kin}} \quad \text{for organic molecules} \quad (2.13)$$

With λ_m as the IMFP in monolayers, λ_d as the IMFP in milligrams per square meter, the monolayer thickness a , and the kinetic energy of the photoelectron E_{kin} .

The conversion to an IMFP in nanometers is given by equations 2.14 and the monolayer thickness a is calculated as shown by equation 2.15:

$$\lambda_n = a\lambda_m = \frac{\lambda_d}{10^{-3}\rho} \quad (2.14)$$

$$a = \sqrt[3]{\frac{A}{\rho n N}} \cdot 10^8 \quad (2.15)$$

Given by the atomic/molecular weight A , the number of atoms in the molecule n and Avogadro's number $N=6.022 \times 10^{23} \text{ mol}^{-1}$.

2.4.2 Ultraviolet photoemission spectroscopy

To specifically probe the valence band of the structures of interest, it is beneficial to probe the electrons of highest energy by ultraviolet photoemission spectroscopy (UPS) as depicted in Figure 2.12a. UPS works with excitation energies of $h\nu < 100 \text{ eV}$. According to the models by Seah and Dench⁹⁴ this leads to a minimal inelastic mean free path (IMFP) λ of the emitted photoelectrons as shown in Figure 2.12b. Therefore, the information depth is confined to the topmost layers which makes this technique especially well-suited for the investigation of interfaces.

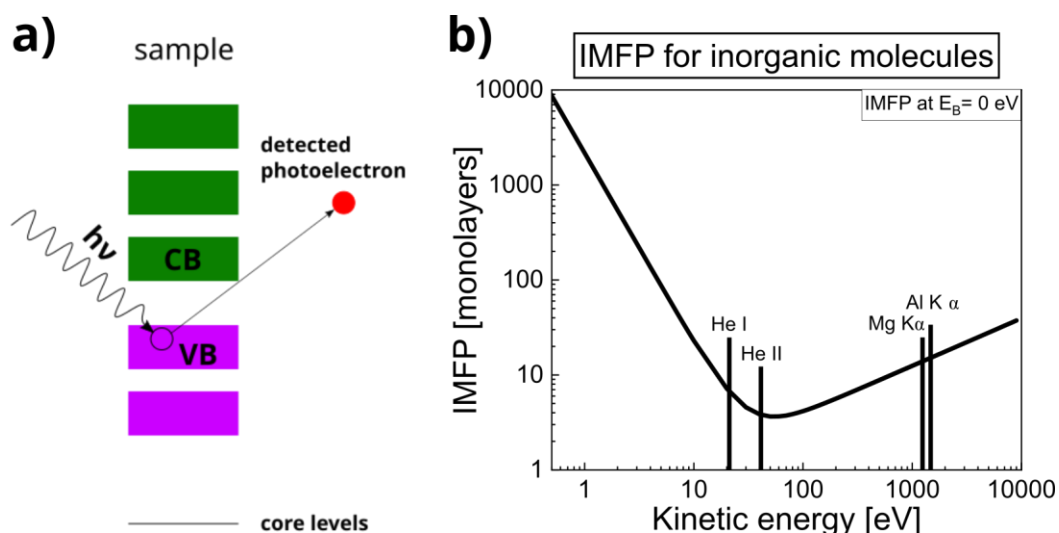


Figure 2.12: a) Formation of photoelectrons in UPS and b) inelastic mean free path (IMFP) at $E_B=0$ eV for common light sources (He I, He II, Al K α , Mg K α). Own representation using the formula given by Seah and Dench for inorganic molecules.⁹⁴

The most common sources of excitation for UPS are helium discharge lamps. By applying a high voltage to a filament, electrons from that metal wire (typically tungsten) are emitted. These are then accelerated towards an anode. During this process they collide with He atoms inside the chamber causing the excitation of bound electrons from the 1s orbital to unoccupied states. Transition from an excited p orbital (2p, 3p, 4p) back to the 1s orbital leads to the emission of ultraviolet (UV) radiation as schematically depicted in Figure 2.13a. Notably, since the selection rule $\Delta l = \pm 1$ applies for electronic transitions, no other paths of relaxation are observed. The most intense transition $2p \rightarrow 1s$ is defined as He I α with an energy of 21.22 eV and is accompanied by satellites stemming from higher transitions called He I β ($3p \rightarrow 1s$) and He I γ ($4p \rightarrow 1s$), also depicted in Figure 2.13c.

If higher filament currents are used, the He atoms can be ionized to He^+ which lowers the energy of the spherically symmetrical s orbitals the most. Therefore, the energy of the $2p \rightarrow 1s$ transition increases to a value of 40.81 eV, which is then called He II α excitation, as schematically depicted in Figure 2.13b and c. This He II excitation leads to almost minimal IMFPs at the valence band, where $E_{\text{kin}} \approx h\nu$ (as shown in Figure 2.12b) which makes it an especially powerful technique for the investigation of interfacial electronic structures.⁹⁵

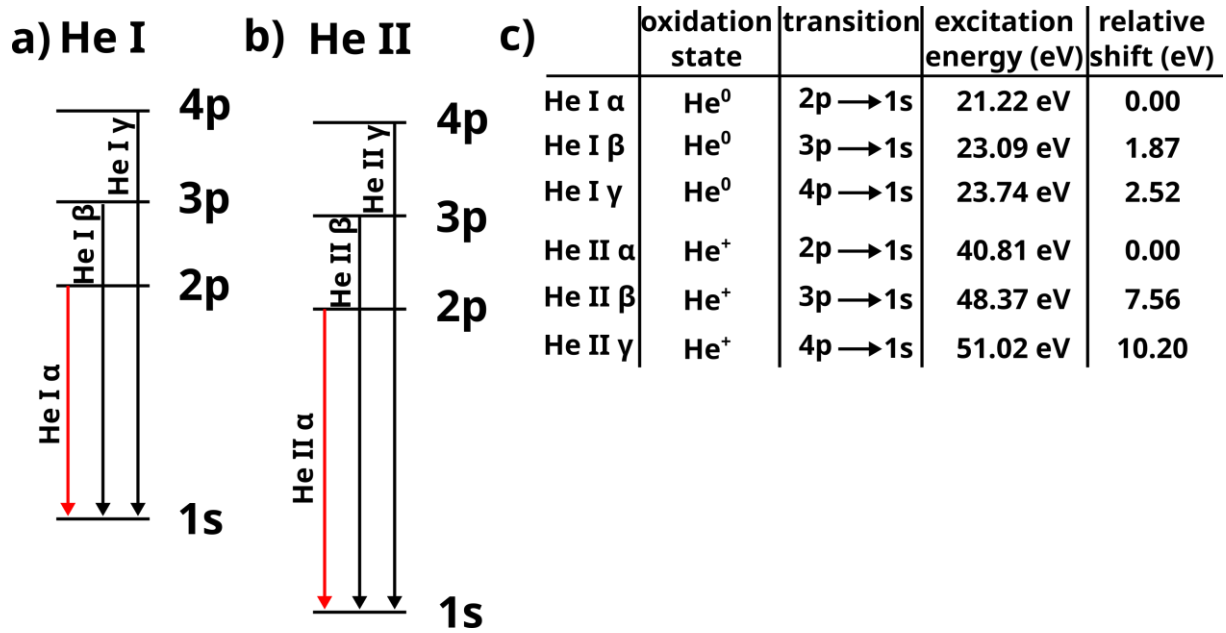


Figure 2.13: Helium discharge lines including satellites for a) Helium I excitation and b) Helium II excitation, c) summarizes the resulting excitation energies, and relative shifts and intensities for the different transitions (values taken from ref⁹⁵).

2.4.3 Angle-resolved photoemission spectroscopy

In order to achieve deeper understanding of the valence band, Angle-resolved PES (ARPES) experiments can be conducted. This technique allows the mapping of the k-space of lateral samples like TMDCs by altering the angle θ between the sample and the analyzer. This is achieved either by turning the analyzer or the sample as depicted in Figure 2.14a. In addition, 2D analyzers can image large areas of reciprocal space.

To interpret the resulting band structures, it is pivotal to understand the most important points of high symmetry in the TMDCs of interest which are depicted in Figure 2.14b.

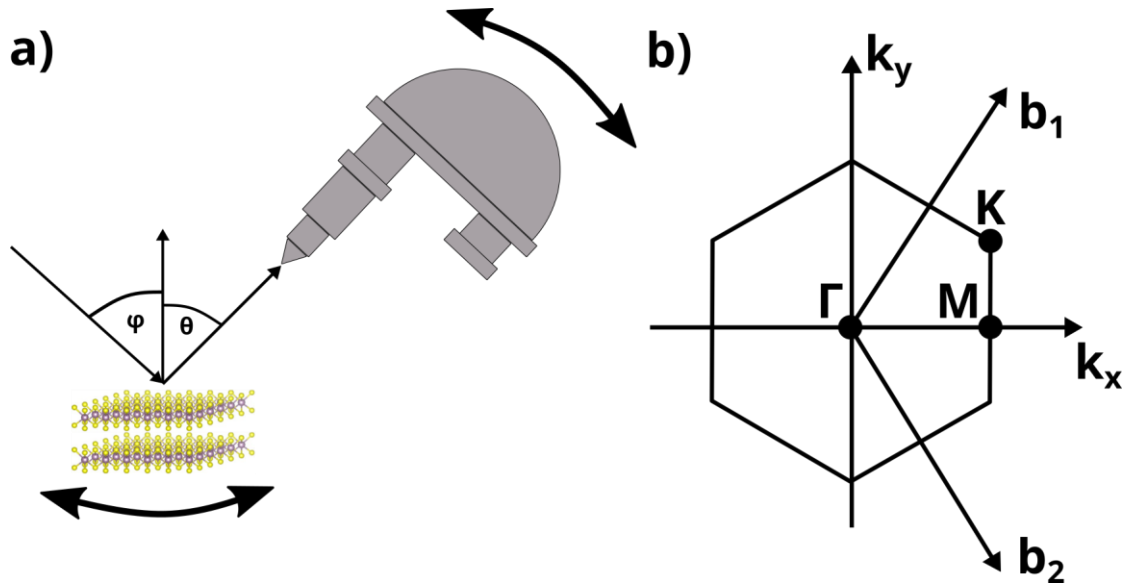


Figure 2.14: a) Geometry of an ARPES experiment with either a movable detector or a movable sample. b) Geometry of k_x - k_y momentum maps of a hexagonal system with the most important points of high symmetry.

The electron wave vector k can be defined by a component perpendicular to the molecular plane $k_{\perp}$ and a component parallel to the molecular plane $k_{\parallel}$.

The latter can be calculated using θ as:

$$k_{\parallel} = \sin \theta \sqrt{\frac{2m_e \cdot E_{\text{kin}}}{\hbar^2}} \quad (2.16)$$

With the electron mass $m_e \approx 9.11 \cdot 10^{-31}$ kg and the Reduced Planck constant $\hbar \approx 1.05 \cdot 10^{-34}$ Js.⁹⁶

Which can then be used to map the reciprocal space via the coordinates k_x and k_y :

$$k_{\parallel} = \sqrt{k_x^2 + k_y^2} \quad (2.17)$$

The lattice vectors of the reciprocal space can be constructed via equations 2.18 and 2.19.⁹⁷

$$\vec{b}_1 = \frac{2\pi}{a_1} \left(\frac{\sqrt{3}}{3} k_x + k_y \right) \quad (2.18)$$

$$\vec{b}_2 = \frac{2\pi}{a_2} \left(-\frac{\sqrt{3}}{3} k_x + k_y \right) \quad (2.19)$$

The distances between the high symmetry points can then be calculated using the coordinates in reciprocal space:⁹⁸

$$\Gamma = (0,0); M = \frac{\vec{b}_1 + \vec{b}_2}{2}; K = \frac{(\vec{b}_1 + 2\vec{b}_2)}{3}$$

$$|\Gamma M| = \frac{2\pi}{\sqrt{3} \cdot a} \quad (2.20)$$

$$|\Gamma K| = \frac{4\pi}{3 \cdot a} \quad (2.21)$$

Using the lattice parameteres given in Chapter 2.1.1, the distances between Γ , K and M can be calculated as depicted in Table 2.2:

Table 2.2: Calculated distances $|\Gamma M|$ and $|\Gamma K|$ for MoS₂ and MoSe₂.

TMDC	$ \Gamma M $ (Å ⁻¹)	$ \Gamma K $ (Å ⁻¹)
MoS ₂	1.15	1.33
MoSe ₂	1.10	1.27

2.4.4 Photoemission electron microscopy

The monolayers investigated in this thesis have a size of about 5–20 μm and can therefore not be resolved by most set-ups due to lacking focus of the beam, and commonly used analyzers that do not allow such a high spatial resolution.

Using photoemission electron microscopy (PEEM), the area of the surface of a solid material is imaged by spatially resolving the emitted electrons after the absorption of photons. This technique was first described by E. Brüche in the early 1930s using UV excitation provided by a mercury lamp.⁹⁹

Nowadays, these experiments are often carried out at synchrotron beamlines using the highly polarized and intense X-rays provided by the electron storage ring. To achieve image contrast, the different work functions of the materials investigated can be utilized. Areas with smaller work functions (e.g., silicon substrates, MoS₂ monolayers) show a brighter contrast when compared to areas with higher work functions (e.g., MoS₂ bulk). Furthermore, elemental contrast allows the mapping using the resonant X-ray absorption at specific photon energies. Regions that contain the absorbing atom are then observed as being brighter than regions without those atoms. By these techniques resolutions down to 30 nm can be achieved.

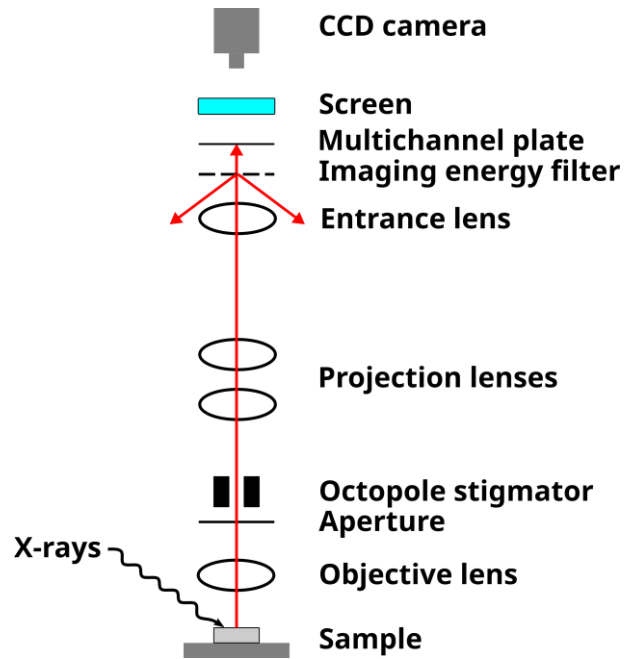


Figure 2.15: Schematic composition of a PEEM set-up with an imaging energy filter (IEF). The emitted photoelectrons are extracted and magnified via the objective lens. Via the aperture stray electrons are filtered out. The octupole stigmator corrects astigmatism. The projection lenses further magnify the image. The electron beam is focused via the entrance lens. The imaging electron filter filters high energy electrons to reduce chromatic aberration. The multichannel plate increases the photoelectron signal. A phosphorous screen transforms the electronic signal into an optical signal which is then detected by the charge-coupled device (CCD) camera.

Figure 2.15 depicts the basic schematic composition of a PEEM set-up. The irradiation of the sample with X-rays leads to the emission of photoelectrons with a specific kinetic energy E_{kin} . These negatively charged electrons are then extracted and focused by an electrostatic objective lens via high electric fields. Via the aperture the angular acceptance of the emitted electrons is changed, which influences the intensity and resolution of the detected signal. To correct astigmatism (different focusing in x and y direction), typically an octupole stigmator is used which further improves the quality of the image. The projection lenses then magnify the image. The entrance lens represents the transition into the analyzer. Here the electron beam is focused before reaching the energy filter. The imaging energy filter acts as a high-pass filter: Electrons with kinetic energies higher than the applied potential can pass the micro grid while electrons with lower kinetic energies are repelled. The electron signal is amplified by the multichannel plate as every electron on the plate triggers an avalanche of further

electrons since otherwise the signal intensity would be too weak. At the phosphorous screen the electron signal is then transformed into an optical image which is detected by the charge-coupled device (CCD) camera.¹⁰⁰

While common photoemission techniques fail to resolve individual TMDC flakes on micrometer scale, the PEEM technique allows spatially resolved analyses even down to nanometer scale. Therefore, not just individual flakes can be resolved but even information on different parts of the same flake can be obtained. Even though the signal is admittedly much weaker when compared to regular PES experiments, a set choice of different ranges of interest (RoI), in this case: areas with the same number of layers on a TMDC flake, gives valuable information about the electronic properties on distinct structures. Besides photoemission, the PEEM set-up can also detect X-ray absorption signals, allowing μ XAS experiments.

2.4.5 X-ray absorption spectroscopy

To determine the local geometry of adsorbed molecules like the TMPcs used in this work, X-ray absorption spectroscopy (XAS) became a feasible method after the establishment of synchrotron beamlines which provide a highly intense continuous spectrum of electromagnetic radiation.¹⁰¹

In X-ray absorption spectroscopy the fine structure of the X-ray absorption coefficient σ_x is measured in dependence of the excitation energy.

According to Beer's law (eq. 2.22) the intensity of the transmitted X-rays I_t depends on the intensity of the incident X-rays I_0 and the sample thickness t as depicted in Figure 2.16a.

$$I_t(t) = I_0 e^{-\sigma_x t} \quad (2.22)$$

At the lowest X-ray energies at which a photon can be absorbed, an electron is excited to an unoccupied bound state, as illustrated in Figure 2.16b.¹⁰²

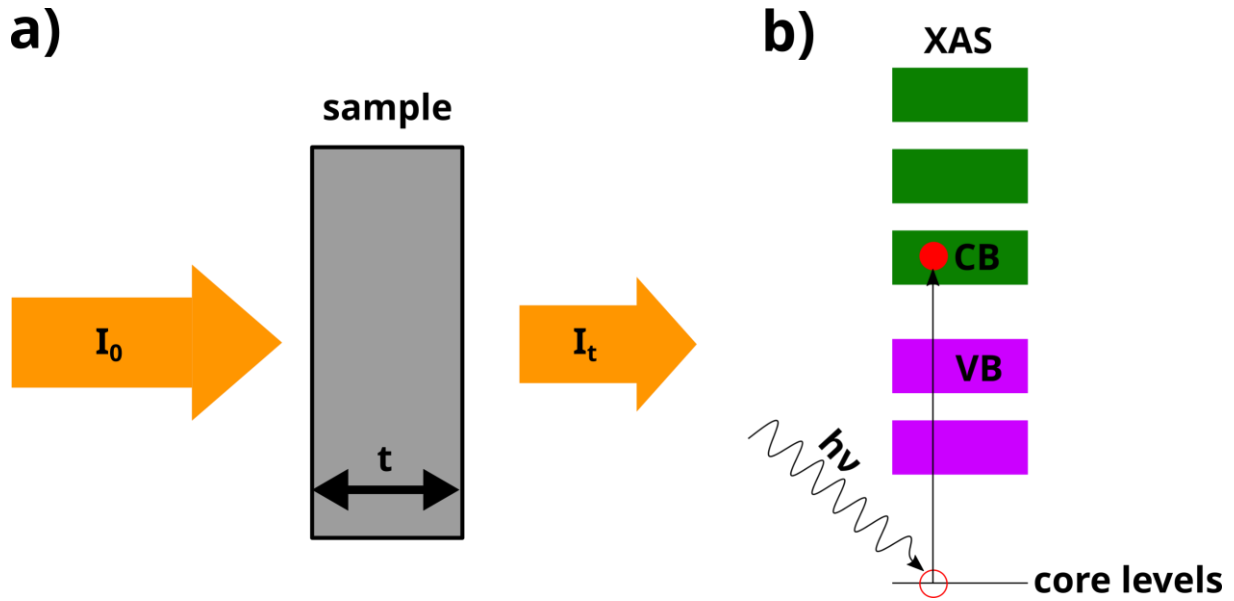


Figure 2.16: Scheme of X-ray absorption: a) Attenuation of the incident intensity of the X-rays according to Beer's law and b) Observed transition of a photoelectron from a core level to an excited state.

According to Fermi's Golden Rule the transition probability P_{if} from the initial state $|i\rangle$ to the final state $|f\rangle$ is given by equation 2.23.

$$P_{if} = \frac{2\pi}{\hbar} |\langle f | \bar{V} | i \rangle|^2 \rho_f(E) \quad (2.23)$$

Where $\bar{V}$ is given by the harmonic time-dependent perturbation $V(t) = \bar{V}e^{-i\omega t}$ and the energy density of final states $\rho_f(E)$.¹⁰³

The resulting spectra as functions of σ_x in dependence of the energy of the X-rays can be split into two regions. The region close to the absorption edge of a specific atom is considered the near edge X-ray absorption fine structure (NEXAFS, also known as X-ray absorption near edge structure XANES). The region beyond the NEXAFS is called the extended X-ray absorption fine structure (EXAFS) and indicates transitions from the bound ground state to a free state or continuum which will not be discussed further in this thesis.

The NEXAFS region is highly sensitive to chemical bonding and the oxidation states in the observed molecule.¹⁰² The NEXAFS spectra are often defined by complex multiplet structures which derive from the presence of a core hole in the final state. For instance, for Co(II) XAS, a transition from Co 2p into Co 3d orbitals is observed ($2p^63d^7 \rightarrow 2p^53d^8$). Due to electron-electron repulsion and spin-orbit coupling, the final

state is split into various states with slightly different energy (as indicated by its different term symbols), leading to a multiplet spectrum.¹⁰⁴

In addition, the resonance intensities reveal an angular dependence in polarization dependent experiments. Even though the symmetry of molecular orbitals (MOs) differs between molecules in free space and adsorbates, their directionality remains. For example, for K-shell excitation (excitation from the 1 s orbital to an unoccupied MO), the spatial distribution of the unoccupied orbitals plays a significant role.¹⁰³

Figure 2.17 depicts the directional geometry for transitions into σ^* - and π^* -orbitals which are common for many organic molecules and for the transition from the highest occupied molecular orbital of a central metal atom where the symmetry of the 3d orbitals (here: d_{z^2} and $d_{x^2-y^2}$) can be assumed.

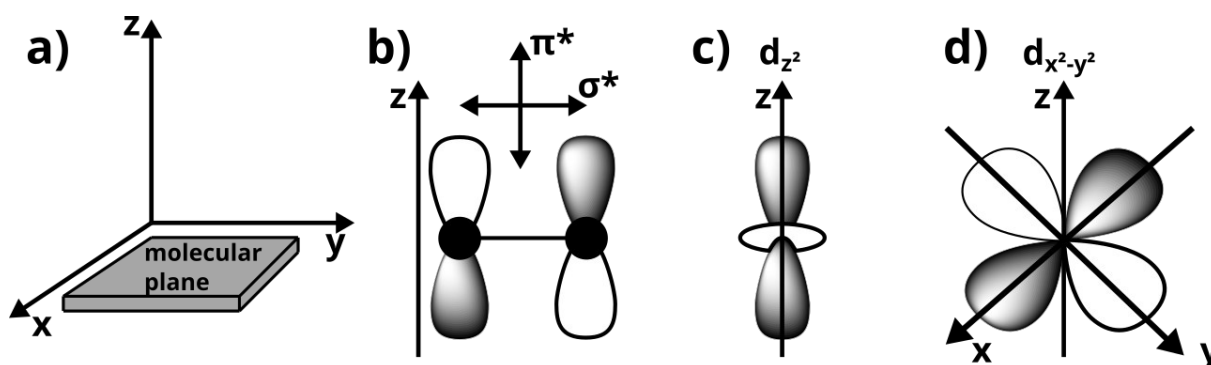


Figure 2.17: Geometry of orbitals with respect to a) the molecular plane, b) π^* and σ^* orbitals, c) d_{z^2} orbital and d) $d_{x^2-y^2}$ orbitals.

For planar organic molecules like TMPcs, the shown σ^* -bond of e.g. a (hetero-)aromatic ring lies in the x-y-orientated molecular plane, while the π^* -bond is orientated perpendicular along the z-axis. For metal atoms like the Co core of CoPc(F₁₆), the d-orbitals are also orientated differently with respect to the molecular plane. While the d_{z^2} -orbital is mostly oriented perpendicular to the x-y-plane, the $d_{x^2-y^2}$ -orbital lies within the molecular plane.

To understand the interaction of the given orbital symmetries with the electric field vector E of the incident light, the vector can be described by two orthogonal components as depicted in equation 2.24.

$$E = E^{\parallel} \cos(kz - \omega t) + E^{\perp} \sin(kz - \omega t) \quad (2.24)$$

With k as the momentum of the X-rays and ω the frequency of the electromagnetic wave. $E^{\parallel} = |E^{\parallel}|e^{\parallel}$ and $E^{\perp} = |E^{\perp}|e^{\perp}$ are the maximum components of the electric field vector in and perpendicular to the molecular plane with e being the corresponding unit vectors in the direction of the electric field vector. For mostly linear polarized light, which was used for the experiments discussed in this thesis, $E^{\perp} \approx 0$ can be assumed.

For linear polarized light, the transition intensity is proportional to the quadratic matrix element as shown via the proportionality relation (2.25):

$$I \propto |e \cdot \langle f | p | i \rangle|^2 \quad (2.25)$$

With $\langle f |$ and $|i\rangle$ representing the final and initial state of the transition and the momentum operator p .

Figure 2.18 serves to explain the geometry at the molecular plane for a vector final state (a) and a plane final state (b).

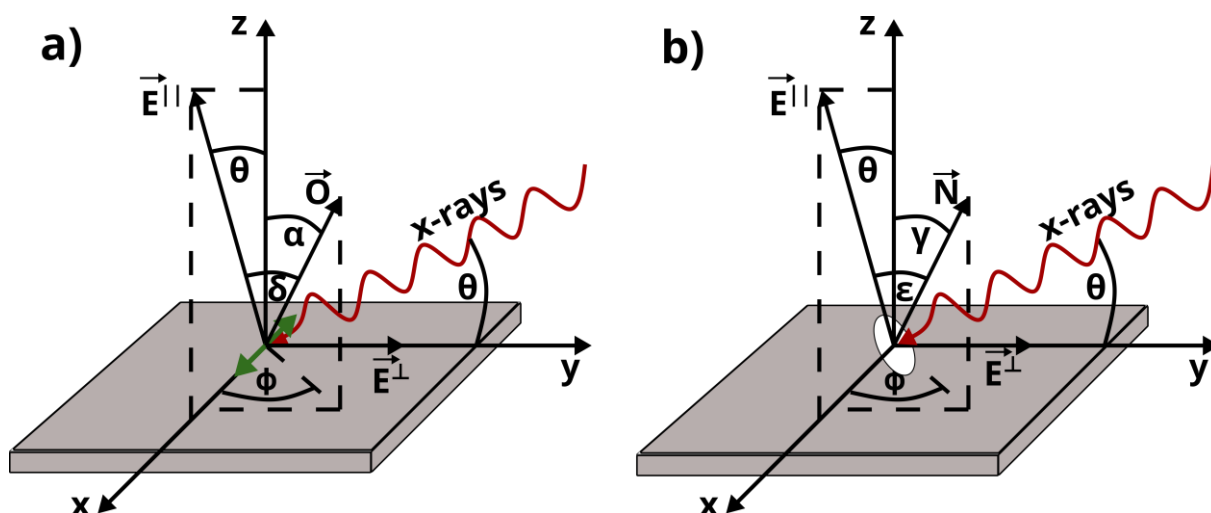


Figure 2.18: Geometry at the molecular plane according to Stöhr.¹⁰³ With θ as the angle of incident which is equal to the polar angle of $\vec{E}^{\parallel}$ and the azimuthal angle ϕ . a) depicts the vector final state (green arrow) in the direction $\vec{O}$ characterized by ϕ and the polar angle α . δ describes the angle between $\vec{O}$ and $\vec{E}^{\parallel}$. For the plane final state (white plane) depicted in b) its direction is given by $\vec{N}$ characterized by ϕ and the polar angle γ . The angle between $\vec{N}$ and $\vec{E}^{\parallel}$ is given as ϵ .

Using (2.25) the intensity of the transition I_v for the vector case can then be described with respect to the angle δ as depicted in equation 2.26.

$$|\mathbf{e} \cdot \langle f | \mathbf{p} | i \rangle|_V^2 \propto I_V = \cos^2(\delta) \quad (2.26)$$

By integrating equation 2.26 over all azimuthal angles the intensity of the transition I_p for the plane case is given as

$$|\langle f | \mathbf{e} \cdot \mathbf{p} | i \rangle|_p^2 \propto I_p = \sin^2(\epsilon) \quad (2.27)$$

I_V and I_p can then be separated into angle-dependent components. The $E^\perp$ components are denoted as $I_V^\perp$ and $I_p^\perp$ respectively, the $E^\parallel$ components as $I_V^\parallel$ and $I_p^\parallel$.

The intensities $I_V^\perp$ and $I_V^\parallel$ can then be expressed using the angles θ , α and ϕ :

$$I_V^\perp = \sin^2(\alpha) \sin^2(\phi) \quad (2.28)$$

$$I_V^\parallel = \cos^2(\theta) \cos^2(\alpha) + \sin^2(\theta) \sin^2(\alpha) \cos^2(\phi) \quad (2.29)$$

$$+ 2\sin(\alpha) \cos(\alpha) \sin(\theta) \cos(\theta) \cos(\phi)$$

For the plane case, the intensities $I_p^\perp$ and $I_p^\parallel$ are expressed using the angles θ , γ and ϕ :

$$I_p^\perp = 1 - \sin^2(\gamma) \sin^2(\phi) \quad (2.30)$$

$$I_p^\parallel = 1 - \cos^2(\theta) \cos^2(\gamma) - \sin^2(\theta) \sin^2(\gamma) \cos^2(\phi) \quad (2.31)$$

$$- 2\sin(\gamma) \cos(\gamma) \sin(\theta) \cos(\theta) \cos(\phi)$$

In the case of flat molecules like the TMPcs of interest, $E^\perp$ is always in the molecular plane, and therefore intensity changes are dependent on the change of $E^\parallel$. At this geometry $\vec{O}$ is perpendicular to the surface plane, leading to $\alpha=0$. Assuming a vector final state, the expression for I_V simplifies using 2.28 and 2.29 as:

$$I_V = I_V^\parallel = \cos^2(\theta) \quad (2.33)^{103}$$

A more simplified understanding of the geometry between the orbitals, the electric field vector of the X-ray beam and its angle of incident θ is given in Figure 2.19:

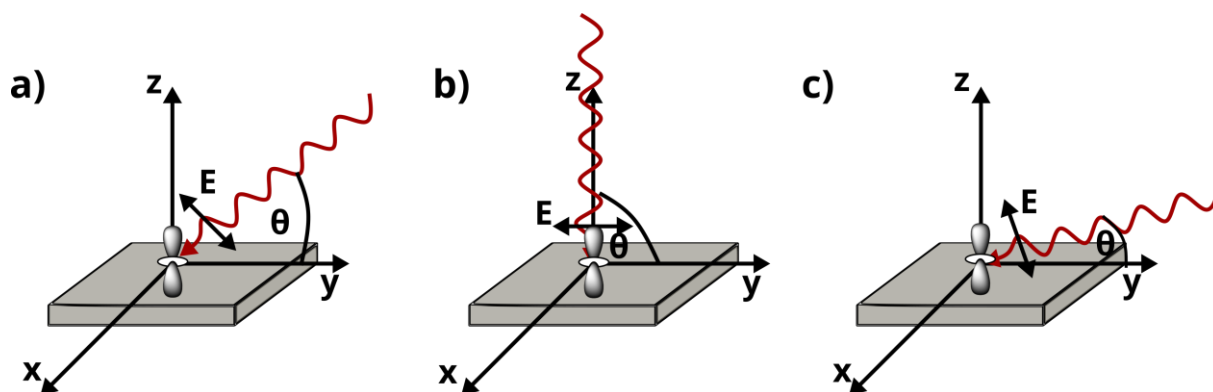


Figure 2.19: Geometry of the electric field vector in comparison to the molecular plane with exemplary d_{z^2} orbital for a) $\theta = 45^\circ$ incidence, b) normal incidence ($\theta = 90^\circ$) and c) grazing incidence ($\theta = 10^\circ$).

Considering Figure 2.19, the molecular geometry of an overlayer molecule on a flat substrate can be determined. For instance, measuring polarization dependent XAS was used to determine the orientation of iron phthalocyanine on Ni(111) by Uihlein et al.¹⁰⁵ At the N K-edges transitions into the (mostly) in-plane σ^* orbitals and the (mostly) out-of-plane π^* orbitals can be observed. Via XAS the intensity of these transitions can be monitored as a function of the direction of the electric field vector E . If E is parallel to the molecular plane, mostly transitions into the in-plane σ^* orbitals are observed, whereas an orientation of E perpendicular to the molecular plane yields mostly transitions into the out-of-plane π^* orbitals. In their study, Uihlein et al.¹⁰⁵ showed that for grazing incidence the intensity for the π^* transition was the highest, while normal incidence leads to the highest intensity of the σ^* transitions, proving a flat-lying geometry of iron phthalocyanine on Ni(111).

3. Publications

3.1 Effects of Annealing on Electrode/MoS₂ Interfaces Studied by Photoelectron Spectroscopy

The first publication discussed in this thesis focusses on the interfaces between bulk MoS₂ and different electrode materials like Au, Cu and Ti in dependence of their respective film thickness. Using an electron beam evaporator the metals were deposited *in situ* onto the TMDC substrate. The changes in electronic structure were investigated by XPS and UPS experiments. In a second step, the heterostructures were annealed for 30 minutes at a temperature of 250 °C, simulating accelerated aging to give insights into the long-term stability of devices based on these structures. In addition, scanning electron microscopy was performed to monitor changes in the structure of the adsorbed metals. After the deposition of different film thicknesses of gold onto the MoS₂ substrate, n-type doping of the TMDC was observed, indicated by the core level shifts of the Mo 3d and S 2p XPS signals. The subsequent annealing step did not lead to changes in doping, indicating that the deposited gold atoms stayed in vicinity to the top-layer(s) of the MoS₂ crystal. The more surface sensitive UPS data showed that after deposition, the valence band structure at the heterointerface is heavily dominated by the deposited gold, independent of the film thickness. After annealing, only minor changes are observed in UPS for the multilayer Au film, while for the single layer Au the valence band features of the MoS₂ substrate become more pronounced. For the MoS₂/Cu interface, similar n-type doping was found pre- and post-annealing. In contrast to the previously mentioned results, the valence band structure shows significant changes after annealing, even for multilayer coverages of Cu, indicating mostly MoS₂ at the surface. The deposition of titanium leads to significant alterations of the MoS₂ crystal under the formation of a reduced Mo species, which prevails even after annealing. This indicates a degradation of the top-layer of the MoS₂ substrate. To further investigate the nature of the annealed MoS₂/Au and MoS₂/Cu interfaces, the location of the metal atoms was probed using CoPcF₁₆. For metal atoms at the surface, a charge transfer between these and the cobalt atom of the CoPcF₁₆ molecule can be expected. Considering the acquired Co 2p XPS spectra it can be shown that after the annealing step the cobalt atoms diffuse below the top layer of MoS₂, independent of their layer number. In contrast, for the MoS₂/Au interfaces a full

diffusion was only found for single layer coverages of Au, while in the multilayer case gold atoms remain at the surface of the MoS₂. As the n-type doping is not affected in any case by the annealing step, it can be assumed that the diffused atoms are still directly below the first layers of MoS₂.

Effects of Annealing on Electrode/MoS₂ Interfaces Studied by Photoelectron Spectroscopy

Eric Juriatti¹, Christoph Späth¹, Heiko Peisert^{1,*}, Marcus Scheele^{1,*}

¹ Institut für Physikalische und Theoretische Chemie, Universität Tübingen,
72076 Tübingen, Germany

* Corresponding author

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3.1.1 Abstract

For optoelectronic devices based on transition metal dichalcogenides (TMDCs) like molybdenum disulfide (MoS_2), contacts with metal electrode materials are of great importance. However, the role of possible interactions at these interfaces for the device performance is often not sufficiently considered. We present an in-depth study of interface properties between MoS_2 and Au, Cu and Ti using photoelectron spectroscopy (PES) and scanning electron microscopy (SEM). By post-deposition annealing, we simulate the potential long-term effects of slow metal diffusion into MoS_2 . A doping of the TMDC was observed at the Au and Cu containing interfaces, as well as the (partial) diffusion of metal atoms into the TMDC substrate after annealing. In the case of Ti, we observe profound changes in the electronic structure, indicating a chemical reaction. The deposition of cobalt(II)-hexadecafluorophthalocyanine (CoPcF_{16}) on the metal covered surface was utilized as a probe for the presence of metal atoms on the topmost TMDC layer before and after annealing.

3.1.2 Introduction

In optoelectronics, the interface between common metal contacts and new semiconducting materials is of pivotal interest. In recent years, the group of transition metal dichalcogenides (TMDCs) as two-dimensional semiconductors gained considerable interest due to their unique and easily tunable electronic properties in combination with a layered structure which makes them exceptionally well suited for the miniaturization of novel photodetectors.^{106–108} While many studies focus on single-layer TMDCs like molybdenum disulfide, recent research underlines the importance of multilayered structures for applications in devices.^{2,10} The most commonly used electrode material is Au and is therefore also of special interest in this work. Since titanium is typically used as an adhesion layer in such devices, in many cases MoS_2/Ti is the actually formed heterostructure.^{11,109} In addition, there has been research on copper as a highly conductive and mechanically durable, low-cost electrode material for semiconducting devices which makes it also interesting in this study.^{110–112} Previous works indicate that the metal contacts made of Au and Ti, which are required for most devices, can alter the electronic structure at the interface.^{18,24} In particular, core level shifts in photoemission have indicated an n-doping at such interfaces.^{18,24} In contrast, the observed photoluminescence quenching at the Au/MoS_2 interface was ascribed to a p-doping of MoS_2 .¹¹³

In the present study, we investigate the change of the position of the Fermi level of a MoS₂ bulk substrate in detail upon deposition of Au, Cu and Ti layers with different thicknesses. We use both, (valence band) ultraviolet photoelectron spectroscopy (UPS) and (core level) x-ray photoelectron spectroscopy (XPS), to determine the exact position of the Fermi level in the gap. A gentle annealing was performed to gain insights into the long-term stability of such interfaces as typically modeled via accelerated aging.¹¹⁴ To this end, microscopic techniques and the deposition of cobalt(II)-hexadecafluorophthalocyanine (CoPcF₁₆) give valuable information about diffusion processes across the interface.

In preliminary studies, the influence of weakly adsorbing, organic transition metal phthalocyanines (TMPcs) such as cobalt(II)-hexadecafluorophthalocyanine (CoPcF₁₆) on various substrates was investigated. Such comparatively weakly interacting organic molecules show a flat-lying growth on both metal and MoS₂ substrates.^{27,115,116} For metal substrates like Au and Cu, a charge-transfer from the substrate towards the Co atom of the organic molecule was described.^{115,116} For the MoS₂/CoPcF₁₆ interface no such interaction was found.²⁰ Therefore, we propose that the molecule which was previously used to modify the electronic structure of given semiconductors can serve as a probe for the existence of metal atoms at the top layer of the given TMDC. To investigate the changes in electronic structure and possible interface interactions, we use photoelectron spectroscopy as a highly surface-sensitive method. In addition, we apply scanning electron microscopy (SEM) as a high-resolution microscopic technique to visualize the TMDC/metal interfaces.

3.1.3 Experimental Section

All PES experiments were conducted at our home laboratory setup under ultrahigh vacuum (UHV) conditions (base pressure $8 \cdot 10^{-10}$ mbar). For XPS, a monochromatized Al K α radiation source (XR 50 M, SPECS GmbH) was used. UPS was carried out using a duoplasmatron type discharge UV light source (UVS 300, SPECS GmbH). In both cases a hemispherical energy analyzer (Phoibos 150, SPECS) was used. The energy calibration was performed using Ar-ion sputtered foils of Au, Ag and Cu (Goodfellow Cambridge Ltd.), calibrating to the binding energies of Au 4f_{7/2} (84.00 eV), Ag 3d_{5/2} (368.21 eV) and Cu 2p_{3/2} (932.63 eV). For UPS, the binding energy of 0.0 eV was calibrated as the point of inflection using a sigmoidal fit of the Fermi edge of the same sputtered gold foil.

Synthetic molybdenum disulfide crystals were purchased from 2D semiconductors Inc. and attached to the sample holders with silver conductive paint. To ensure the cleanliness of the pristine MoS₂ crystals, the *in situ* scotch tape method was used. A contamination-free surface was confirmed by UPS work function measurements and the absence of carbon- and oxygen-signals in XPS.

The deposition of the metals was carried out by electron beam evaporation via an EFM 3S (Focus GmbH). Copper and gold films were evaporated at a pressure of 5·10⁻⁹ mbar from a molybdenum crucible, titanium directly from a rod (all metals are purchased from Goodfellow Cambridge Ltd.). A quartz crystal microbalance (QCMB) was used to ensure a deposition rate of approximately 0.1-0.2 nm per minute. In a secondary step, the samples were annealed under UHV conditions via resistance heating to approximately 250–270 °C for a total time of 30 minutes. The temperature was controlled using an IMPAC IGA 15 plus pyrometer (LumaSense Technologies GmbH).

In a separate chamber, cobalt(II)-hexadecafluorophthalocyanine (CoPcF₁₆) (BLD Pharmatech LTD.) was evaporated at a temperature of 450–470 °C and a pressure of approximately 1·10⁻⁷ mbar using a Knudsen cell. The deposition rate of 0.1–0.2 nm per minute was again monitored via a quartz crystal microbalance.

The nominal layer thicknesses of both the metal and the organic layer were determined by comparing core level intensities of the overlayer (C 1s, Cu 2p, Au 4f or Ti 2p) to the intensity of the substrate related Mo 3d signal. Photoionization cross sections were taken from Yeh and Lindau,¹¹⁷ the inelastic mean free paths of the photoelectrons were calculated by the formulas for organic molecules (CoPcF₁₆) and atoms (Au, Cu, Ti) given by Seah and Dench.⁹⁴ For the calculation of the layer thicknesses of the organic molecule (CoPcF₁₆) from C 1s and Mo 3d spectra, the attenuation of Mo 3d signals due to the intermediate metal layers was considered according to

$$I = I_0 \cdot e^{-d/\lambda} \quad (3.1)$$

with the measured intensity I , the intensity without attenuation I_0 , the layer thickness of the metal layer d and the inelastic mean free path of the photoelectron λ .

All XPS peak fits were performed with the software Unifit (Unifit Scientific Software GmbH) using Voigt profiles (a convolution of Gaussian and Lorentzian line shapes) and Shirley backgrounds.

3.1.4 Results and discussion

3.1.4.1 Studying the Electronics of the MoS₂/Metal Interface by Photoelectron Spectroscopy

XPS is a valuable method for the investigation of chemical interactions at interfaces and the interfacial electronic structure. Since the reference level in photoemission is the Fermi level, energetic shifts of the spectra may indicate not only a change of the local electron density at the considered atom, but also a shift of the surface Fermi level due to doping. In the latter case, a rigid shift of valence band features and all core levels is expected. Since valence band features can be hidden by structures of overlayers, the monitoring of substrate-related core level shifts is useful for the investigation of Fermi level shifts at interfaces.¹¹⁸

In Figure 3.1 the Mo 3d core levels are shown to investigate possible shifts in Fermi level. Mo 3d was chosen since it is the peak with the highest intensity and lowest full width at half maximum (FWHM) of the MoS₂ crystal. It consists of the Mo 3d_{5/2} peak at approximately 229 eV and the Mo 3d_{3/2} peak at approximately 232–232.5 eV. In addition, the spectrum shows the S 2s peak at approximately 226.5 eV. The fit parameters are listed in Table 7.1.

Figure 3.1 shows Mo 3d core level spectra before and after the deposition of a) gold, b) copper and c) titanium (sub-)monolayers and subsequent annealing. The corresponding XPS spectra of the given metals for (sub-)monolayer coverages are depicted in Figure 7.1.

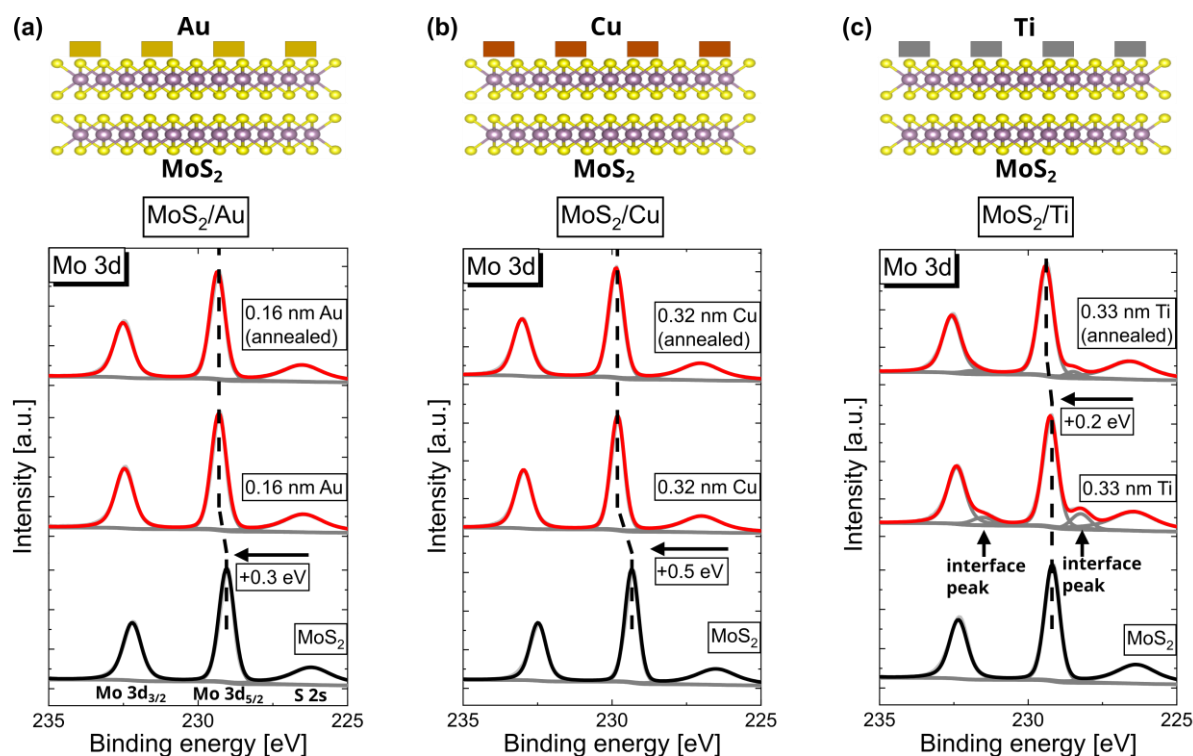


Figure 3.1: Mo 3d core level spectra for the MoS₂/metal interface for (sub-)monolayer coverage of (a) gold, (b) copper and (c) titanium. Interface peaks are observed after deposition of titanium (arrows in Fig. 3.1c), indicating a chemical interaction.

The Mo 3d peak shape in Figure 3.1a and 3.1b does not change after the deposition of the noble metals. Only a shift to higher binding energies of 0.3 eV for gold, and 0.5 eV for copper is visible. Also, in the corresponding S 2p spectra (supporting information, Figure 7.2; Table 7.2) comparable shifts are visible, whereas no changes of the shape can be detected. Therefore, these shifts indicate an n-type doping of MoS₂ upon deposition of Au or Cu. For gold, the results are in good agreement to recently studied multilayer films.^{18,23} The magnitude of the shift and thus the n-type doping effect was somewhat higher in those cases. After the annealing step, no further change in structure or binding energy can be observed in the core level spectra for Au/MoS₂ or Cu/MoS₂.

Mo 3d spectra after the deposition of the base metal titanium in Figure 3.1c exhibit new interface peaks indicated by black arrows pointing to a stronger chemical interaction between the metal and the MoS₂ surface. In line with previous results by McDonnell et al.²⁴, this may be attributed to the formation of Mo(0) metal as a result of the charge-transfer from the deposited titanium atoms. These interface peaks decrease after the

annealing step. A reason for this can be a reaction with oxygen caused by the increased pressure during heating.²⁴

Further information can be gained from the UPS valence band spectra (excited by He I radiation) shown in Figure 3.2. To minimize the superposition to features of interest by satellites arising from He I β and He I γ excitation, we take spectra at an angle of 30° with respect to the analyzer. The corresponding spectra taken at 0° (normal emission) are shown in the supporting information (Figure 7.3). The spectra depicted in Figure 7.3 are close to the Γ -point in k-space and therefore exhibit high intensities at binding energies of >1 eV. Since the satellites arising from He I β and He I γ excitation are found at approximately 1.9 and 2.5 eV smaller binding energies the region around 0 eV is covered by those as shown in Figure 7.3. By the rotation of 30° the detected emission does not emerge from the electron density at the Γ -point leading to much less intensity originating from the satellites making it much more feasible to analyze the Fermi edge which can be seen as independent of the analyzed angle. To make metal related features visible, we choose thicker metal films (the corresponding XPS spectra for the given metals are depicted in Figure 7.4) compared to Figure 3.1, but we note that comparable results are obtained for (sub-)monolayer coverages (Figure 7.5).

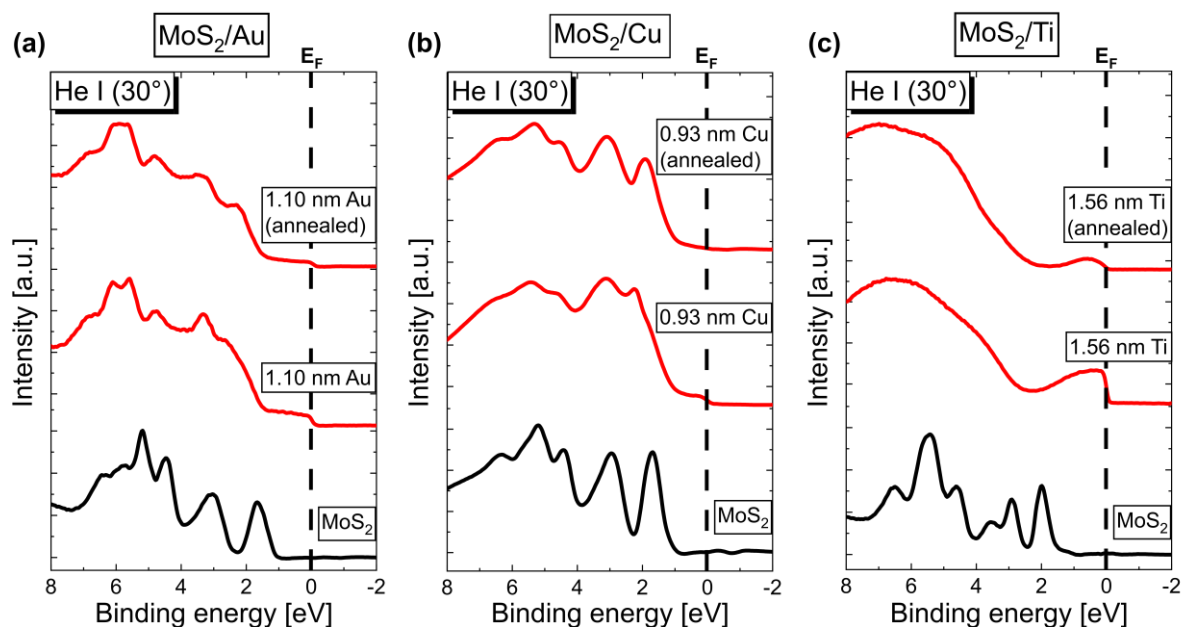


Figure 3.2: Valence band (He I excitation) spectra recorded at an angle of 30° with respect to the analyzer for a multilayer coverage of a) gold, b) copper and c) titanium.

Generally, the spectral shape after the deposition of metals is significantly altered due to the superposition with metal related features, which makes the assignment of MoS₂

structures complicated. The pronounced Fermi edge of the metals at a binding energy of 0 eV is clearly visible. After annealing, the valence band structure changes only slightly, the relative intensity of the Fermi edge is reduced. This can indicate a slightly decreased concentration of the metals on top of the MoS₂ substrate or the formation of islands. Comparing Au and Cu (Figure 3.2a+b), this effect is more pronounced in the case of Cu. For the MoS₂/Cu interface, even MoS₂ features re-appear after annealing, suggesting that the concentration of copper on the top-layer is drastically reduced, possibly due to a diffusion of Cu atoms into deeper layers. Similar effects were observed for Ag/MoS₂ in a previous report.¹¹⁹

For MoS₂/Ti (Figure 3.2c), substrate related features completely vanish after metal deposition, and they do not re-appear after annealing. This confirms the deterioration of the MoS₂ structure after the interaction with Ti, in good agreement with the XPS results (Figure 3.1c).

We now use the UPS spectra for the extraction of electronic interface parameters. We apply a linear extrapolation of the lower binding energy edge of the valence band to define the energy of the valence band maximum (VBM) as shown in Figure 7.3. The energies were calculated as 0.8 eV before deposition of Au and Cu and 0.9 eV before deposition of Ti. We calculate the work function ϕ of the different MoS₂ surfaces and the metals using the energy of the secondary electron cutoff (SECO) depicted in Figure 7.6 as

$$\phi = h\nu - E_{\text{SECO}}. \quad (3.2)$$

A shift in the position of the SECO directly indicates the existence of an interface dipole. The work function of the pristine MoS₂ (5.3 eV) as well as the ionization potential IP ($\Phi + \text{VBM}$) of 6.1–6.2 eV are in good agreement with previously reported data for clean surfaces.²²

The resulting energy level alignment (ELA) diagrams are summarized in Figure 3.3 for all three interfaces. Notably, for all experiments the Fermi level before metal deposition is located above the center of the band gap, corresponding to an n-type behavior, as often observed for clean, synthetic MoS₂ crystals.^{20,22} We extract the band bending in MoS₂ upon metal deposition with a thickness between 0.9-1.6 nm (cf. Figure 3.2) from the XPS core level shifts (supporting information, Figures 7.7 and 7.8; Tables 7.3 and 7.4). The chosen thicknesses correspond to multilayer coverages of given metals.

Similar shifts can be extracted from experiments investigating (sub-)monolayer coverages. Since the determined work functions for the thicker layer thicknesses of given metal are less affected by the MoS₂ substrate it was chosen to depict the multilayer coverages in Figure 3.3. Notably, the observed shifts for the (sub-)monolayer thicknesses depicted in Figure 3.1 vary slightly from the shifts resulting by multilayer coverages which are used in the following figure. We argue that the observed absolute differences in shifts are derived from the different surfaces of MoS₂ before deposition which alter between every experiment. The work functions for the metals are in good agreement with literature data,^{120,121} pointing to a coverage of large areas of the substrate. Interface dipoles increase from Au via Cu to Ti. The formation of such dipoles can be ascribed to different effects, including the push back or pillow effect, charge transfer or a more complex, bidirectional redistribution of electrons at the interface (for detailed discussions, see, e.g. Refs.^{13,82,122–124}). However, the downward band bending for MoS₂/Au and MoS₂/Cu hints strongly to an involvement of electron transfer from the metal to MoS₂.

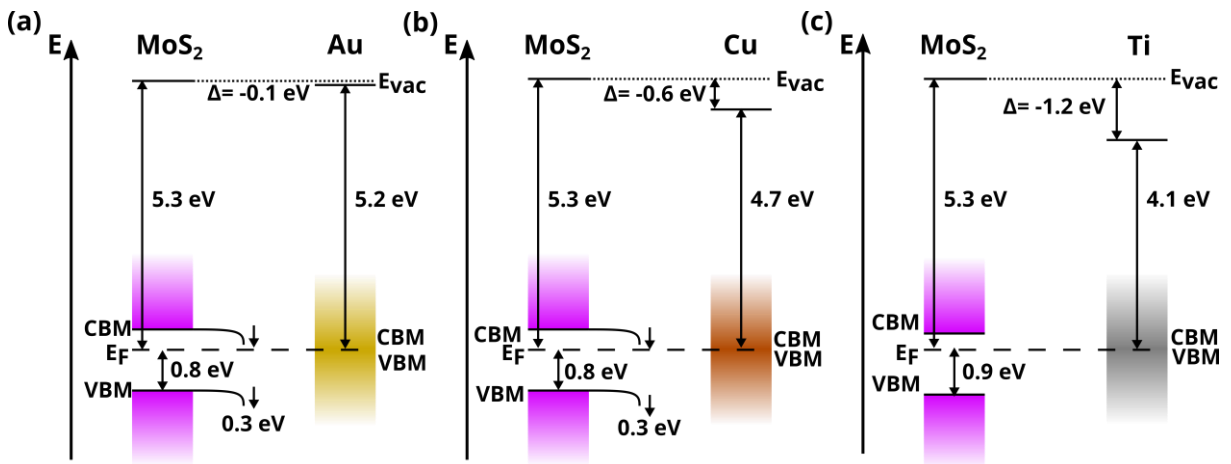


Figure 3.3: Energy level alignment (ELA) diagrams of the MoS₂/metal interfaces for coverages of a) 1.10 nm Au, b) 0.93 nm Cu and c) 1.56 nm Ti.

3.1.4.2 Structural Investigation of the MoS₂/Metal interface

We apply scanning electron microscopy (SEM) to gain additional information about the morphology of the metal films as depicted in Figure 3.4. In the case of titanium, we deposit it onto MoS₂ without annealing to perform SEM experiments on the interface due to the strong chemical interaction between titanium and MoS₂ discussed in 3.1.4.1.

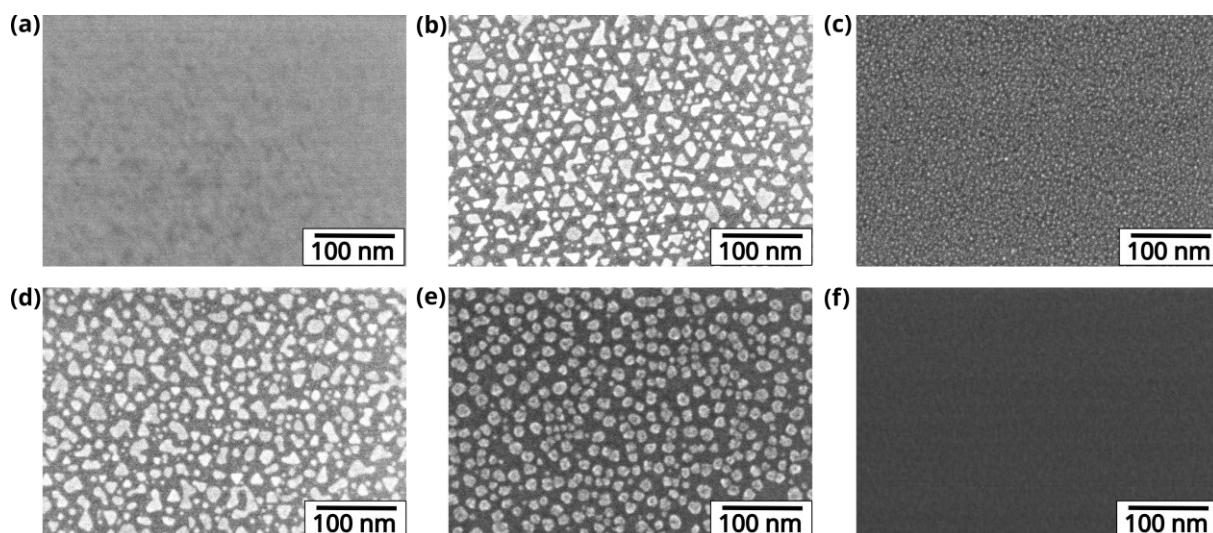


Figure 3.4: SEM images for a) pristine MoS₂, b) MoS₂+1.5 nm Au, c) MoS₂+0.4 nm Au (annealed at 250 °C), d) MoS₂+0.9 nm Cu, e) MoS₂+0.8 nm Cu (annealed at 250 °C) f) MoS₂+0.4 nm Ti

Figure 3.4a shows the pristine MoS₂ substrate, distinctive structures cannot be identified. After the deposition of Au with a nominal thickness of 1.5 nm, island of a size of approximately 10–15 nm form, indicating a Volmer-Weber growth mode (Figure 3.4b). Their triangular shape is typical for crystalline Au(111) surfaces, which was recently also observed for gold deposited at elevated temperatures (350 °C) on MoS₂ cleaved in air.¹²⁵ The deposition of lower coverages of Au in the monolayer range and a subsequent annealing result in significantly smaller structures (Figure 3.4c). This indicates the formation of smaller Au clusters with undefined shape on top of MoS₂. However, a diffusion below the topmost MoS₂ layer cannot be completely ruled out.

The behavior of Cu deposited on MoS₂ (Figure 3.4d,e) is apparently similar to MoS₂/Au. After deposition of 0.9 nm Cu, islands form and a crystalline structure is noticeable, even if the triangular shape is less pronounced compared to MoS₂/Au. The (111) orientation is in agreement with the literature.¹¹⁰ After annealing (Figure 3.4e), the shape of the islands changes, suggesting amorphous Cu clusters on top, near the MoS₂ surface. We do not observe an agglomeration of islands as reported for Cu film on MoS₂, annealed to 500 K.¹²⁶

In contrast to MoS₂/Au and MoS₂/Cu, the SEM image for MoS₂/Ti (Figure 3.4f) does not show any nanoscale features. It seems that Ti atoms directly react with MoS₂ top atoms, in agreement with the XPS and UPS results discussed above. Consequently, the formation of metal clusters or crystalline islands is suppressed.

3.1.4.3 Diffusion of Metal Atoms into Deeper MoS₂ Layers

For electronic application of MoS₂, an important question is whether or not metal atoms can diffuse into deeper MoS₂ layers, especially for MoS₂/Au and MoS₂/Cu. To investigate the presence of metal atoms on the surface, we use CoPcF₁₆ as a probe molecule, which is deposited subsequently on the metal-covered MoS₂ surfaces. It is known that the central Co atom of CoPcF₁₆ interacts strongly with Au and Cu (interfacial charge transfer), visible as an additional interface component in the corresponding Co 2p XPS spectra.^{115,116} In contrast, the absence of a charge-transfer was proven for the MoS₂/CoPcF₁₆ interface.²⁰ For this reason, we propose that the CoPcF₁₆ molecule can act as a highly surface-sensitive method to probe the location of metals before and after annealing.

Figure 3.5 shows the Co 2p_{3/2} photoemission spectra for different thicknesses of CoPcF₁₆ on MoS₂/Au. The bottom spectra (red curves) before CoPcF₁₆ deposition confirm that there are no background features in this energy range. The top spectra (dark green) are representative for thicker films, where the influence of the substrate can be neglected considering the inelastic mean free path of electrons of approximately 1.58 nm.⁹⁴ Their spectral shape is determined by multiplet effects (see e.g. Ref.¹⁰⁴). Light green curves for thicknesses below 1 nm correspond to a coverage of about 2-3 monolayers of flat lying molecules (in the following called “few layer”), in which possible interface interactions become visible.

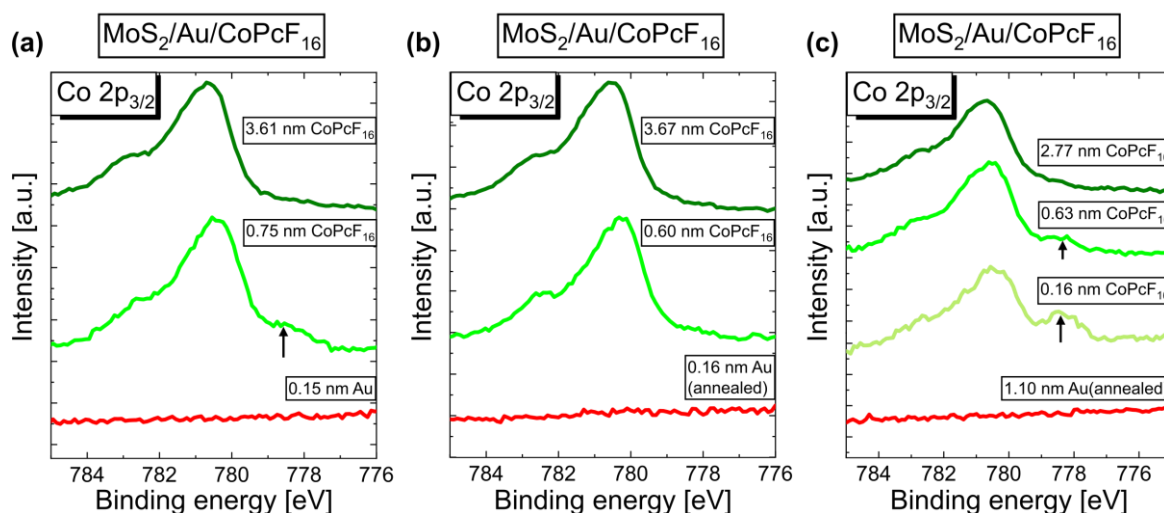


Figure 3.5: Co 2p_{3/2} spectra of MoS₂/Au/CoPcF₁₆ interfaces for a) (sub-)monolayer coverage of Au (not annealed); b) (sub-)monolayer coverage of Au (annealed); c) multilayer coverage of Au (annealed).

Figures 3.5a and 3.5b compare gold coverages in the sub-monolayer range on MoS₂ with and without annealing. A distinct interface compound in the Co 2p spectrum for the few layer CoPcF₁₆ spectrum is only visible before annealing (black arrow, Figure 3.5a). The intensity of the interface component is weak, indicating that only for few molecules the Co atoms are in vicinity to a gold cluster. For the annealed sub-monolayer gold coverage (Figure 3.5b), no interface peak can be detected after the deposition of CoPcF₁₆, implying that the amount of gold on the surface is significantly decreased due to annealing of the sample. Since a desorption of gold is rather unlikely at the gentle annealing temperature, we conclude that gold must diffuse into deeper MoS₂ layers upon annealing. Repeating the same experiment for an annealed, thicker gold film on a MoS₂ substrate (Figure 3.5c), interface components are clearly visible in the corresponding Co 2p spectra (light green corresponds to a monolayer CoPcF₁₆ coverage), indicating that the (larger) gold clusters cannot completely diffuse into the MoS₂ substrate upon annealing.

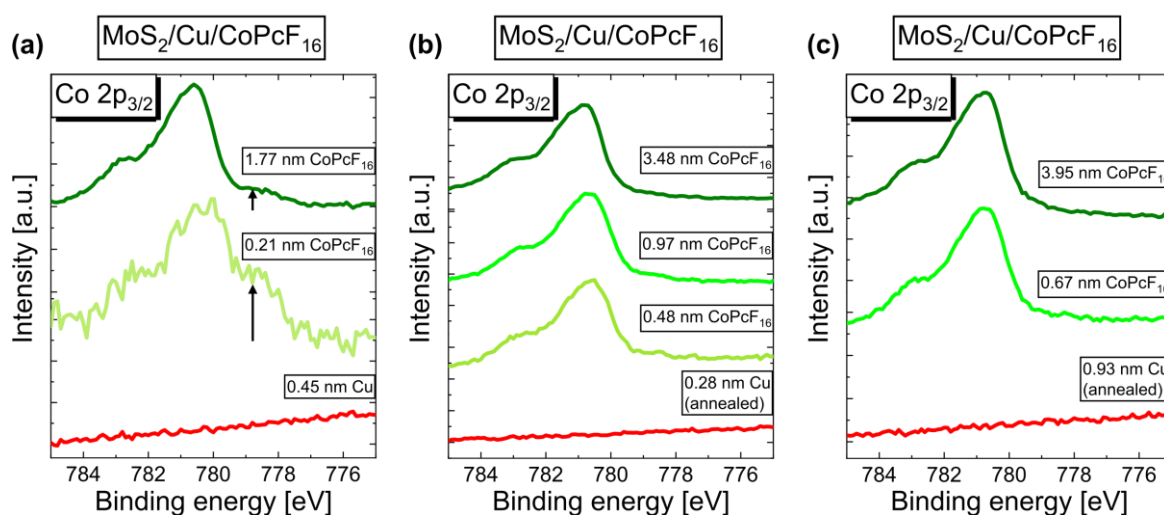


Figure 3.6: Co 2p_{3/2} spectra of MoS₂/Cu/CoPcF₁₆ interfaces for a) (sub-)monolayer coverage of Cu (not annealed); b) (sub-)monolayer coverage of Cu (annealed); and c) multilayer coverage of Cu (annealed).

In Figure 3.6, the Co 2p_{3/2} spectra for the MoS₂/Cu interface are presented. Again, the unannealed surface, the annealed monolayer and the annealed multilayer are depicted.

For the unannealed MoS₂/Cu interface shown in Figure 3.6a, the comparably intense interface peak (black arrow) hints to large numbers of Co atoms of CoPcF₁₆ interacting with Cu clusters. Even for a multilayer of a nominal thickness of 1.77 nm the interface

component does not completely vanish. In contrast, for the annealed copper layers of different thicknesses of Cu on MoS₂ (Figure 3.6b,c) the Co signal does not show any signs of interaction with the substrate. This indicates that copper can diffuse much easier into deeper layers of the MoS₂ substrate compared to gold. Diffusion processes of coinage metal atoms (or also germanium) into deeper layers, often discussed in context with intercalation, are very common for layered substrates and were intensively studied for graphite or graphene. As a mechanism, a diffusion through defects and step edges or even a local reaction through the graphene layer were discussed.^{127–131} The copper diffusion into graphite or MoS₂ seems to be very effective, if the number of defects is high.^{131,132} Our results suggest that a diffusion might also occur on surfaces with a lower number of defects.

3.1.5 Conclusion

This study serves to give a deeper understanding of the behavior of MoS₂/metal interfaces. For the application in electronic devices, it is crucial to obtain more knowledge on the interfaces created by the deposition of electrode materials such as Au, Cu and Ti. We have derived the energy level alignment to get deeper insights into the band bending of the MoS₂ energy levels and the total electron transfer between the TMDC substrate and the metal. We show that copper on the surface behaves as an n-type dopant similar to gold. By annealing, we seek to probe the thermodynamically stable electronic environment at such interfaces, simulating the long-term scenario in a device. We find that the n-type doping for Au and Cu does not change, implying that the metals are still in the vicinity of the top-layer of the TMDC. Our data indicates the diffusion of the noble electrode materials to deeper layers. While gold only seems to partially diffuse as the coverage increases, copper fully diffuses even at multilayer coverage. To probe the exact position of the metal, CoPcF₁₆ was used. The charge-transfer towards the Co atom of the organic molecule is a clear indicator for given metal at the surface which makes it an exceptionally well-suited probe to localize the presence of the noble metals.

3.2 Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes

In the second publication of this thesis the heterostructure between the organic molecules CoPc or CoPcF₁₆ and single- or multilayered MoS₂ are investigated. To yield the MoS₂ flakes mechanical exfoliation with scotch tape was performed. The samples were transferred via a PDMS stamp onto silicon wafers with overlayers of the native oxide and titanium. Afterwards the flakes were characterized by photoluminescence spectroscopy and atomic force microscopy to determine the number of layers. As the obtained flakes are at a micrometer scale, the electronic structure was investigated using photoemission electron microscopy coupled with μ XAS. After the deposition of any of the organic molecules, no significant change in the electronic structure of the substrates of varying layer number was found in the XPS core level spectra. The Co L_{2,3} X-ray absorption spectra showed no signs of charge transfer between the substrates and the organic molecules. However, the orientation of the molecules probed by XAS revealed a clear layer dependence at the interfaces. While CoPc and CoPcF₁₆ showcase a flat-lying geometry on multi-layered or bulk-like MoS₂ flakes, the same molecules appear to lie tilted on single or few-layered MoS₂. This finding is highly significant for designing heterostructures of single layered MoS₂ and weakly adsorbing molecules like CoPc and CoPcF₁₆, as the orientation between substrate and overlayer are crucial for possible interactions at the interface. Furthermore, the results of these experiments show that the orientation of molecules on single layered TMDCs cannot simply be derived from the bulk-like case as typically assumed.

Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes

Philipp Haizmann^{1,#}, Eric Juriatti^{1,#}, Maren Klein¹, Katharina Greulich¹, Peter Nagel^{2,3}, Michael Merz^{2,3}, Stefan Schuppler^{2,3}, Amir Ghiami^{2,3}, Ruslan Ovsyannikov⁴, Erika Giangrisostomi⁴, Thomas Chassé¹, Marcus Scheele^{1,*}, Heiko Peisert^{1,*}

1 Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

2 Institute for Quantum Materials and Technologies (IQMT), Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany

3 Karlsruhe Nano and Micro Facility (KNMF), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

4 Institute for Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

These authors contributed equally (P.H., E.J.).

* Corresponding author

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3.2.1 Abstract

Heterostructures consisting of transition metal dichalcogenides (TMDCs) and organic molecules are currently of enormous interest for a variety of applications. Comparably weakly interacting molecules, like phthalocyanines, exhibit a high potential for tuning of electronic properties of TMDCs. Knowledge of the molecular orientation is a prerequisite for the understanding of the nature and strength of the interfacial interaction. We study the molecular orientation of cobalt phthalocyanine (CoPc) and perfluorinated cobalt phthalocyanine (CoPcF₁₆, also denoted F₁₆CoPc), on both large molybdenum disulfide (MoS₂) single crystals and small MoS₂ flakes, using synchrotron-based techniques: X-ray absorption spectroscopy (XAS) at the Co L₃ edge, and spectromicroscopy in a photoemission electron microscope (PEEM). We show that the orientation can be radically different on both substrates. Whereas on large crystals an almost flat-lying orientation is observed, significant tilt angles were found on smaller flakes. It is proposed that the orientation depends crucially on the number of MoS₂ layers and/or the smaller size of atomically flat terraces on flakes compared to bulk crystals.

3.2.2 Introduction

Due to their remarkable physical and chemical properties, layered transition metal dichalcogenides (TMDCs) are a promising class of materials for future applications in modern semiconductor devices for electronics, lighting, solar energy, and communication. In particular, it is expected that these materials will enable the further miniaturization of electronic devices according to Moore's law^{107,108} and promote the establishment of flexible electronic devices.¹³³ The layered structure allows for the exfoliation down to two-dimensional layers with unique electronic properties compared to their bulk counterparts; in the case of MoS₂, the nature of the band gap changes from direct to indirect.^{134–136} Especially, TMDC monolayers and heterostructures are of interest for a broad variety of devices.^{2,26,107,137}

One approach for tuning of electronic properties is the formation of TMDC/organic semiconductor heterostructures. Recent research on conjugated organic molecule/TMDC interfaces has been mainly focused on strong molecular electron acceptors.^{138,139,13,25} However, weaker interacting, physisorbed organic molecules

may also interact with TMDCs. Such systems are expected to offer new opportunities for tuning both optical and electronic characteristics.¹⁴⁰ For example, a quenching of the low-temperature defect photoluminescence of MoS₂ was observed after the adsorption of metal-phthalocyanines, depending strongly on the central metal atom of the phthalocyanine.¹⁴¹ The nature of such interactions is currently being increasingly discussed,¹⁴² and one crucial parameter in this regard is the orientation of the molecules with respect to the substrate surface. For example, the coupling between nickel phthalocyanine (NiPc) and graphene is supported by the flat geometry of the NiPc complexes.¹⁴³ Especially for anisotropic organic semiconductor films, the orientation of the individual molecules at the heterostructure is of particular significance, since it influences the electronic properties of the film and, therefore the overall interaction at the interface.^{144,145}

We study the molecular orientation of cobalt phthalocyanine (CoPc) and perfluorinated cobalt phthalocyanine (CoPcF₁₆) on MoS₂ bulk crystals and on exfoliated pieces, often called flakes, which have fewer and even monolayer thickness — a system, where weak interactions at interfaces (i.e., the absence of an integer charge transfer) can be expected. Representatives of the family of transition metal phthalocyanines (TMPcs) were chosen due to their advantageous chemical and physical properties, including stability, film growth, and tunability of electronic parameters due to the variation of the central metal and the selection of the peripheral substituents.^{54,146–148} Fluorination of the Pc moiety increases the ionization energy by more than 1 eV,^{149–152} which may significantly affect electronic interactions at interfaces, even in the case of metal surfaces passivated by graphene.⁶⁴ Numerous studies on the growth of phthalocyanines were carried out on a broad variety of substrates. On single-crystalline substrates, the almost planar phthalocyanine molecules typically prefer a predominantly flat-lying orientation (see, e.g., Refs.^{22,146,153–158}); this includes also van der Waals substrates like GeS or MoS₂, and graphene-covered metal substrates.^{22,154,156–158} In contrast, on polycrystalline substrates, the molecular orientation can be radically different, depending crucially on the substrate roughness.^{153,154} The different growth modes observed on various substrates can be understood in terms of different molecule-substrate and molecule-molecule interactions at the interface.^{153,159–161} In conclusion, higher tilt-angles for phthalocyanines on single crystals were in particular found if the molecule-substrate

interaction is weaker, e.g., for van-der-Waals solids or passivated semiconductor surfaces.^{156,162}

In this study, we demonstrate that the orientation of CoPc and CoPcF₁₆ on molybdenum disulfide flakes can diverge from that on the bulk MoS₂ single crystal. Therefore, the prediction of the molecular orientation on thin flakes from literature data obtained with bulk crystals only could be misleading for differing structural situations.

3.2.3 Methods

Cobalt phthalocyanine (CoPc, Sigma-Aldrich Chemie GmbH) and perfluorinated cobalt phthalocyanine (CoPcF₁₆, Sigma-Aldrich Chemie GmbH) were deposited on synthetic bulk 2H-phase MoS₂ (2D Semiconductors Inc. USA) by thermal evaporation under ultra-high vacuum (UHV) conditions (base pressure about $1 \cdot 10^{-9}$ mbar). The evaporation chamber was directly attached to the spectrometer chamber. The nominal film thickness was determined using a quartz crystal microbalance (QCM), setting the mass density of CoPc and CoPcF₁₆ at 1.6 g/cm³ and 2.0 g/cm³, respectively,^{163,164} and checked by the comparison of X-ray photoelectron spectroscopy (XPS) peak areas for bulk MoS₂ sample experiments.

For the studies on bulk MoS₂, the crystals were cleaved by adhesive tape in UHV. No further annealing was performed. The cleanliness was checked by XPS. These experiments were conducted at the PM4 beamline of the BESSY II electron storage ring operated by the Helmholtz-Zentrum Berlin (HZB) using the LowDosePES endstation.¹⁶⁵ Polarization-dependent X-ray absorption spectroscopy (XAS) measurements at the N K and Co L edges were carried out in total electron yield mode, measuring the sample drain current and orienting the sample at different polar angles with respect to the incoming beam of fixed horizontal polarization. The correction for beamline characteristics of the photon flux was carried out using the drain current from the last beamline mirror, or XAS spectra of pristine gold substrates. The XAS spectra were normalized to the same step height, well above the absorption edge.

For determining the orientation of CoPc and CoPcF₁₆ on MoS₂ flakes, laterally resolved spectromicroscopy experiments in a photoemission electron microscope (PEEM) were conducted at the Institute for Quantum Materials and Technologies soft x-ray beamline WERA at the KIT Light Source, Karlsruhe, Germany. The degree of linear polarization was set to nominal values between 72 and 93%, all giving sufficient orientational contrast of the Co L edge with photon energies between 770 eV – 800 eV. The energy

resolution was set to 490 meV. The PEEM (FOCUS GmbH) has an integrated sample stage (IS), an imaging energy filter (IEF) using a retarding field, and operates in a fixed geometry; the angle between the p-polarized incident photon beam and the normal of the sample was 65°. Since the fixed geometry does not allow a direct determination of the molecular orientation, the adsorption geometry was estimated from the known angular dependence of polarization dependent XAS spectra (measured, for example, on bulk MoS₂). Flat and dark field corrections were considered in the post-processing of the measured image stacks. The incident photon flux was monitored using a clean gold mesh.

Ultraviolet photoelectron spectroscopy (UPS) measurements at our laboratory spectrometer were performed inside a multichamber UHV system (base pressure of 1·10⁻⁹ mbar) equipped with an ultraviolet source (UVS 300, Specs) and a Phoibos 150 hemispherical photoelectron analyzer (Specs). The energy calibration was performed using argon-sputtered and annealed Ag foils at the Fermi edge. The energy resolution was 150 meV.

MoS₂ flakes, containing regions with varying numbers of layers, were prepared *ex-situ* for PEEM measurements using the top-down scotch tape method, starting with synthetic bulk MoS₂ (2D Semiconductors Inc., USA).¹⁶⁶ Since MoS₂ crystals used for both exfoliation and experiments on bulk MoS₂ were purchased from the same company, we assume a similar quality of MoS₂ layers for both types of experiments. Exfoliated flakes were transferred onto a polydimethylsiloxane stamp (PF Gel Film®, Teltec GmbH). The stamp is pressed onto substrates, leaving thin-layers of TMDC on them. As substrates we used commercially available silicon wafers. Part of the silicon wafers were coated with 50 nm of titanium at an evaporation rate of 0.1 nm/s, determined by QCM, and used after exposure to environmental conditions as a substrate for the transfer of the flakes. The XPS analysis reveals that the native oxide covers the surface completely; no metallic Ti was detectable. To fit the dimensions of the PEEM sample holders, 7.5 x 7.5 mm substrates were cut from these wafers. Native titanium oxide and silicon oxide layers were found on both surfaces, as evidenced by photoemission measurements (Figure 7.9–11, Supporting Information). The substrates were ultrasonically cleaned with a solvent cascade, starting with acetone, followed by hexane, ethyl acetate, and isopropanol. As a final cleaning step, the substrates were placed in a UV oven (Photo Surface Processor PL16-110B-1, Sen Lights Corp) for 15 minutes. Successful transfers of the MoS₂ flakes were evaluated by optical microscope

images. Those images were taken with an Olympus BHM microscope equipped with an EOS600D camera (Canon) and a NeoDPlan 50 (Olympus) objective. As this preparation method yields a large number of flakes with different thicknesses on the substrates, we selected the most promising ones based on contrast assessments. The images of the flakes selected for later experiments are shown in Figure 3.8a–c. Prior to the deposition of phthalocyanines, the samples were annealed under UHV conditions to 250 °C for 12 h to remove contamination from preparation and ensure a clean surface, as verified by PEEM measurements (see Figure 7.9–11).

For the evaluation of the PEEM results and optical microscopy images, we used the software ImageJ/Fiji^{167,168} with the plugin FeatureJ from Erik Meijering.

3.2.4 Results and Discussion

Polarization-dependent X-ray absorption spectroscopy (XAS) offers an optimal method for studying the adsorption geometry of molecular adsorbates.^{103,153} For the planar TMPcs having D_{4h} symmetry, both $C1s-\pi^*$ or $N1s-\pi^*$ excitations are suitable for determining molecular orientation.¹⁵³ If the electric field vector of the incoming light is oriented parallel to the atomic p_z wave functions forming the molecular π^* orbital (i.e., out of the molecular plane), the absorption is maximal. In contrast, the transition is forbidden in the case of a perpendicular orientation.^{103,169} However, in our case, the analysis of N K edge absorption spectra is hindered by the overlap with features from the MoS_2 substrate. An example of a N K edge spectrum of a $CoPcF_{16}$ monolayer in superposition with Mo $M_{3,2}$, is shown in Figure 7.12a (Supporting Information) and for a thicker $CoPcF_{16}$ film in Figure 7.12b. Also, the analysis of the C K edge is very difficult due to common carbon contaminations of beamline components and residual carbon in *ex-situ* prepared samples, especially for monolayer coverages. However, Co L edge XAS spectra also show a pronounced angular dependence (see, e.g., Refs.^{62,157}). They are determined to a large extent by multiplet effects due to the strong overlap between core level and valence wave functions.¹⁰⁴ Nevertheless, in-plane and out-of-plane transitions can be distinguished (for details, we refer to the literature, e.g. Refs.^{170,171}). In the following, we will use the shape of the Co L_3 XAS spectra for the estimation of the molecular orientation. We note that the shape of these spectra is almost independent on the fluorination of CoPc (see, e.g., Refs.^{116,157}).

In Figure 3.7, polarization-dependent Co L₃ edge spectra of (Figure 3.7a) CoPcF₁₆ and (Figure 3.7b) CoPc on bulk MoS₂ are shown for two different film thicknesses, measured at two different incidence angles of the p-polarized light. Transitions polarized perpendicular to the molecular plane (z-polarized) are denoted A, whereas B features are polarized within the molecular plane (xy-polarized). Consistent with the considerations above, the intensity of the out-of-plane feature A is maximal close to grazing incidence (20°), whereas the in-plane transitions B are most intense at normal incidence (90°). This indicates a preferred orientation of the molecule parallel to the substrate surface (referred to as face-on). The spectral shape of the Co L₃ edge is almost identical for the coverage in the monolayer range (0.34 nm) and the multilayer film, indicating that the orientation of the first molecular layer is maintained in the thin film. This behavior on bulk MoS₂ substrates is identical for CoPc and CoPcF₁₆. A more detailed comparison of the spectral shapes in Figure 3.7 with literature data (e.g., Refs.^{62,116,157}) reveals that tilt angles between the molecules and the substrate surface are rather small or even negligible. Thus, we can conclude that an orientation close to a face-on configuration of CoPc and CoPcF₁₆ is favored on bulk MoS₂.

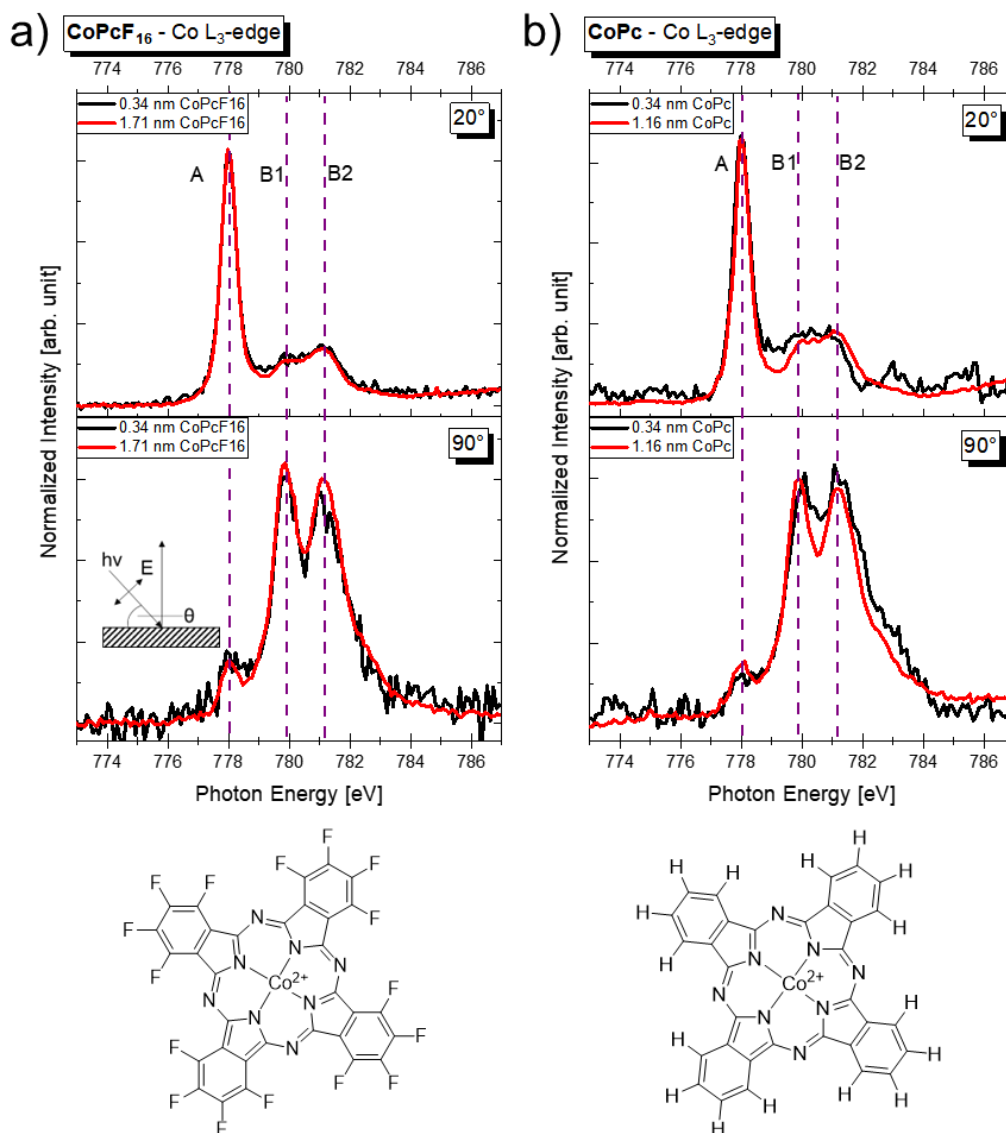


Figure 3.7: Angle-dependent XAS measurements in the Co L₃ region show intensity differences of features A and the two B features depending on the orientation of the electric field with respect to the sample for CoPcF₁₆ shown in (a) and CoPc shown in (b) on bulk MoS₂, with the respective structural formula below each spectrum.

The observed predominant face-on alignment of cobalt phthalocyanines is in good agreement with related systems, such as the previously studied FePc(F_x) molecules on MoS₂.²² However, it is essential to recognize that this orientation could be influenced by numerous factors on more frequently studied MoS₂ samples, like, e.g., 2D layers or flakes. For instance, the roughness of the substrate surface and the size of its atomically flat terraces can significantly impact the alignment of molecules.¹⁵³ This leads to the question whether the determined molecular orientation of cobalt phthalocyanines on bulk MoS₂ applies also to smaller MoS₂ flakes, which are of

particular interest for applications. Due to the small dimensions of the MoS₂ flakes, a microscopic technique is needed. A certain PEEM measurement mode, spectromicroscopy, is particularly useful here. Spectromicroscopy essentially means taking stacks of PEEM images while scanning the incoming photon energy or the kinetic energy of the emitted electrons. By tracing a pixel (or lateral region) through the image stack the former yields laterally resolved (μ -)XAS spectra, the latter laterally resolved (μ -)PES spectra. The resulting local spectra can be summed over regions of interest (Rols) with freely defined shapes as applied on measurements discussed in the following. In particular, microscopic measurements of the work function contrast have proven to be a very sensitive method for distinguishing monolayer and few-layer regions of TMDC flakes.^{172–174}

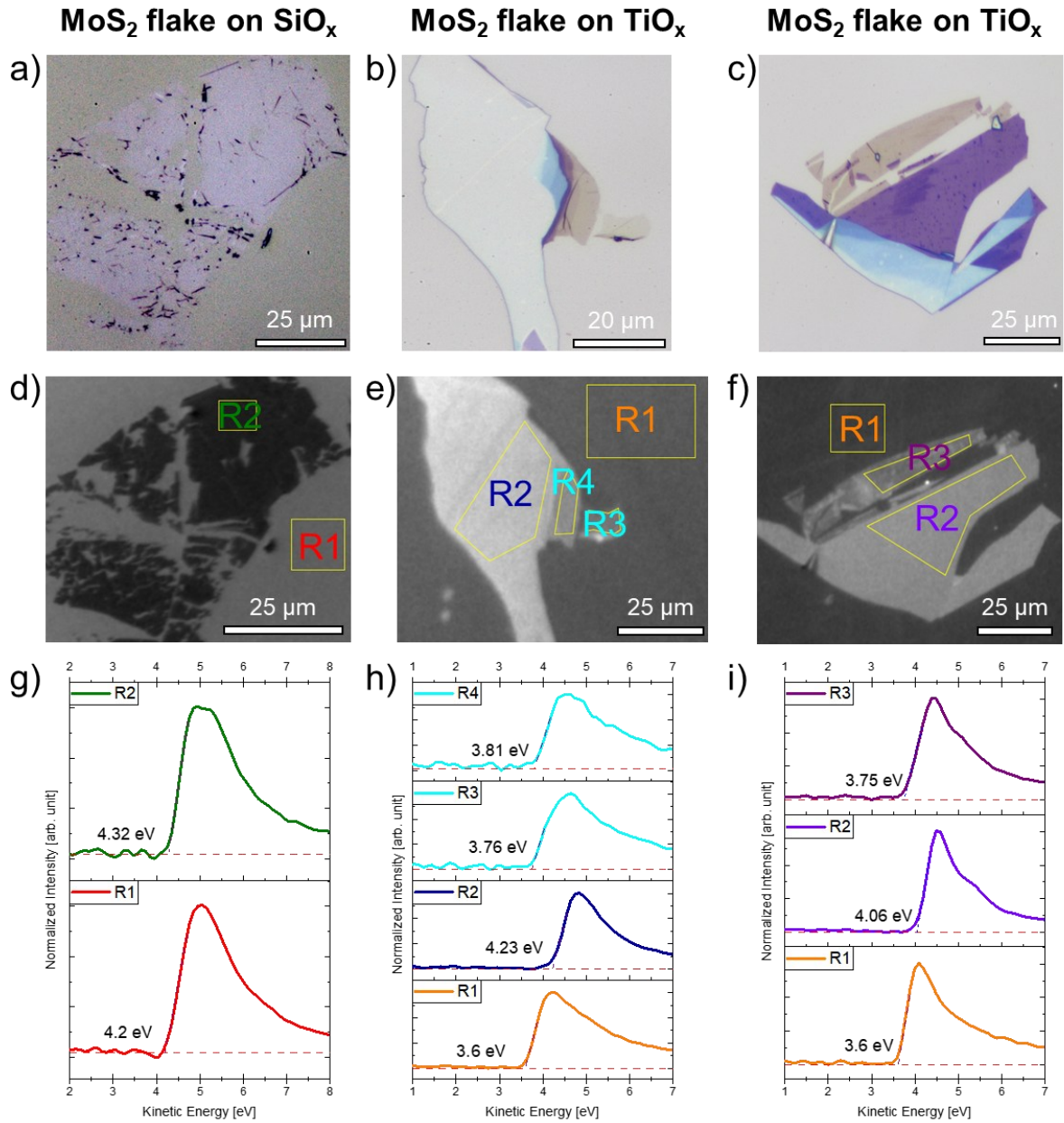


Figure 3.8: (a – c) Optical microscope images of MoS₂ flakes on SiO_x (a, flake 1) and on TiO_x substrates (b) and (c), flake 2 and flake 3 respectively. Averaged images of the work function contrast sequence for the samples containing flake 1, flake 2 and flake 3 are shown in (d), (e) and (f) respectively. The grayscale is arbitrary to maximize contrast. (g – i) μ -PES spectra of the secondary electron cutoff and the calculated work functions.

In Figure 3.8, we show optical microscopy images, PEEM images, and corresponding μ -PES spectra of the secondary electron cutoff. In the following, we will refer to the flake on the oxidized silicon substrate (Figure 3.8a, d, and Figure 7.9) as flake 1, while

the two flakes on the oxidized titanium substrates are referred to as flake 2 (Figure 3.8b, e, and Figure 7.10) and flake 3 (Figure 3.8c, f, and Figure 7.11).

An initial indicator for estimating the number of layers can be provided by optical microscopy images. Differences in contrast between the substrate and the various layers in the flake (Figure 3.8a–c, Figure 7.13, and Figure 7.14) can be used to estimate the number of layers.^{175,176} A detailed analysis of the red channel of optical microscope images (cf. Figure 7.13) reveals a distinct difference between regions R3, which is assumed to be a single MoS₂ layer based on the photoluminescence,^{177,178} and R4 in Figure 3.8e.

Furthermore, we will discuss the work function contrast of selected MoS₂ flakes prepared on naturally oxidized silicon and titanium substrates. Figures 3.8e–i show PEEM images (the total diameter of the field of view is 126 μm for the measured circular images; the figures shown are cutouts, and the scales are adjusted accordingly) together with the normalized $\mu\text{-PES}$ spectra of the secondary electron cutoff. Generally, differences in intensity of PEEM images are attributable to secondary electrons and, to a lesser extent, spectral features. Regions of interest (denoted R1 - R4 in Figure 3.8) were selected based on previously acquired optical microscope images and observable color variations (Figure 3.8a–c). Average spectra in Figure 3.8g–i were generated over all pixels in the chosen regions marked in Figures 3.8d–f. For a better comparison of the work functions, we measured the secondary electron cutoff from the pure substrates with UPS at our laboratory spectrometer. We found a work function of 4.2 eV for the silicon and 3.6 eV for the titanium substrates, respectively (Figure 7.15g). This difference is in good agreement with literature data and the relative differences we found in our PEEM measurements on the substrate regions (Figure 7.15d–f), marked R1 in each experiment. Therefore, we referenced the measured work functions of the substrate regions R1 to the values measured in the UPS experiments on the bare substrates. The energy scales of the MoS₂ flake regions are based on this calibration procedure.

We find almost the same work function for the pristine titanium substrate regions (R1) for the measurements containing flake 2 and flake 3, and a higher work function for the silicon substrate region containing flake 1. A comparably high work function Φ is expected for MoS₂; a value of 5.4 eV was recently reported for single-crystalline bulk substrates.²² However, for monolayer or few-layers on oxidized silicon, significantly lower values were observed ($\Phi \sim 4.5$ eV) by both PEEM and Kelvin probe force

microscopy (KPFM).^{179,180} We note that KPFM measures relative work functions, which may complicate a direct comparison of absolute values. Furthermore, a comparison to literature data has to take into account difference in the preparation method, the influence of contaminations in the case of measurements under ambient conditions,¹⁷⁹ as well as the choice of the substrate, which may alter the work function of MoS₂ flakes by several tenths of eV.¹⁸⁰ However, and most importantly, all methods agree in that the work function increases from single to few-layer MoS₂.^{173,180,181} Using PEEM under UHV conditions, for MoS₂ on oxidized silicon differences of 60 meV and 80 meV were observed from 1 to 2 and 2 to 3 monolayers, respectively. Thus, the lower work function of regions R3 and R4 in Figure 3.8b, c clearly indicates a lower number of MoS₂ layers.

From these investigations, we estimate that flake 1 on the oxidized silicon substrate is a bilayer, region R3 of flake 2 on oxidized titanium is a monolayer, and region R4 is a trilayer. For region R3 of flake 3, we estimate it to consist of four layers. We note that this estimation is associated with a high degree of uncertainty. However, we were able to prepare samples that exhibit regions with a few layers of MoS₂, as well as thicker, bulk-like regions (R2 in Figure 3.8e and f).

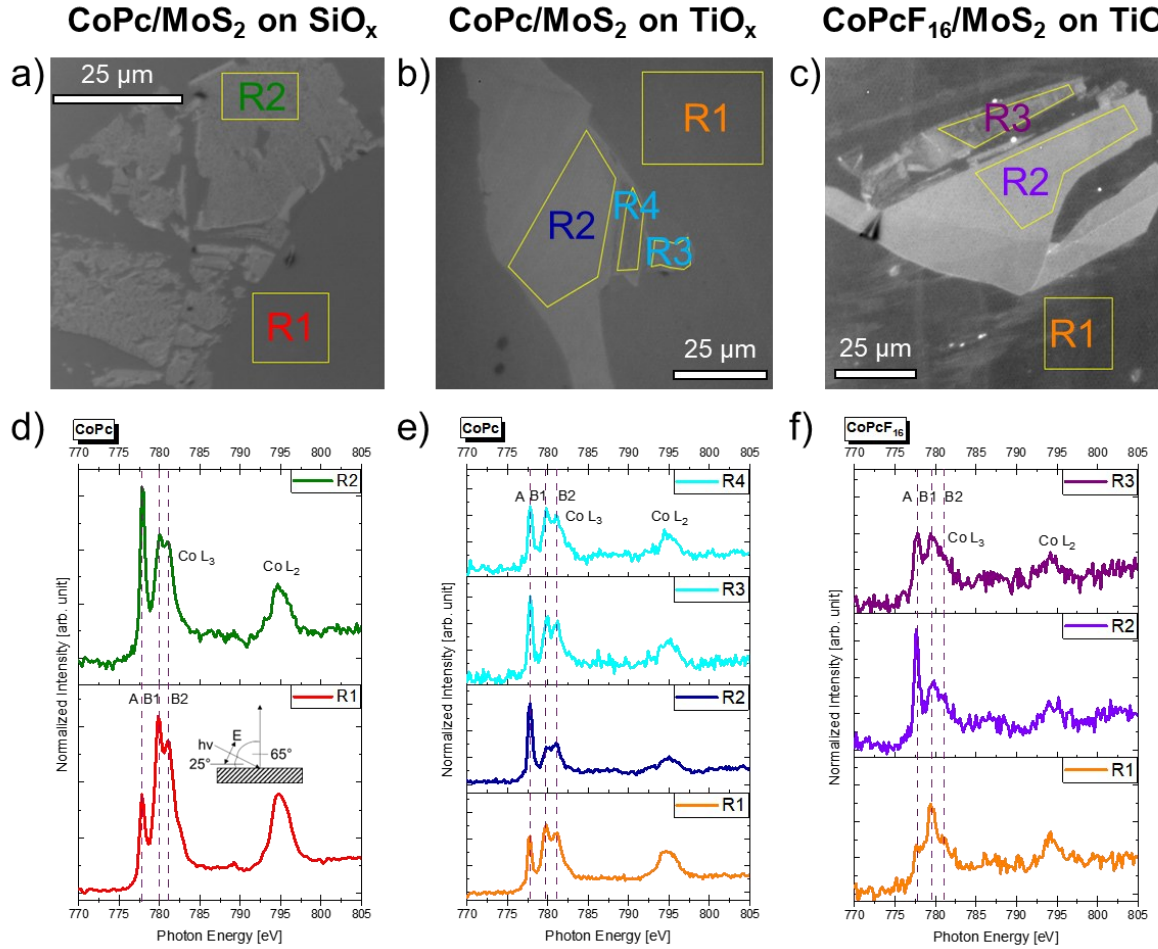


Figure 3.9: PEEM XAS measurements at an incident angle of 25° in the region of the Co L edge. (a – c) show average intensity images with an arbitrarily chosen grayscale to maximize contrast. Intensity differences are mostly based on secondary electron counts and to a lesser extent on spectral features. Selected regions of interests in these images are like those chosen for work function contrast measurements shown in Figure 3.8. (d – f) show the normalized spectra of the respective RoI for the flakes 1–3 above.

In a next step, we deposited CoPc on the samples containing flakes 1 and 2, and CoPcF₁₆ on the sample containing flake 3 and measured PEEM-XAS in the Co L_{3,2} region. According to the QCM data, the thickness was in the monolayer range. The corresponding PEEM images, together with the averaged Co L_{3,2} edge spectra of the selected regions, are shown in Figure 3.9. The XAS spectra in Figure 3.9d–f were obtained by the analysis of PEEM images taken at different excitation energies. Generally, the XAS features discussed in Figure 3.7 are also visible in the μ -XAS spectra of Figure 3.9. Due to the fixed measurement geometry, all spectra were taken

at an incident angle of 25° with respect to the surface of the sample. This is relatively close to the grazing incidence angle for the measurements of CoPc and CoPcF₁₆ on bulk MoS₂ single crystals (20°). Thus, for preferred predominantly flat-lying molecules only a slight increase in the relative intensity of the in-plane polarized features B1 and B2 might be expected compared to bulk MoS₂ single crystals, discussed in Figure 3.7 (cf., e.g., Refs.^{62,157} for the angular dependence of Co L₃ spectra). A further reason for a slightly increased intensity of B1 and B2 could be a different degree of the polarization of the synchrotron light. Considering these minor technical limitations, the μ -XAS spectra of CoPc and CoPcF₁₆ on large MoS₂ terraces (R2) in Figure 3.9 are very similar to the related spectra on bulk MoS₂ single crystals at grazing incidence (20°) in Figure 3.7. In both cases, the out-of-plane polarized feature A clearly dominates the spectrum. In contrast, on the oxidized silicon and titanium surfaces (regions R1 in Figure 3.9), the molecules grow obviously in a different manner: The dominating in-plane features B1 and B2 indicate a preferred standing (edge-on) adsorption geometry, which can be related to the weaker molecule-substrate interaction with increasing (micro-)roughness of the substrates (i.e., the substrates are not atomically flat). Such effects were reported for different molecules (see, e.g., Refs.^{153,159}). Most importantly, the ratio of A/B intensities of the Co L₃ spectra for the regions R3 (flake 2 and flake 3) and R4 (flake 2) deviate distinctly from the regions R2 of the MoS₂ flakes on oxidized titanium (Figure 3.9e and f), indicating significant tilt angles of the molecules to the surface plane or a disordered growth. This effect is observed to some weaker extent also in the region R2 on oxidized silicon (Figure 3.9d), where Figure 3.9a suggests a more inhomogeneous MoS₂ layer. The regions R3 (flake 2 and flake 3) and R4 (flake 2) are characterized by i) a lower number of MoS₂ layers and ii) by a smaller size compared to regions R2. Both could affect the molecular orientation of the deposited CoPc or CoPcF₁₆ molecules. The lower number of MoS₂ layers may affect the surface energy of the substrate, and the flexibility of the thin-layer MoS₂ may cause a certain corrugation due to the alignment at the substrate surface. The small lateral size of the thin MoS₂ regions might limit the favorable flat-lying adsorption geometry to a certain number of molecules, and step-edge effects might become important. Another factor that can influence the surface energy, and consequently molecule-substrate interactions, particularly in mechanically exfoliated flakes of MoS₂, is defects.¹⁸² Further investigation is needed to understand the different adsorption geometry of Co phthalocyanines on smaller MoS₂ terraces.

3.2.5 Conclusion

In conclusion, we found that the orientation of cobalt phthalocyanines on small-sized thin-layers of MoS₂ flakes is significantly different compared to bulk MoS₂. This demonstrates that the molecular orientation on small sized (mono- to few-layers) TMDC flakes cannot be simply deduced from the orientation of organic molecules on related bulk substrates. For the understanding of electronic and optic interactions at such interfaces, different molecular orientations should be considered. From our perspective, this could also affect TMDC-based devices as the situation between electrodes with small distances could lead to a similar restricted situation, in particular if the evaporation of molecules occurs after the deposition of electrode structures. In addition, defects in the flakes and the high cleanliness of in situ cleaned substrates might be important. Although our studies are focused on monolayer coverages, more extended growth studies varying the temperature, film thickness, and deposition rate are of high interest. Also, a systematic variation of the lateral size of atomically flat MoS₂ terraces may help to understand the observations discussed in this study. Thus, further research is needed to reveal the exact underlying mechanism for the different molecular orientation on bulk MoS₂ and flakes.

3.3 Tuning the electronic properties of defect-rich MoS₂

The third publication of this thesis serves to achieve further understanding on the properties of highly defective molybdenum disulfide and the heterostructures formed with CoPcF₁₆. To control the amounts of defects on the MoS₂ surface the substrate was sputtered *in situ* with Ar and Ne gas. Subsequently, CoPcF₁₆ was deposited first at a monolayer coverage and afterwards a multilayer coverage. The electronic structure of the yielded surfaces was investigated by angle-resolved photoemission spectroscopy, X-ray absorption spectroscopy and (surface-sensitive) X-ray photoemission spectroscopy. After sputtering with argon for one or four minutes, the MoS₂ surface was slightly p-type doped, while sputtering with neon for one minute lead to a slightly n-type doped surface. In addition, the formation of monosulfur vacancies, as seen by a decreased Mo:S ratio and the formation of a reduced Mo⁰ species was found. The data show that both the amount of monosulfur vacancies and Mo⁰ atoms increase with an enhanced dose of sputtering. The deposition of CoPcF₁₆ onto the Ne sputtered substrates allowed further tuning of its electronic properties involving p-type doping as seen by the according shift in Fermi level. This indicates that defect healing is possible even for those very defect-rich substrates. For the Ar sputtered substrates, no significant further tuning of the Fermi level could be achieved by the deposition of CoPcF₁₆. In addition, a charge transfer between any of the sputtered substrates and the cobalt atom of the CoPcF₁₆ molecule was found as depicted in the XAS spectra acquired at the Co L_{2,3} edge and the Co 2p XPS spectra. For higher sputter doses this charge transfer appears to be more pronounced, most likely highlighting the significance of the metallic Mo⁰ atoms in this process. In conclusion, this work shows that even for highly defective TMDCs the tuning of its electronic properties is possible and the possibility to transfer charge between deposited molecules and the created defects.

Tuning the electronic properties of defect-rich MoS₂

Eric Juriatti¹, Martina Binninger¹, Carolin Schüle¹, Maren Zirwick¹, Katarina Margetic¹, Erika Giangrisostomi², Marcus Scheele^{1,*}, Heiko Peisert^{1,*}

1 Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

2 Institute Methods and Instrumentation for Synchrotron Radiation Research, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, 12489 Berlin, Germany

* Corresponding author, heiko.peisert@uni-tuebingen.de, Tel.: (+49) 07071 / 29-76931, Fax: (+49) 07071 / 29-5490 and marcus.scheele@uni-tuebingen.de

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3.3.1 Abstract

Transition metal dichalcogenides (TMDCs), including molybdenum disulfide (MoS₂), have emerged as a promising candidate for novel semiconducting devices. However, in many cases structural defects significantly affect the electronic properties of the material. The present study utilizes angle resolved photoelectron spectroscopy (ARPES) and surface sensitive core level spectroscopy (SXPS, XAS) with synchrotron radiation to investigate the interfaces between defect-rich MoS₂ and perfluorinated cobalt phthalocyanine (CoPcF₁₆). Defects were introduced in synthetic MoS₂ bulk crystals by gentle argon and neon sputtering. Although the band structure is still visible after sputtering, especially SXPS reveals structural and electronic disturbances of the topmost MoS₂ layer. We show how the Fermi energy in such defect-rich MoS₂ can be tuned by the subsequent deposition of CoPcF₁₆, which is verified by a shift in Fermi level for the Ne sputtered surface, under complex charge rearrangements including a charge transfer from all the substrates towards the cobalt atom of the organic molecule.

3.3.2 Introduction

In the pursuit for novel semiconducting materials, the group of transition metal dichalcogenides (TMDCs), including molybdenum disulfide (MoS₂), has emerged as a promising candidate due to their distinctive properties as layered 2D materials with broadly tunable electronic structure.^{106–108} While numerous studies have focused on single-layer MoS₂ sheets, recent research has underscored the pivotal role of multilayer TMDCs in the fabrication of ultrafast photodetectors.^{10,183} To tune their electronic structure for such applications, the adsorption of organic molecules is a versatile strategy (e.g., refs ^{13,14}), resulting e.g. in a dipole-induced doping or (complex) charge transfer.¹⁵ Photoelectron spectroscopy (PES), X-ray absorption spectroscopy (XAS), and angle-resolved photoelectron spectroscopy (ARPES) are powerful techniques for studying their interfacial electronic structure with different surface sensitivities, the orientation of the molecules in the heterostructure, and the band structure in proximity to the Fermi level. Using these techniques, heterostructuring with (fluorinated) transition metal phthalocyanines (TMPcs) has been shown to modify the interfacial electronic properties of pristine TMDCs.^{15,20,22} For the interface between CoPcF₁₆ and defect-free MoS₂, a slight doping in the TMDC was recently observed, however without strong local interactions accompanied by (integer) charge transfer.²⁰ A convenient side-effect of this heterostructure is the strong interaction of the central

Co atom of CoPcF₁₆ with many metals such as Au, Ag, Cu or Ni (e.g. refs ^{21,157,184–187}), such that it can be used as a probe for PES studies of TMDC layers.²¹ Since interaction mechanism depend strongly on the central metal atom and the ionization potential of the phthalocyanine, we focus specifically on CoPcF₁₆ and vary the properties of the substrate.

In general, electronic defects play a crucial role in novel optoelectronic devices, as they represent, e.g., traps for charge carrier transport.⁴⁶ However, it is challenging to produce nearly defect-free TMDC monolayers or multilayers. In particular, natural, exfoliated MoS₂ crystals exhibit a variety of intrinsic defects.¹⁸⁸ Moreover, p- and n-type defects can be formed intentionally by sputtering with noble gases, yielding conflicting results in different reports, apparently depending on detailed experimental conditions and the source of the substrates.^{69,70,188,189} Recently, a TMDC surface cleaning by noble gas ion bombardment was considered.¹⁹⁰ Amongst other strategies, such defects can be healed by appropriate surface modifications. For instance, the adsorption of thiol-bearing molecules has been demonstrated to remove the S-vacancies inherent to MoS₂ grown by chemical vapor deposition (CVD).¹⁹¹ It has been shown that the adsorption of different TMPcs can significantly affect surface-enhanced Raman scattering (SERS) and photoluminescence (PL) properties of MoS₂.^{141,192} Furthermore, it has been reported that the adsorption of titanyl phthalocyanine (TiOPc) might be an effective defect passivation method for MoS₂.¹⁹³

In the present study, we intentionally create defects in multilayered MoS₂ by gentle ion sputtering with argon or neon and analyze the electronic structure after each treatment with PES, XAS and ARPES. Subsequently, cobalt(II) hexadecafluorophthalocyanine (CoPcF₁₆) is deposited, and the interfacial electronic structure of the defect-rich MoS₂/TMPc heterostructure is determined. It is proposed that the electronic properties at the interface of defect-rich surfaces can be tuned by the interaction with the deposited molecule.

3.3.3 Experimental section

All experiments were conducted either at our home laboratory set-up or at the LowDosePES endstation of the PM4 beamline (BESSY II, Helmholtz-Zentrum Berlin, Germany) under ultrahigh vacuum (UHV) conditions (base pressure at our home laboratory: 8×10^{-10} mbar and 1×10^{-10} mbar at the LowDose PES endstation). The spectrometer at the home laboratory is equipped with a monochromatized Al K α

radiation source (XR 50 M, SPECS GmbH) and a hemispherical analyzer (Phoibos 150, SPECS). The energy was calibrated to the binding energies of Au 4f_{7/2} (84.00 eV), Ag 3d_{5/2} (368.21 eV) and Cu 2p_{3/2} (932.63 eV) using Ar-ion sputtered foils of Au, Ag and Cu (Goodfellow Cambridge Ltd.). At the LowDosePES endstation the samples were investigated by XAS and (angle-resolved) PES using an angle-resolved time-of-flight detector (ARTOF). For XAS, the total electron yield of the sample current was measured. The energy resolution for the Co L-edges was 263 meV at a photon energy of 790 eV. For photoemission at excitation energies of 900, 500, 370, 300, 230 and 75 eV the energy resolution was 592, 230, 156, 114, 118 and 66 meV, respectively. A sputtered gold crystal was used for energy calibration. After every change of energy, the Au 4f spectra (XPS) calibrated to 84.00 eV or the Au Fermi edge, calibrated to 0.00 eV, was acquired.

Synthetic molybdenum disulfide crystals (2D Semiconductors, Phoenix, AZ, USA) were attached to the sample holders using silver conductive paint. To ensure cleanliness, the crystals were cleaved *in situ* by scotch tape. By the absence of carbon- and oxygen-signals in the XPS, a contamination-free surface could be confirmed. The samples were sputtered with a IQE 10 ion source (SPECS GmbH, Berlin, Germany) using Ar and Ne gas (purity: 4.5, Linde plc, Dublin, Ireland and Westfalen AG, Münster, Germany). The pressure in the vacuum chamber was maintained at a constant level of 5×10^{-5} mbar during the sputtering process. The kinetic energy of the ions was set to 500 eV at the synchrotron facility and 250 eV at the home laboratory. The sputter time was varied. Subsequently, CoPcF₁₆ (95 %, BLD Pharmatech LTD., Shanghai, China) was deposited in a separate chamber at temperatures of 450 °C and a pressure of approximately 1×10^{-7} mbar using a Knudsen cell. Via a Quartz crystal microbalance (QCMB) the deposition rate was determined as 0.1–0.2 nm per minute. The nominal layer thickness of the deposited CoPcF₁₆ molecule on the MoS₂ substrate was calculated by comparing core level intensities of the overlayer (C 1s) to the intensity of the substrate related Mo 3d signal. The photoionization cross sections were taken from Yeh and Lindau¹¹⁷ and the inelastic mean free path was calculated using the formula given by Seah and Dench⁹⁴ for organic molecules.

The XPS spectra were fitted using Unifit software (Unifit Scientific Software GmbH, Leipzig, Germany). The Voigt profile as a convolution of Gaussian and Lorentzian line shapes and a Shirley background was chosen.

The ARPES data were processed using IGOR Pro software, subtracting a detector image for intensity correction. The 2D images shown in this study were extracted from 3D images in Γ -K and Γ -M direction, i.e. the most important points of high symmetry within the reciprocal space.

3.3.4 Results and Discussion

3.3.4.1 Effects of sputtering on the MoS₂ surface and interface properties of MoS₂/CoPcF₁₆

In Figure 3.10, the variations of the position of the Fermi level of MoS₂ upon Ar⁺ and Ne⁺ ion bombardment and subsequent deposition of CoPcF₁₆ in the monolayer range are monitored using ARPES M- Γ -K maps of three different experiments: Ne ion sputtering for 1 min (Fig. 3.10a,d,g), Ar ion sputtering for 1 min (Fig. 3.10b,e,h), and Ar sputtering for 4 mins (Fig. 3.10c,f,i). A low energy of 500 eV was used to avoid more severe radiation damage of MoS₂ (For further details, e.g. the corresponding k_x-k_y maps, see Figure 7.16 in the Supporting information.). To ascertain the valence band maximum as the energy of the highest occupied state, the Fermi edge of a sputtered gold foil was measured prior to each experiment to calibrate the Fermi level to 0.00 eV. The exact position of the valence band maximum was determined utilizing the integrated band maps at the located Gamma point as shown in Figure 3.10j-l.

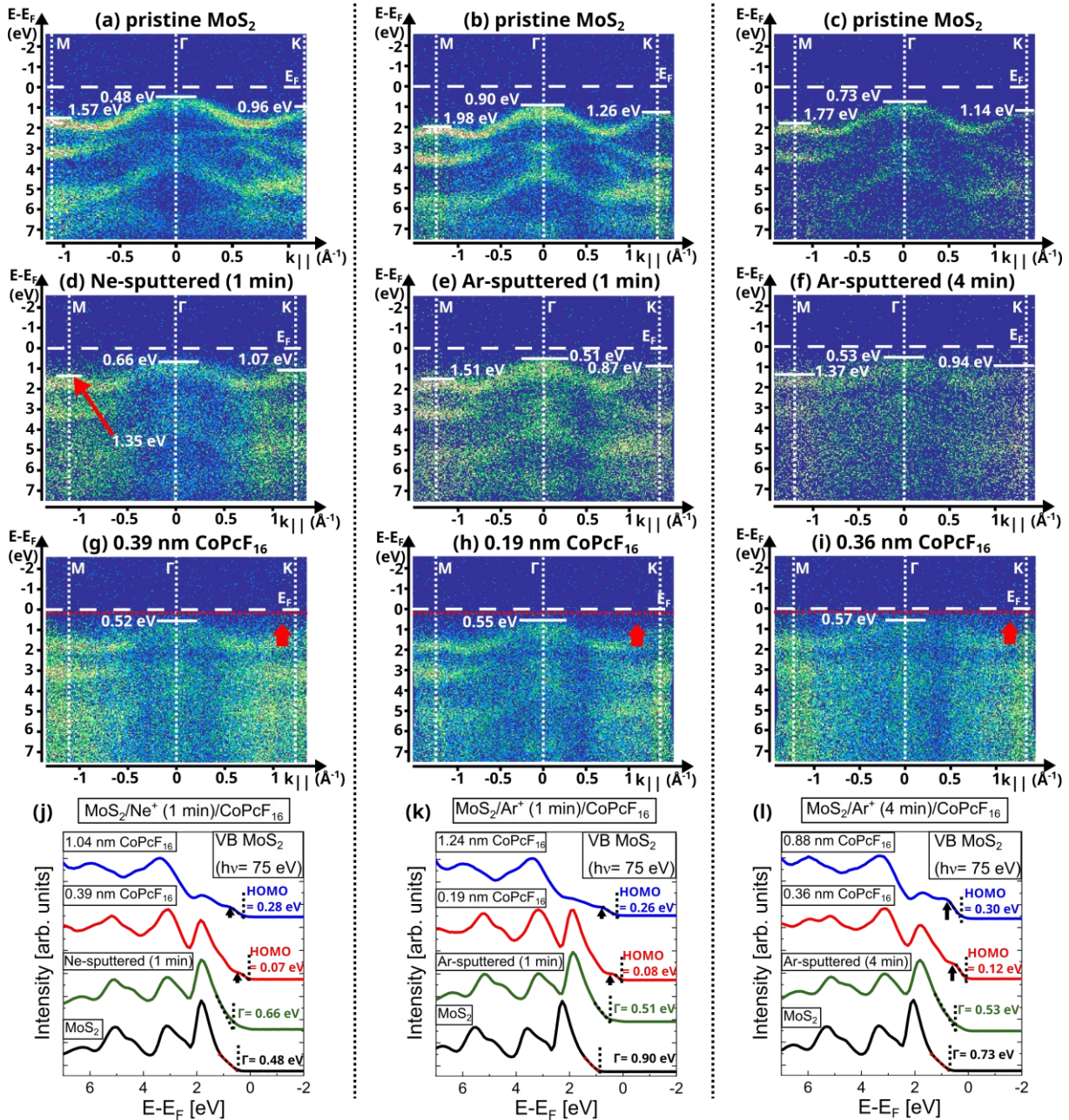


Figure 3.10: ARPES band structure of MoS₂ before (a, b, c) and after sputtering (d, e, f) and the subsequent deposition of a monolayer film of CoPcF₁₆ (g, h, i) and the integrated valence band structures (j, k, l) measured at an excitation energy of $h\nu=75$ eV.

In general, energetic shifts of core levels or valence band features in photoemission can be attributed to different origins including a change of the electron density at the considered atom, different screening of the remaining photo-hole, or shifts of the reference (Fermi) level. Screening effects by additional adsorbates depend strongly on the dielectric constant and the distance would cause a lowering of the binding energy. The magnitude might be estimated to maximal 0.1–0.2 eV for an atom directly at the

interface to an organic molecule.¹⁹⁴ Since the observed energetic shifts are similar for different substrate related core levels and the signal is not limited to the uppermost atoms only, we discuss them in the following in the frame of a shift of the reference (Fermi) level due to band bending. This change in the Fermi level is referred to as (relative) p- or n-doping.

It is important to note the varying initial Fermi level positions at 0.48, 0.90 and 0.73 eV above the valence band maximum for the three experiments (Figure 3.10a–c). Assuming an (indirect) band gap of 1.23 eV,^{36,195} this indicates initial p-doping for the first sample, as well as n-doping for the other two samples. The ion bombardment causes energetic shifts to these initial Fermi level positions without compromising the integrity of the band structure. In experiment one, the sputtering with Neon, the Gamma point shifts to 0.7 eV (Figure 3.10d), now indicating a slight n-doping. In contrast, after Ar sputtering for 1 or 4 min, the Gamma point is located about 0.5 eV below E_F , which corresponds to a slight p-doping (Figure 3.10e,f; integrated spectra: k,l).

Subsequent deposition of roughly a monolayer of CoPcF₁₆ on the sputtered substrates causes further energetic shifts, which are small but above the energetic resolution of our experiment, after which the valence band maximum at the Gamma point (Fig. 3.10g–i) lies between 0.5–0.6 eV in all three cases. In addition to the band structure derived from the MoS₂ substrate, new non-dispersive bands emerge below the Fermi level, marked by the red dotted lines and arrows in Fig. 3.10g–i and best visible in the integrated valence band spectra (Fig. 3.10j–l, red curves) highlighted by black arrows. These effects are attributed to the molecular orbitals of CoPcF₁₆ at the interface. In accordance with this interpretation, an even more pronounced manifestation of such additional energy levels is observed for thicker molecular coverages, exemplified in Fig. 3.10j–l with the blue curves (and in more detail in Figure 7.16, Supporting information). With increasing molecular deposition, their position shifts to higher energies until reaching the position of the HOMO of the free CoPcF₁₆ molecule at approximately 0.3 eV below the Fermi level.

The results presented in Figure 3.10 are largely consistent with previous studies on the subject of sputtering MoS₂ surfaces: Both, Ne⁺ and Ar⁺ ion bombardment of MoS₂, have been reported to cause changes in the electronic structure.^{69,70} However, depending on the gas and the precise sputtering conditions, the mechanisms are somewhat different and the results not always comparable. It was reported that Ar

sputtering at high energies (10 keV) yields a p-doped substrate accompanied by the formation of Mo⁰ islands.⁶⁹ For Ne sputtered MoS₂, the literature is much less clear. For 1 keV Ne⁺ bombardment, Lince et al.⁷⁰ reported slight shifts of the Mo 3d core levels towards lower binding energies and more intense shifts towards higher binding energies for the S 2p signals, precluding any conclusions on possible doping. Further results in the context include the observation of distinct defects in the microstructure already upon low ion dosing,^{16,189} as well as significant alterations of the Mo/S atomic ratio.^{69,70,189}

We ascribe the variations of the initial doping level in our samples to the presence of step edges and/or non-detectable traces of adsorbates. However, considering that even low doses of ion sputtering can result in a significantly higher number of defects, we presume that these sample-dependent fluctuations do not relevantly affect the qualitative trends found after sputtering and the deposition of CoPcF₁₆.

Overall, the results of this study indicate that sputtering is a viable method for shifting the Fermi level in MoS₂, thereby affording slight p- (Ar) or n- (Ne) doping. In addition, the thickness-dependent results after deposition of CoPcF₁₆ indicate a surface interaction with the sputtered MoS₂ which will be expanded in the following sections.

3.3.4.2 Interaction mechanism at the interface between the sputtered MoS₂ substrate and CoPcF₁₆

In the case of TMPCs, two distinct interaction channels are possible involving the macrocycle and/or the central metal atom.¹⁵⁷ First, the interaction via the Co atom of CoPcF₁₆ will be examined utilizing XAS at the Co L_{2,3} edge.

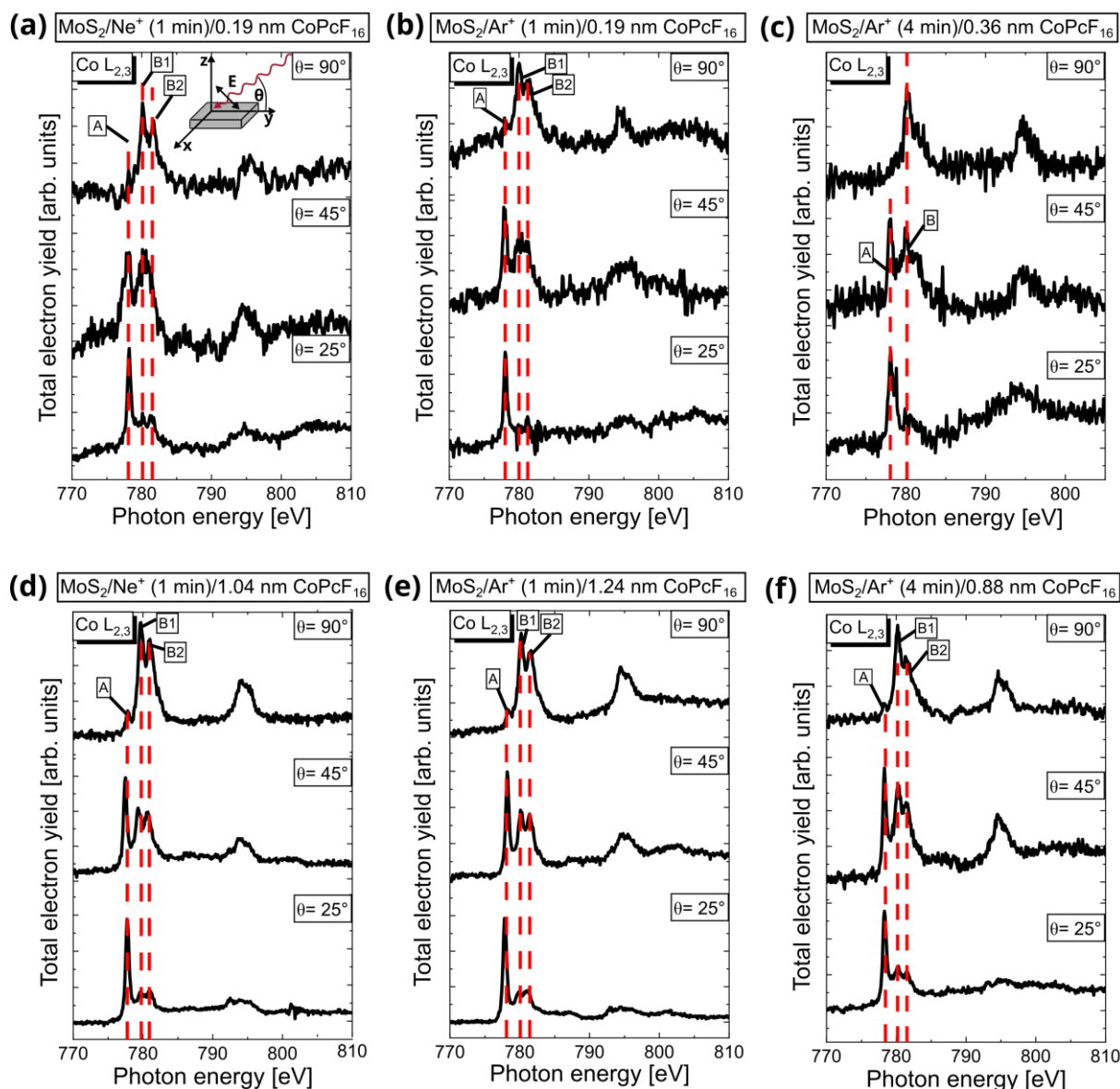


Figure 3.11: Co $L_{2,3}$ -XAS spectra of CoPcF₁₆ coverages in the mono- or multilayer range on Ne⁺ or Ar⁺ sputtered MoS₂.

Co $L_{2,3}$ edge XAS are sensitive to the interfacial electronic structure and provide information on molecular orientation. Co $L_{2,3}$ spectra of CoPcF₁₆ exhibit a typical multiplet structure; analogously to refs^{116,157} with three primary features: A (polarized orthogonal to the molecular plane, z), B1, and B2 (polarized within the molecular plane, xy).

The Co $L_{2,3}$ -XAS results are interpreted using p-polarized synchrotron light in Figure 3.11 in the context of these three features, which are highlighted by dashed red lines. For all three substrates and approx. monolayer CoPcF₁₆ coverage (see Figure 3.11a-c), the largest intensity is observed at grazing beam incidence ($\theta=25^\circ$) at feature A.

Changing the angle of incidence to 45° and 90° strongly diminishes the intensity of feature A, while the features B1 and B2 gain relative intensity.

Increasing the CoPcF₁₆ thickness has no major effects on the Co L_{2,3}-XAS results for the Ne⁺(1 min) and Ar⁺ (1 min) sputtered samples (compare Fig. 3.11a vs. 3.11d, and Fig. 3.11b vs. 3.11e, respectively). In general, these spectra are similar to bulk-like spectra, suggesting the absence of strong interfacial interactions. In contrast, for the more defect-rich, 4 mins Ar⁺ sputtered MoS₂ substrate, we detect significant changes of the spectral shape. Most notably, the relative intensity of B2 at normal incidence (90°) is substantially weaker than B1 with 2-3 layers of CoPcF₁₆ (Fig. 3.11f) and almost completely vanishes for a monolayer coverage (Fig. 3.11c).

These results indicate almost planar, flat lying CoPcF₁₆ molecules on the MoS₂ surface, enabling generally strong interactions of the central Co atom of CoPcF₁₆ with the substrate. Such interactions can include a redistribution of the d-electrons, charge transfer or even the formation of new states in the case of a strong chemisorption.¹⁵⁷ The latter was observed for CoPc on reactive metal surfaces like Ag or Ni.¹⁵⁷ However in the present case, such interactions exclusively manifest for the heavily sputtered Ar⁺(4 min)-sample. This behavior is more in line with the previously documented interactions of CoPcF₁₆ with relative inert metals, oxygen terminated copper or graphene covered Ni (e.g. refs ^{116,157,196}). Based on these similarities, we suggest that charge transfer and/or electron redistribution at the Co atom in the vicinity of such defect-rich MoS₂ is responsible for our observations in Figure 3.11c+f.

Figure 3.12 substantiates the study of the interaction between CoPcF₁₆ and heavily sputtered MoS₂ surfaces.

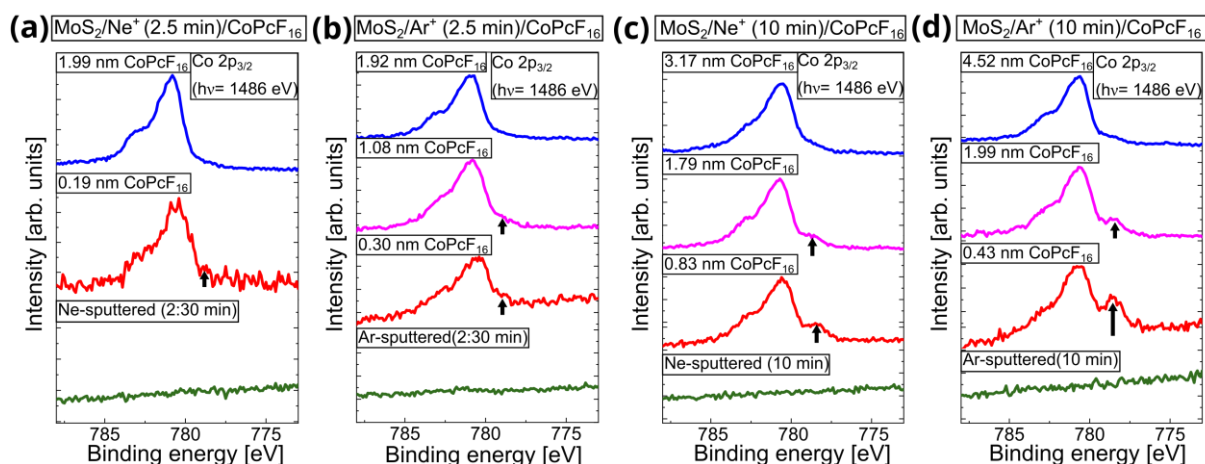


Figure 3.12: Co 2p XPS spectra before and after the deposition of mono- and multilayer films of CoPcF₁₆ after a) 2.5 min Ne sputtering b) 2.5 min Ar sputtering c) 10 min Ne-sputtering and d) 10 min Ar sputtering.

To this end, we recorded Co 2p XPS spectra with the home lab instrument of MoS₂ surfaces sputtered with Ne or Ar gas for 2.5 min or 10 min, and after deposition of a gradually increasing number of CoPcF₁₆ layers. Consistent with the XAS results in Figure 3.11, an additional peak was found at 778–779 eV (see black arrows in Figure 3.12) for a monolayer coverage, which decreases in intensity as the thickness rises. The peak is particularly prominent for the longest sputtering times (Fig. 3.12c+d), corroborating that strong Co-MoS₂ interactions require a high defect density. A similar peak for CoPcF₁₆ at interfaces with metal substrates like Au and Cu and also WSe₂ was found which was ascribed to a reduced Co species resulting from the charge transfer from the substrate to the central metal atom of the organic molecule.^{21,88,115} For the unspattered MoS₂ substrate, this charge transfer was neither observed in the XAS Co L_{2,3} edges nor in the Co 2p photoemission spectra.^{20,27} This demonstrates that the high concentration of surface defects is crucial for such an interaction. For multilayer coverage, e.g. when the effect of the substrate becomes negligible, the Co 2p spectra exhibit the typical multiplet structure for Co²⁺.^{104,157,186,197}

Figure 3.13 presents the results into an alternative interaction mode between the sputtered MoS₂ surface and CoPcF₁₆ by XPS: that of the carbon- and nitrogen-rich macrocycle.

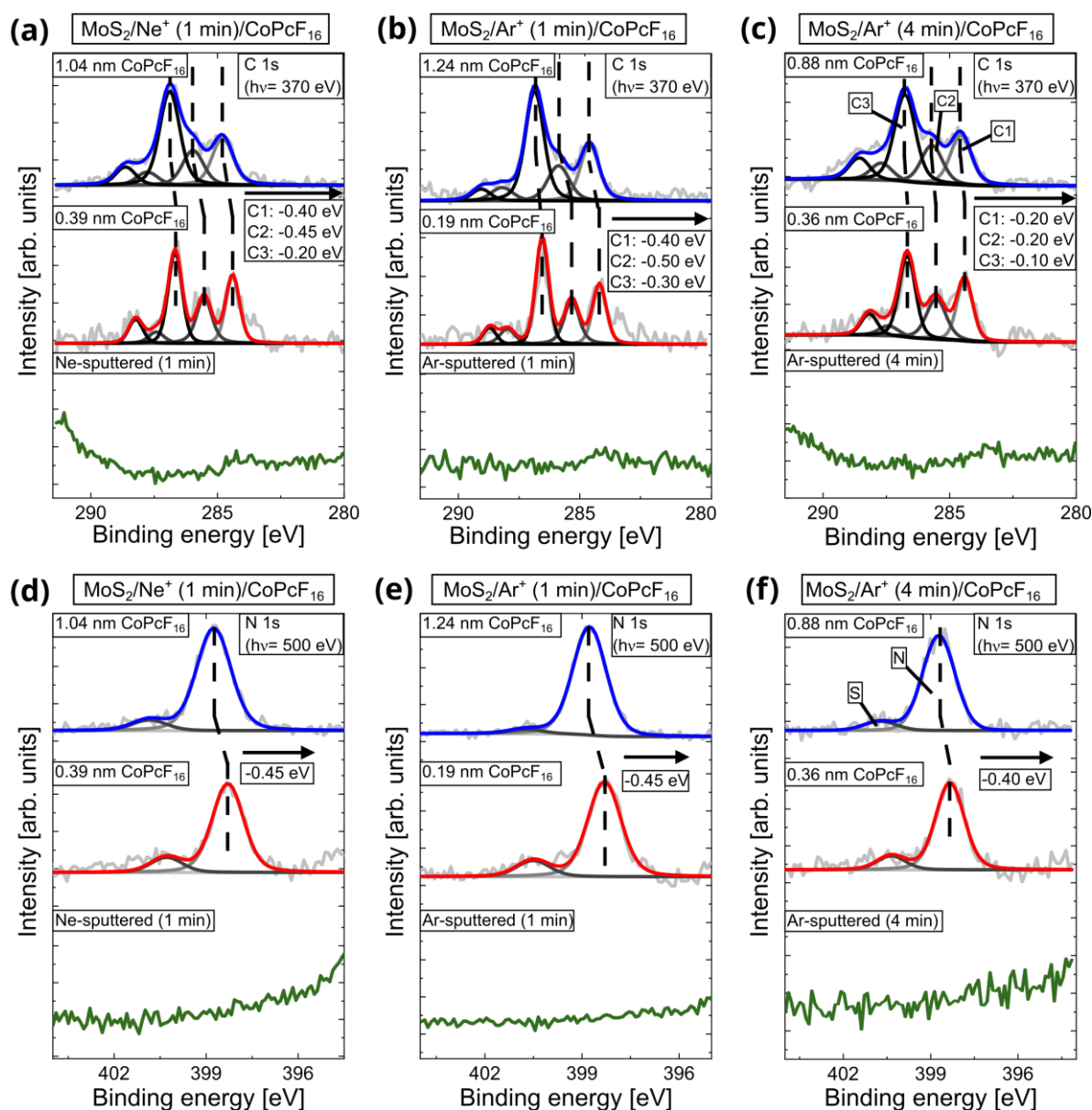


Figure 3.13: Molecule-related C 1s (a,b,c) and N 1s (d,e,f) core level spectra on differently sputtered MoS₂ surfaces. The absence of additional interface peaks indicates the absence of strong, local interactions.

In summary, the C 1s- (Fig. 3.13a-c) and N 1s-spectra (Fig. 3.13d-f), following the deposition of CoPcF₁₆ of varying thicknesses onto MoS₂ substrates, sputtered with Ne⁺ or Ar⁺ and varying durations up to 4 min, exhibit no signs of strong interactions like bond breaking or local charge transfer to a particular atom. The molecules remain intact and possible interactions of the macrocycle are most likely limited to complex (bidirectional) charge rearrangements at the interface, as observed for many similar systems.^{115,123,198,199} The shift towards lower binding energies between the free molecule, indicated by the thicker film (blue line) and the interface (red line) can be

mostly attributed to commonly observed screening of the photohole at the interface.^{20,22,200}

For details on the fitting procedure underlying this conclusion, refer to the supporting information.

3.3.4.3 Surface sensitivity of substrate-related energetic shifts

In Figure 3.14, we use Mo 3d core level spectra (accompanied by S 2p spectra in Figure 7.17), measured with excitation energies of 900 eV or 300 eV, to study how far the effects of sputtering and CoPcF₁₆ deposition extend into the bulk of the MoS₂ substrate. The corresponding mean-free-paths, λ , calculated for the two energies according to ref ⁹⁴ for inorganic materials, are 2.5 nm (“low surface sensitivity”) and 0.9 nm (“high surface sensitivity”). All spectra consist of Mo 3d_{5/2} and Mo 3d_{3/2} doublets at binding energies of 228–229 eV and 232–232.5 eV, respectively, and the S 2s peak at 225.5–226.5 eV. All fit parameters are summarized in Tables 7.9 and 7.10 (supporting information).

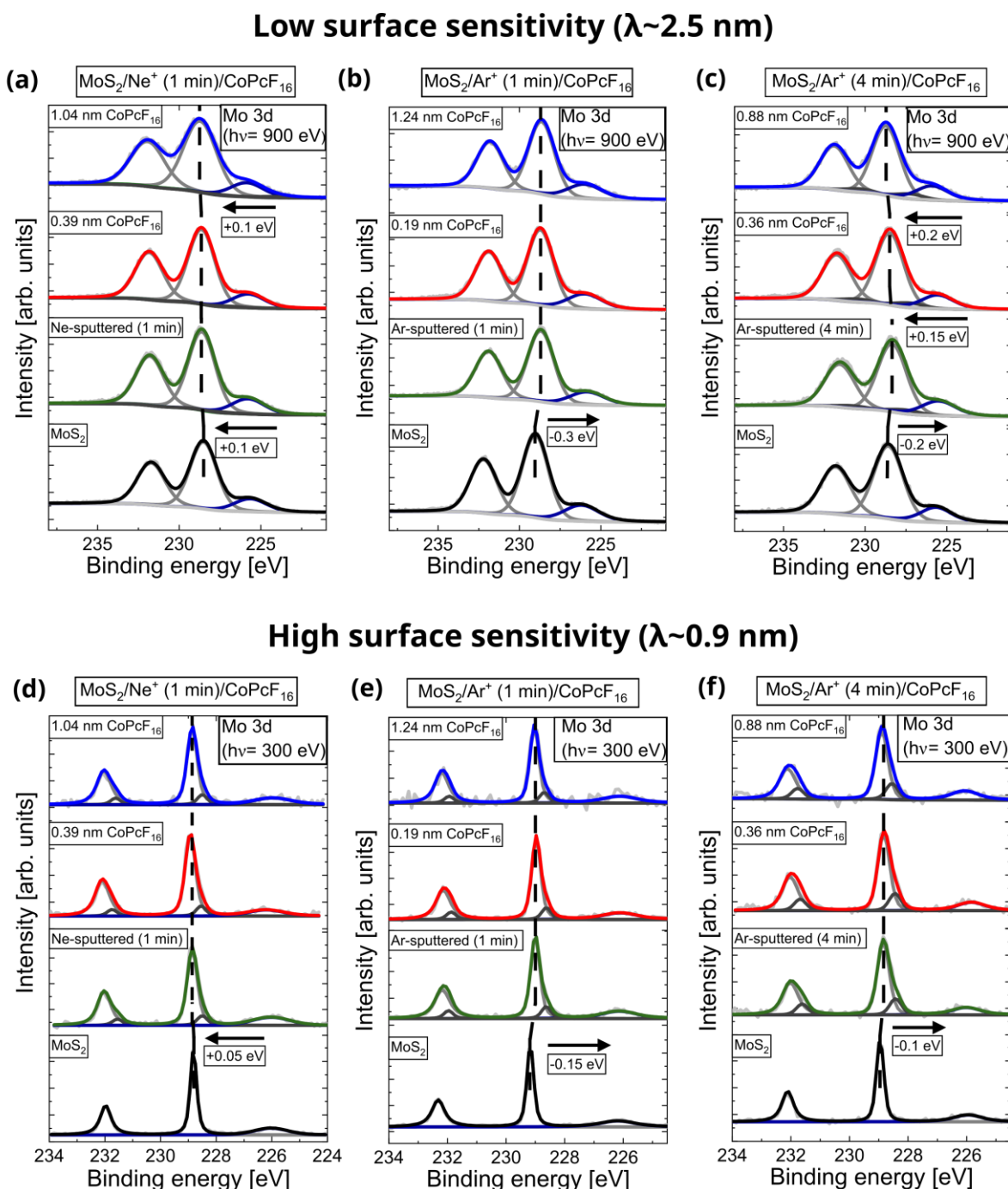


Figure 3.14: X-ray photoelectron spectroscopy (XPS) measurements of the Mo 3d core levels of MoS₂ following the sputtering with Ar⁺ and Ne⁺ and the deposition of CoPcF₁₆ measured at excitation energies of 900 and 300 eV, resulting in different inelastic mean free paths λ of the detected photoelectrons and thus a different surface sensitivity. Additional peaks after sputtering (dark grey lines) are attributed to Mo⁰ species. Shifts towards higher(lower) binding energies are indicated by black arrows.

With low surface sensitivity, the shifts of the Mo 3d (Figure 3.14a-c) and S 2p core level spectra (Figure 7.17) after sputtering and molecular deposition (Figure 3.14a,b,c) are

in reasonable agreement with the shifts of the valence band spectra in Figure 3.10 and corroborate our previous interpretation as p- or n-doping. A further consistence between these two experiments is found in the partial reversal of the sputter-induced energetic shifts by a subsequent deposition of CoPcF₁₆. Monitoring the Mo:S ratios (Table 7.12, supporting information) yields no significant difference inflicted by sputtering, indicating that these actions do not change the composition of the bulk.

In contrast, with high surface sensitivity we find an increasing Mo:S ratio (Table 7.12; especially for Ar⁺(4min) sputtering) and the appearance of an additional Mo-species, which we attribute to Mo⁰ (Figure 3.14d-f).^{69,70} These findings are consistent with recent microscopic studies that have demonstrated structural surface changes due to sputtering,^{16,189} as well as reports on the formation of Mo⁰ after sputtering at higher energies or with relatively high doses of various noble gases.^{69,70,190} The effect of Ar⁺ sputtering on the Mo:S ratio is larger than for Ne⁺ for the same sputtering time. These results indicate a severe degradation of the topmost layer of sulfur atoms during sputtering.

It is noted that – based on the mean-free-path – one would expect similar surface sensitivities for the valence band spectra in Figure 3.10 ($\lambda = 5\text{--}10\text{ \AA}$)^{201–203} and the core level spectra in Figure 3.14d,e,f. However, the core level shifts seen with high surface sensitivity – although qualitatively identical – are quantitatively less pronounced than the changes in the valence band. We suggest that this could be an indication that these uppermost fragments do not determine the electronic structure depicted in Figure 3.10. The sharp features shown therein may originate to a large extent from deeper layers, broadened and attenuated due to scattering at the topmost atoms. Contributions from the top layer appear as background intensity in Figure 3.10, and do not contribute to the well-defined bands due to the lack of periodicity over larger distances.

On the other hand, an exact agreement between the core level shifts acquired with low surface sensitivity and the valence band shifts in Figure 3.10 cannot be expected either, since for $\lambda=2.5\text{ nm}$ the topmost layer still contributes significantly to the spectra.

3.3.5 Conclusion

By this study, a deeper understanding of defect-rich MoS₂ heterointerfaces is given. It has been demonstrated that by sputtering with different noble gases (Ar, Ne), the

structure and electronic properties of the top layer are significantly disturbed. Energetic shifts in valence band and core level spectra reveal p- or n- type doping effects, most likely due to the presence of sulfur vacancies and metallic Mo. Nevertheless, the deposition of CoPcF₁₆ affects the position of the Fermi energy, which illustrates that a tuning of electronic properties is also possible in the case of MoS₂ substrates with a high density of surface defects. The molecules remain intact and a local charge transfer to the Co atom is observed for a small fraction of molecules only, especially for high defect concentrations (4 mins Ar⁺). Most likely complex (bidirectional) charge rearrangements occur at the interface.

4. Non-peer-reviewed Results

4.1 Interfaces between Cobalt Phthalocyanines and MoSe₂: Conditions for charge transfer and the Nature of Gap States

Besides the already published results, this thesis includes an additional manuscript which is not published at the time this thesis is submitted. In this work, the interface between the TMDC MoSe₂ and the organic molecules CoPc and CoPcF₁₆ were investigated. Utilizing synchrotron experiments like ARPES, XAS and surface sensitive XPS at the WERA beamline at KARA in combination with monochromatic XPS and UPS recorded at the home laboratory, new insights in the discussed heterostructures could be achieved. Additional photoluminescence experiments give further information about the optical properties of the molecules at the interface. In summary, it can be deduced from the results that the CoPc molecule does not show strong interactions with the MoSe₂ substrate while a pronounced charge transfer between the Co atom of the CoPcF₁₆ molecule and the MoSe₂ substrate was observed via X-ray absorption and photoemission spectroscopy. Via angle-resolved photoemission, the nature of newly formed gap states could be studied, indicating a (partial) occupation of the former LUMO or even LUMO+1 of the CoPcF₁₆ molecule. Furthermore, by using n-type doped MoSe₂ as a substrate the dependence of the Fermi level position of the substrate on this interaction could be studied. At the n-MoSe₂/CoPcF₁₆ interface a similar charge transfer and occurrence of gap states was found when compared to the interface with the undoped substrate, but the observed effects were even more pronounced. The findings were concluded by optical experiments that show a reduction in photoluminescence for CoPcF₁₆ on MoSe₂ or n-MoSe₂ when compared to a silicon substrate which was used as reference, which can be explained by the partial filling of d-orbitals of the organic molecule.

Interfaces between Cobalt Phthalocyanines and MoSe₂: Conditions for charge transfer and the Nature of Gap States

Carolin Schüle^{1,#}, Eric Juriatti^{1,#}, Peter Nagel², Tim Parker¹, Michael Merz², Alfred J. Meixner¹, Thomas Chassé¹, Dai Zhang¹, Stefan Schuppler², Marcus Scheele^{1,*}, Heiko Peisert^{1,*}

1 Institut für Physikalische und Theoretische Chemie, Universität Tübingen,
72076 Tübingen, Germany

2 Institute for Quantum Materials and Technologies (IQMT), Karlsruhe Institute
of Technology (KIT), 76021 Karlsruhe, Germany, and Karlsruhe Nano and Micro
Facility (KNMF), Karlsruhe Institute of Technology, 76344 Eggenstein-
Leopoldshafen, Germany

These authors contributed equally.

* Corresponding author, heiko.peisert@uni-tuebingen.de, Tel.: (+49) 07071 / 29-
76931, Fax: (+49) 07071 / 29-5490 and marcus.scheele@uni-tuebingen.de

4.1.1 Abstract

The recently increasing research efforts devoted to layered transition metal dichalcogenides (TMDCs) derive from their novel electronic properties, which might be further tuned by the adsorption of molecules. However, the nature of interactions is often not fully understood, especially for comparably weakly interacting molecules, such as transition metal phthalocyanines (TMPcs). We studied interface properties between cobalt phthalocyanine (CoPc) or perfluorinated CoPcF₁₆ and molybdenum diselenide (MoSe₂) using photoelectron spectroscopy (PES), angle resolved photoelectron spectroscopy (ARPES), X-ray absorption spectroscopy (XAS) and photoluminescence spectroscopy. We found that a significant number of gap states is induced by the adsorption of CoPcF₁₆. In the case of n-doped MoSe₂ even the LUMO of CoPcF₁₆ can be occupied at the interface.

4.1.2 Introduction

Layered transition metal dichalcogenides (TMDCs), such as molybdenum disulfide and diselenide (MoS₂ and MoSe₂), as well as their alloys are currently the focus of interest due to their novel electronic properties including tunable band gaps in the optical or near infrared regime, large charge carrier mobilities and high exciton binding energies.^{10,204–206} These aspects make the materials well-suited for application in optoelectronic devices such as photodetectors or field-effect transistors (FETs).^{10,207} While many earlier studies focused on MoS₂, related TMDCs, including MoSe₂, appear to be even better suited for applications due to their physical properties such as conductivity or interlayer spacing.²⁰⁸ Although MoSe₂ is a structural analogue of MoS₂, the ionization potential of MoSe₂ is up to 0.8 eV smaller and the band gap is reduced compared to MoS₂ (Refs.^{21,22} and Figure 4.1), which will affect also interface properties.

The adsorption of molecules results in TMDC/organic semiconductor hybrid interfaces which can lead to hybrid localized Frenkel- and delocalized Wannier-type excitons, enabling ultrafast interfacial charge transfer.²⁰⁹ The choice of the TMDC/molecule combination affects crucially the interfacial electronic coupling and charge-transfer dynamics.^{14,210} In the case of the adsorption of strong molecular electron acceptor molecules, such as 1,3,4,5,7,8-hexafluorotetracyanonaphthoquinodimethane (F₆TCNNQ), the difference in the ionization potentials can result in a (integer) charge transfer from the substrate to the LUMO of the molecule.¹³ The interaction mechanism

for weakly interacting, physisorbed carbon molecules are still under investigation. Besides charge transfer, possible mechanisms also include dielectric screening and electronic hybridization at the interfaces under investigation.^{142,211} It was demonstrated that optical properties can be distinctly affected by the adsorption of “weakly interacting” molecules (e.g. refs^{14,140,141,212,213}). For example, a quenching of the low-temperature defect photoluminescence of MoS₂ was observed for heterostructures with transition metal phthalocyanines (TMPcs), depending strongly on the central metal atom of the phthalocyanine.¹⁴¹ It is expected that these relatively overlooked molecular properties offer unique opportunities for tuning optical and electronic characteristics.¹⁴⁰ Recently, it was demonstrated that the electrical characteristics of MoS₂ based FETs is distinctly affected by organic molecule adsorption.²⁰⁷ Especially TMDC/TMPc heterostructures may exhibit novel electronic properties, which could be of high interest for efficient and flexible electronics, photonics and spintronics.^{14,25,108,214}

Moreover, due to the chemical tunability of their electronic properties, TMPcs might be especially suited for systematic studies of the interfacial electronic structure. Generally, two different interaction paths are possible, via the central metal atom or the macrocycle. CoPcF_x (X = 0,16) often behaves differently, when compared to phthalocyanines with other transition metals, since the interaction might be governed by a local interaction between the Co 3d_{z²} orbital and electronic states of the substrate.^{157,215} The fluorination causes a distinct increase of the ionization potential by about 0.7-1.0 eV depending on the specific interface.^{20,64,216} As a consequence, electronic interface properties like dipoles or charge transfer may change drastically.

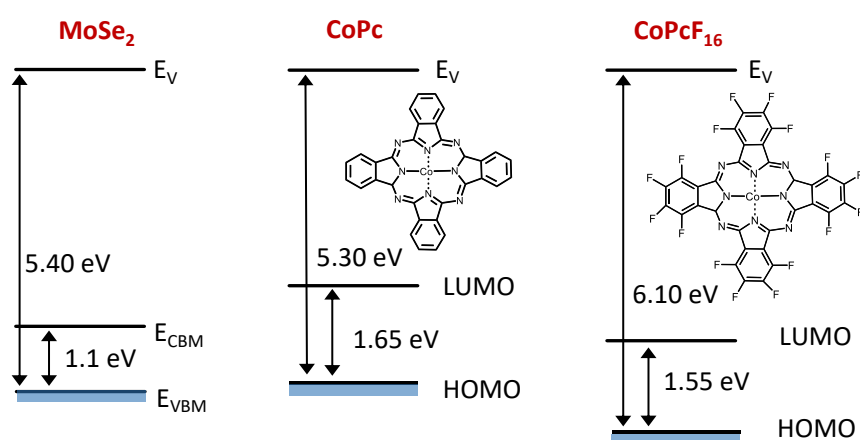


Figure 4.1: Position of important energy levels of the MoSe₂ substrate and the molecules CoPc and CoPcF₁₆ with respect to the vacuum level E_V as obtained from

ultraviolet photoemission spectroscopy (UPS). The CoPc or CoPcF₁₆ film thickness on MoSe₂ was > 1.8 nm. The indirect band gap ($E_{\text{VBM}} - E_{\text{CBM}}$) for MoSe₂ and the optical gaps of the molecules $E(\text{HOMO}) - E(\text{LUMO})$ were taken from the literature (rounded to a half tenth of an eV).^{20,217,218}

In the present study, we investigate interfaces between CoPc or CoPcF₁₆ and MoSe₂ bulk crystals. The position of the energy levels of these materials with respect to the vacuum level E_v is compared in Figure 4.1. Since the lowest unoccupied orbital (LUMO) is higher in energy than the valence band maximum (E_{VBM}) and the highest occupied molecular orbital (HOMO) is lower than the conduction band minimum (E_{CBM}) of MoSe₂, no integer charge transfer might be expected according to the integer charge transfer model.²¹⁹ We note that optical gaps were used for the determination of the $E(\text{HOMO}) - E(\text{LUMO})$ distance in Figure 4.1, which exhibit an excitonic character. For related phthalocyanines, it was demonstrated that transport gaps determined from photoemission and inverse photoemission are 0.2-0.6 eV higher, which shifts the LUMO closer to E_v .²²⁰ In the present study we show that despite the relative positions of the important energy levels interfacial charge transfer can be observed and/or gap states can be formed, crucially depending on both the ionization potential of the molecule and the doping of MoSe₂.

4.1.3 Experimental section

MoSe₂ and n-doped MoSe₂ (Re dopant, $c = 10^{18} - 10^{19} \text{ cm}^{-3}$) single crystals (2DSemiconductors Inc. (USA), grown by chemical vapor transport) were cleaved by adhesive tape in ultrahigh vacuum (UHV). The cleanliness and the azimuthal orientation of the surface were checked by X-ray photoelectron spectroscopy (XPS) and angle resolved photoelectron spectroscopy (ARPES).

CoPc (Sigma Aldrich) and CoPcF₁₆ (BLD Pharmatech) were evaporated at rates of 0.05 – 0.2 nm/min and a temperature of 700 – 760 K from a home-built Knudsen cell. The evaporation rates were estimated from a quartz microbalance and the nominal film thicknesses was calculated from XPS intensity ratios using sensitivity factors from Yeh and Lindau¹¹⁷ and the inelastic mean free path for organic molecules from Seah and Dench assuming layer-by-layer growth for each deposition step.⁹⁴

Synchrotron based photoelectron spectroscopy (PES), angle resolved photoelectron spectroscopy (ARPES) and X-ray absorption spectroscopy (XAS) measurements have

been performed at the WERA beamline at the KIT Light Source, Karlsruhe Research Accelerator (KARA, Karlsruhe, Germany). The base pressure was $2 \cdot 10^{-10}$ mbar. For ARPES experiments the chosen photon energies were 135 eV (for the MoSe₂/CoPc interface) and 142.5 eV (for the (n-)MoSe₂/CoPcF₁₆ interfaces). The energy resolution for XAS and PES was set to about 220 meV at a photon energy of 400 eV. The absorption was monitored indirectly by measuring the total electron yield (sample current). The x-ray absorption spectra have been normalized to the same step height well above the ionization threshold. For photon energy calibration the energy of the Ni-L₃ absorption edge of NiO at 853.0 eV was taken as a reference. For the evaluation of ARPES data we used the software ImageJ/Fiji.^{167,168}

The PES measurements in the home lab (XPS and UPS) were performed using a multi-chamber UHV system (base pressure of $9 \cdot 10^{-10}$ mbar) equipped with a Phoibos 150 Hemispherical Energy Analyzer (SPECS), an X-ray source with monochromator (XR 50 M, SPECS) and a UVS300 helium discharge lamp (SPECS). The energy resolution for XPS (excitation energy $h\nu = 1486.6$ eV) and UPS ($h\nu = 21.22$ eV), were 400 meV and 150 meV, respectively. The energy scale of PES was calibrated to reproduce the binding energies (BE) of Au 4f_{7/2} and Ag 3d_{5/2} (84.0 and 368.2 eV) and the Fermi level of the gold foil $E_F = 0.0$ eV.

The peak fitting of XPS spectra was performed using the program Unifit.²²¹ A Voigt profile peak shape (convolution of Gaussian and Lorentzian peaks) and a Shirley model background were used.

Luminescence measurements were performed on a home-built confocal optical microscope. The samples are excited with a 532 nm continuous wave laser (name, company). The excitation beam was focused onto the sample using a parabolic mirror with a numerical aperture of 0.998, which also collected the emitted signal. The luminescence spectra were detected using a Teledyne Princeton Instruments HRS-500 spectrometer with a Teledyne Pixis 100 CCD camera using a 150 line/mm grating. All spectra were recorded with an excitation power of 150 μ W in front of the parabolic mirror and an acquisition time of 30 s. For each sample a spectral map of 64 spectra was recorded using automatic positioning of the sample with an RHK Technologies SPM 100 controller. Optical images were recorded with a Perkin Elmer SPCM-AQR-14 avalanche photodiode.

4.1.4 Results and Discussion

4.1.4.1 Interfacial electronic structure from ARPES

ARPES is an ideal tool for the momentum-dependent analysis of the electronic structure at surfaces and interfaces. The formation of interface states with lower concentration can be monitored depending on the thickness of the deposited material.

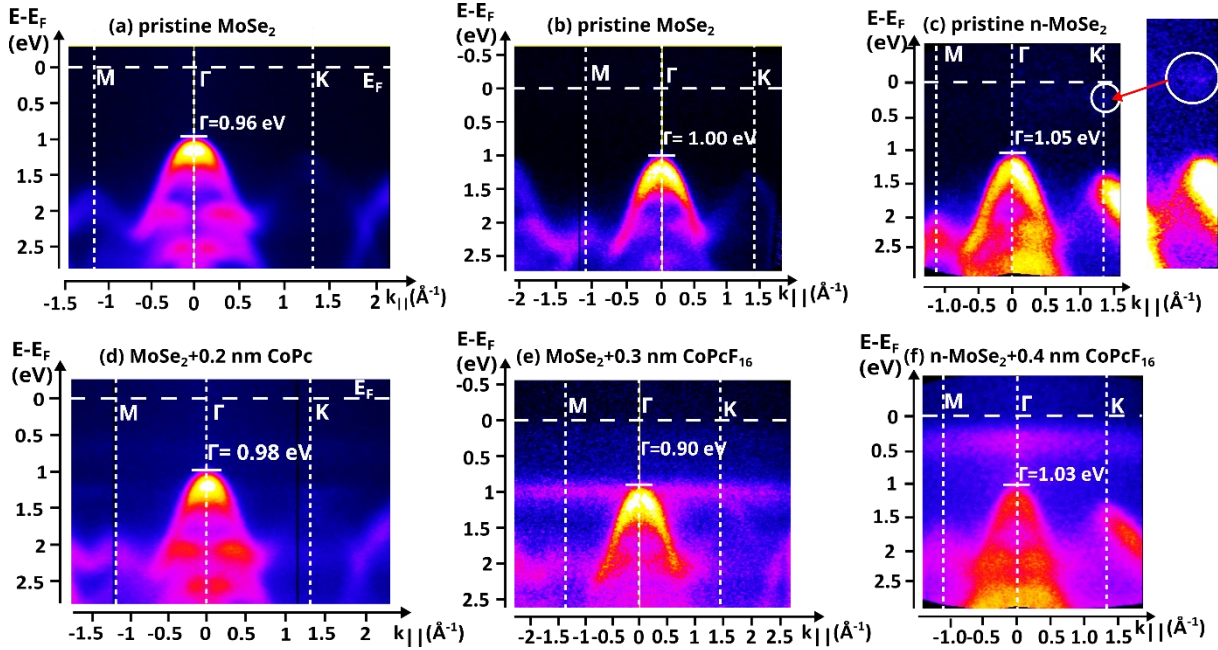


Figure 4.2: Comparison of ARPES band structures before and after deposition of CoPc or CoPcF₁₆: a-c) pristine substrates, d-f) coverages in the monolayer range. The same crystal was used for a) and b), the slight energy shift is ascribed to inhomogeneities of the crystal. For the n-doped crystal (c), intensity at the doping level can be seen in vicinity to the K point.

In Figure 4.2, band structures (ARPES M- Γ -K maps) of pristine MoSe₂ substrates and CoPc(F₁₆) covered MoSe₂ are shown. The corresponding integrated 2D valence band spectra together with thicker coverages are depicted in Figure 7.18 (supporting information). We note that the initial position of the Fermi level for the undoped substrates deviates distinctly from the mid-gap position (Figure 4.2a,b) considering the indirect band gap of 1.10 eV for bulk MoSe₂.^{36,217,218} Also, the maximum of the Γ point of the pristine substrates is not exactly at the same position when comparing the two pristine cleaves. We may ascribe this behavior to step edges and/or non-detectable traces of adsorbates which could already induce n-doping of the substrate. For the doped MoSe₂ (Figure 4.2c), the position of the Γ point indicates a strong n-doping.

Even occupied states close to the Fermi level can be detected (see inset of Figure 4.2c).

After deposition of CoPc (Figure 4.2d), additional non-dispersive features can be detected. The origin of these features can be ascribed to the molecule, intensity close to the Γ point arises from the highest molecular orbital (HOMO). For CoPc and CoPcF₁₆, the HOMO is essentially formed from orbitals of the macrocycle while features arising from the Co central atom appear at about 0.85 eV higher binding energy (see, e.g. refs^{151,157}). Also, for CoPcF₁₆ on MoSe₂ (Figure 4.2e), the non-dispersive HOMO close to Γ is clearly visible. Most importantly, additional intensity within the gap of MoSe₂ is detectable, which can be interpreted as molecule-induced gap states. The formation of additional states in the gap is even more evident for CoPcF₁₆ on n-MoSe₂ (Figure 4.2f), where a non-dispersive line is clearly visible at a distance <0.5 eV to the Fermi level.

The possible formation of gap states can be also traced in the integrated 2D valence band spectra (Figure 7.18). The HOMO-onset for monolayer coverages is hardly visible due to the supposition with the valence band maximum of MoSe₂ in all three cases. Only for the MoSe₂/CoPcF₁₆ interfaces (Figures 7.18b and 7.18c) interface states are clearly visible, more pronounced for n-MoSe₂/CoPcF₁₆ interface (Figure 7.18c), indicating a strong interfacial interaction.

4.1.4.2 Involvement of the Co atom of the TMPcs in the interface interaction

An interaction via the central cobalt atom of phthalocyanines can be detected by the analysis of Co L edge XAS spectra or Co 2p XPS spectra as a function of film thickness. Especially Co L edge XAS spectra are very sensitive to the electronic structure of the Co atom. The shape of the spectra is determined to a large extent by multiplet effects; the reason is the strong overlap of the core wave function with the valence wave functions.¹⁰⁴ Depending on the orientation of the electric field vector of the incoming synchrotron light/beam and the orientation of the molecules, transitions into orbitals with mostly out-of-plane (d_{xz} , d_{yz} , and d_{z^2}) or mostly in-plane components ($d_{x^2-y^2}$ and d_{xy}) are possible, which explains their strong angular dependency (e.g. ref¹⁵⁷). For flat lying, planar TMPcs with D_{4h} symmetry and p-polarized synchrotron radiation, we probe transitions at normal incidence ($\theta = 90^\circ$) into orbitals lying in the molecular plane and at grazing incidence ($\theta = 20^\circ$) preferentially into orbitals with out-of-plane character. From the angular dependence of both Co L and N K spectra of

thicker films (thickness about 2 nm, at such film thicknesses influences of the substrate are negligible), we conclude that CoPc and CoPcF₁₆ are oriented preferentially flat-lying on MoSe₂ bulk substrates (Supporting Information, Figure 7.19). Unfortunately, N K spectra for monolayer coverages are dominated by the substrate related absorption at the Mo M edge, which makes a detailed analysis difficult.

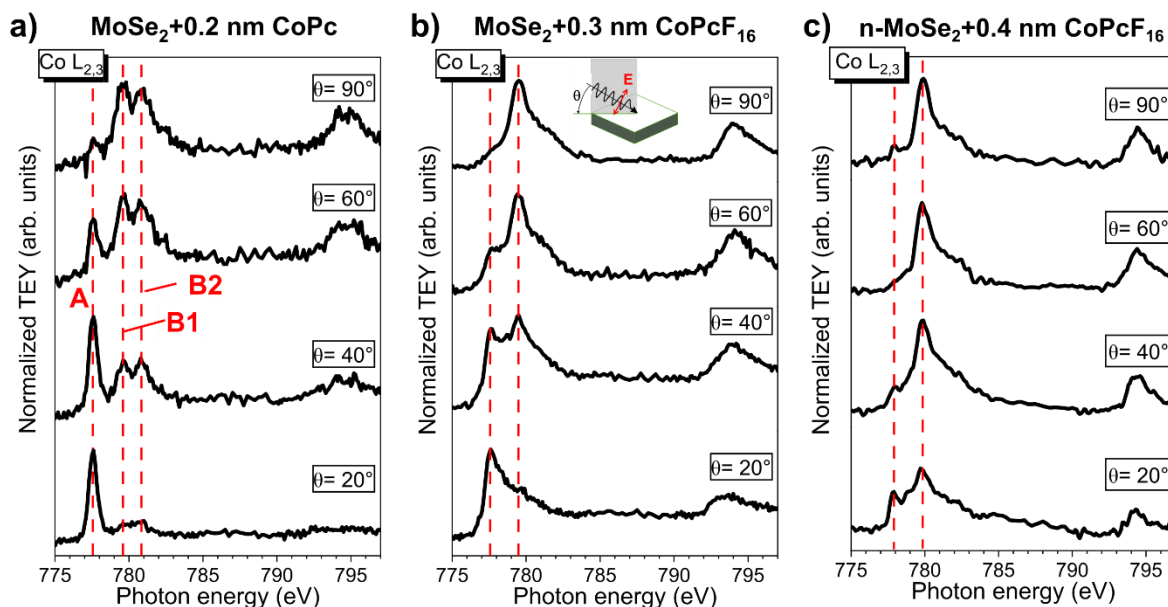


Figure 4.3: Angle-dependent Co L_{2,3} edge XAS spectra for coverages in the monolayer range a) CoPc/MoSe₂, b) CoPcF₁₆/MoSe₂, c) CoPcF₁₆/n-type MoSe₂. Only for CoPc/MoSe₂ the spectral shape is very similar to the bulk indicating the absence of charge transfer across the interface involving the Co atom of CoPc.

In Figure 4.3, we show angle dependent Co L_{2,3} edge XAS spectra for CoPc or CoPcF₁₆ coverages in the monolayer range on (n-) MoSe₂. The L₃ edge transitions between 770 and 785 eV that are polarized perpendicular to the molecular plane are denoted “A”, and features that are polarized within the molecular plane are denoted “B” (Figure 4.3a). The measurement geometry is shown as an inset in Figure 4.3b. The shape and the angular dependence for CoPc on MoSe₂ is in very good agreement to preferentially flat lying molecules in bulk-like films (e.g ref¹⁵⁷), indicating the absence of interactions involving the Co atom of CoPc at the MoSe₂ interface. In contrast, the shape of the XAS spectra for CoPcF₁₆ on (n-)MoSe₂ (Figures 4.3b,c) is distinctly different. First, the relative intensity of A at about 777.5 eV is clearly suppressed at grazing incidence, an observation which seems to be even more pronounced for CoPcF₁₆ on n-MoSe₂ (Figures 4.3c). Second, feature B2 (780.8 eV) almost disappeared, only B1 (779.6 eV) remains. Such behaviour was observed for cobalt

phthalocyanines on other substrates (e.g. ref¹⁵⁷), indicating a redistribution of the d-electrons at the central metal atom of the phthalocyanine at the interface to MoSe₂, which might be accompanied with interfacial charge transfer.

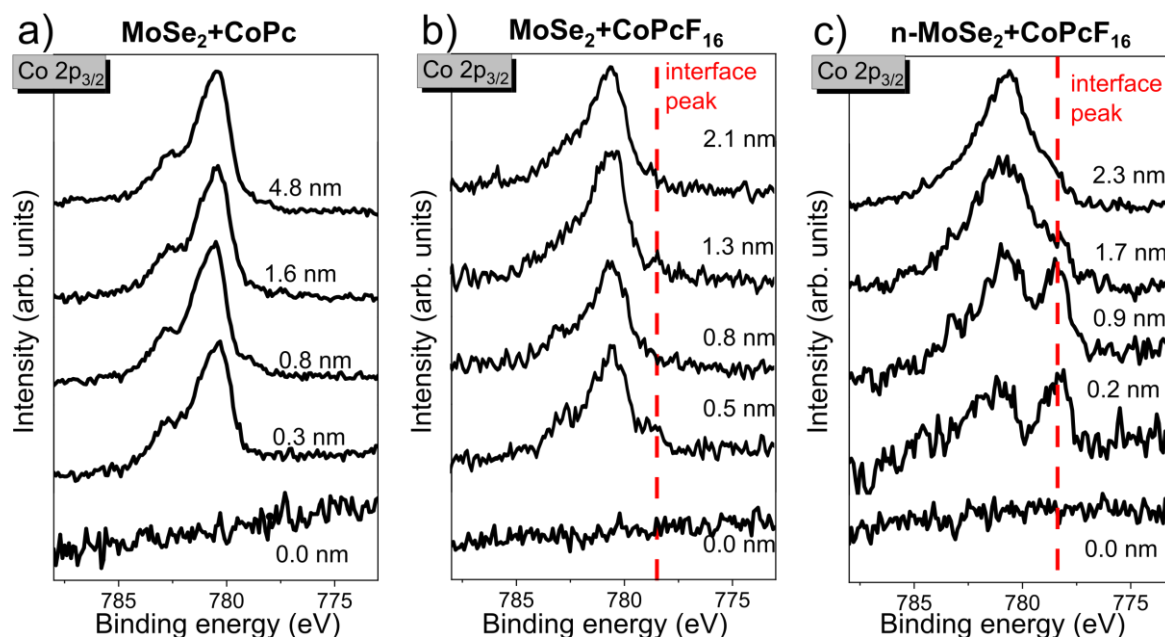


Figure 4.4: Co 2p_{3/2} core level spectra ($h\nu = 1486.6$ eV) of a) CoPc/MoSe₂, b) CoPcF₁₆/MoSe₂, and c) CoPcF₁₆/n-MoSe₂ for thicknesses ranging from (sub-)monolayer to several multilayers. The additional interface peak for CoPcF₁₆/n-MoSe₂ indicates a charge transfer to the Co ion of CoPcF₁₆.

The XAS results are supported by complementary XPS measurements in the home lab. In Figure 4.4, we show Co 2p_{3/2} core level spectra for the three interfaces as a function of the film thickness ranging from (sub-)monolayer to several multilayers. The peak shape is almost independent of the thickness for CoPc/MoSe₂ (Figure 4.4a). For the CoPcF₁₆/MoSe₂ interface (Figure 4.4b) a secondary peak at a lower binding energy of 778 eV is detectable at low coverages. This strongly suggests an electron transfer from the substrate to the Co ion of the CoPcF₁₆ molecule. Such an interface peak is also visible for the CoPcF₁₆/n-MoSe₂ interface but with distinctly higher intensity. This supports the results in Figure 4.3, from which a stronger interaction for the n-MoSe₂ substrate was supposed, and confirms occurrence of an interfacial charge transfer involving the Co ion, at least for a part of the molecules directly at the interface. We note that at the substrate site, no interface peaks could be detected, even in the most surface sensitive Se 3d spectra (Figure 7.20). This may indicate that no localized bonds between Co and the topmost Se atoms are formed. Alternatively, the intensity

of possible interface peaks is below the detection limit due to very few (interacting) Co atoms in CoPcF₁₆.

4.1.4.3 Involvement of the macrocycle of the TMPcs in the interface interaction and interface energetics

While interactions of the macrocycle can involve carbon or nitrogen atoms, here we exemplarily discuss only molecule-related C 1s core level spectra (Figure 4.5). Corresponding N 1s spectra can be found in the supporting information (Figure 7.21). C1s spectra of phthalocyanines can be well described by one component for carbons bound to carbon and hydrogen atoms (CC, blue curves in Figure 4.5) and one component for pyrrolic carbon (CN, magenta). In the case of fluorinated components, an additional component at higher binding energy must be introduced for carbon bond to fluorine atoms (CF, green). All components are accompanied by shake-up satellite features; a single satellite peak, arising from $\pi \rightarrow \pi^*$ transitions, is sufficient to describe the spectra.^{20,152,222}

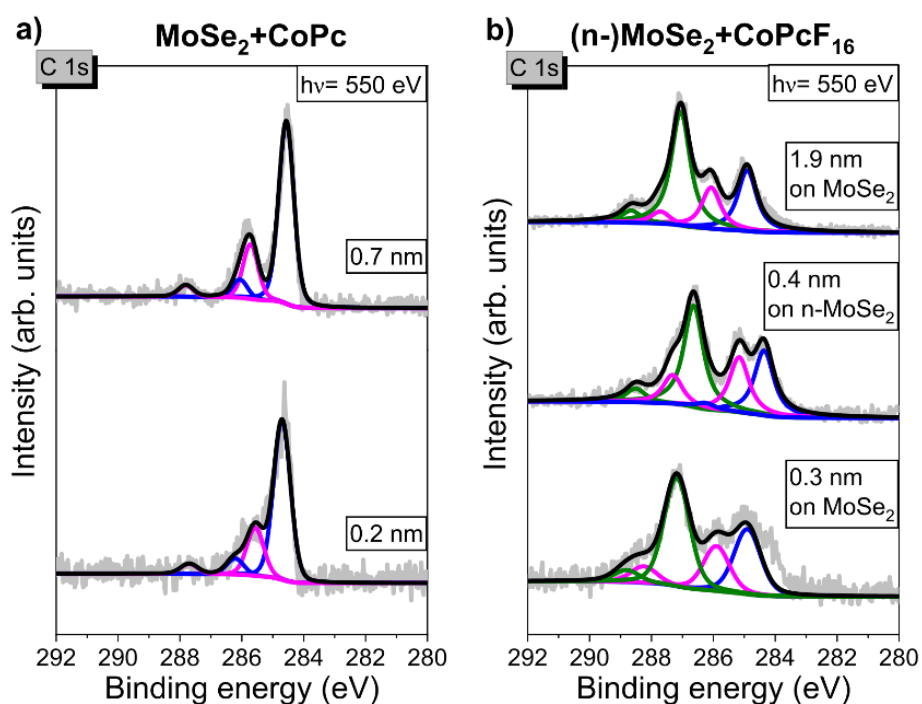


Figure 4.5: Molecule related C 1s core level spectra. a) CoPc/MoSe₂, b) CoPcF₁₆/(n-)MoSe₂. The spectral shape is very similar to the bulk indicating the absence of strong interactions involving the carbon atoms of the macrocycle of the molecules.

The C 1s spectra in Figure 4.5 can be essentially described by the same fitting model, independent of the film thickness. The detailed fitting parameters are summarized in Table 7.12 (supporting information), the fitting parameters for the N 1s spectra are

depicted in Table 7.13 (supporting information). We note that the aromatic carbon component CC is in superposition with carbon from minor traces of contamination, resulting in an apparently higher intensity of this component for the lowest coverages. In addition, the CC-CN distance is smaller at the interface compared to the thicker films. Such an effect was visible for phthalocyanine/ metal interfaces, but also for CoPc and CoPcF₁₆ on MoS₂ and can be ascribed to site-dependent screening effects at the interface and/or a possible redistribution of electrons within the molecule at the interface.^{20,223} Most important, no additional interface component has to be introduced in the spectra for low coverages, indicating the absence of strong interactions due to bond formation/chemisorption and localized charge transfer to specific carbon atoms.

Using the photoemission results in Figure 4.2, we extract the energy level alignment at the interfaces and depict the results in Figure 4.6 for coverages in the monolayer range for CoPc/MoSe₂ (a), CoPcF₁₆/MoSe₂ (b), and CoPcF₁₆/n-type MoSe₂ (c). We determine the work functions from the secondary electron cutoff (SECO) of complementary UPS measurements performed in the home lab. For the distance between the vacuum level (E_{vac}) and the valence band maximum of pristine MoSe₂ substrates we obtain 5.4 eV as an average of several measurements. Interface dipoles in Figure 4.6 were directly extracted from SECO shifts for comparable CoPc or CoPcF₁₆ coverages, as schematically depicted in Figure 7.24 (supporting information) for thicker CoPc(F₁₆) films.

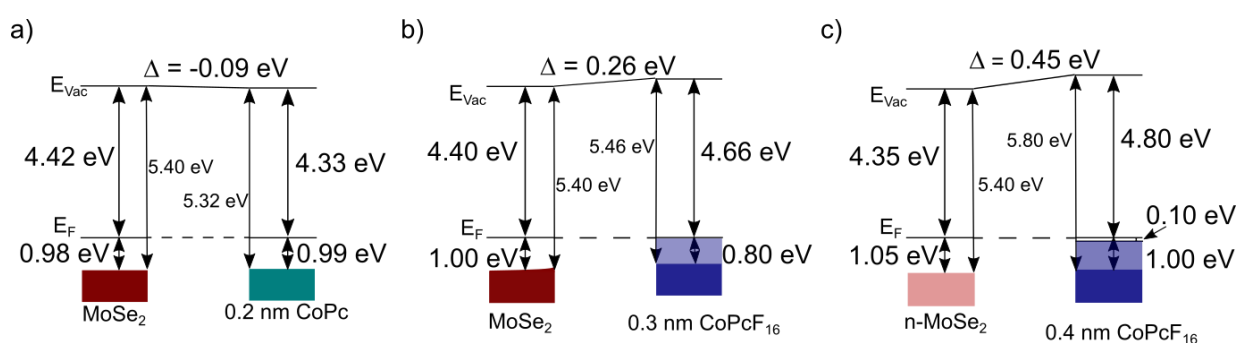


Figure 4.6: Energy level alignment for coverages in the monolayer range: a) CoPc/MoSe₂, b) CoPcF₁₆/MoSe₂, c) CoPcF₁₆/n-type MoSe₂.

The formation of interface dipoles is visible in Figure 4.6 for (n-)MoSe₂/CoPcF₁₆ (Figures 4.6b+c). Even if several effects contribute to the work function modification at interfaces (e.g. Refs.^{123,224}), the observed charge transfer to the central Co atom of CoPcF₁₆ (Figure 4.3 and Figure 4.4) may contribute to positive dipoles. We note that

interface formation is not yet complete at these low coverages, which is also reflected in the lower ionization potential ($E_{\text{vac}}-E_{\text{HOMO}}$) of CoPcF₁₆ compared to the bulk material (Figure 4.1). Formed dipoles for thicker films are even larger (Figure 7.25).

The slight shift of the top of the G point from 1.0 to 0.9 eV upon deposition of CoPcF₁₆ on undoped MoSe₂ (Figure 4.2b,e) is faintly indicated in Figure 4.6b. Shifts to lower binding energies were reproduced several times in the home-lab for this interface; they are even more pronounced in the substrate-related core levels (Figures 7.22, 7.23). In contrast, small energetic shifts for MoSe₂/CoPc and n-MoSe₂/CoPcF₁₆ are not significant. Shifts to lower binding energies can be understood by an interfacial relative p-doping of the substrate, which supports the contribution of charge transfer to the interface dipoles in Figures 4.6 and 7.25. In the case of n-MoSe₂, the high concentration of charge carriers at the doping level (Figure 4.2c) may suppress a possible doping at this interface.

As already briefly discussed (Figure 4.2) interface states extending to the vicinity of the Fermi level were detected in the gap of MoSe₂ upon deposition of CoPcF₁₆; they are depicted in light blue in Figures 4.6b+c. Since the corresponding integrated ARPES spectrum (Figure 7.18) shows even a well-defined peak close to the Fermi level in the case of n-MoSe₂, one interpretation of this peak is the representation of the molecular HOMO. However, we rule out this hypothesis, since its distance to the C 1s core level peak (C-F component) is about 1 eV larger than C-F to HOMO (286.2 eV). An alternative explanation is the occupation of formerly unoccupied molecular states (LUMO and even LUMO+1) at the interface, observed for several molecule/metal interfaces (e.g. refs^{225,226}). We note, however, that in the case of highly ordered films the intensity maximum in ARPES energy-momentum maps (cf. Figure 4.2f) would not be expected at Γ but around $1.5 - 1.7 \text{ \AA}^{-1}$.^{20,227–229} Further, an assignment to the (former) LUMO only seems to be unlikely considering the strong involvement of the Co ion in the interaction at the interface. Thus, the most likely scenario in our opinion is the formation of new hybrid states at the CoPcF₁₆/MoSe₂ and CoPcF₁₆/n-MoSe₂ interfaces. Their intensity might be more pronounced for CoPcF₁₆/n-MoSe₂ due to the large number of available electrons in the gap of n-doped MoSe₂.

The interfacial charge transfer also affects the optical properties of the adsorbed CoPcF₁₆ molecules. In Figure 4.7a we show the photoluminescence (PL) spectra taken from CoPcF₁₆/MoSe₂ and CoPcF₁₆/n-MoSe₂ using a home-built optical microscope

4. Non-peer-reviewed Results

(Figure 7.26). To ensure comparability, all measurements are performed with identical laser excitation power and spectra integration time. To obtain an overview of the sample, 64 spectra are taken at different sample positions. The reproducibility of the spectral intensity is calculated from the deviations of the 64 spectra taken for each sample and is shown in Figure 4.7a as grey (CoPcF₁₆/Si), red (CoPcF₁₆/ MoSe₂), and blue (CoPcF₁₆/n-MoSe₂) shadows.

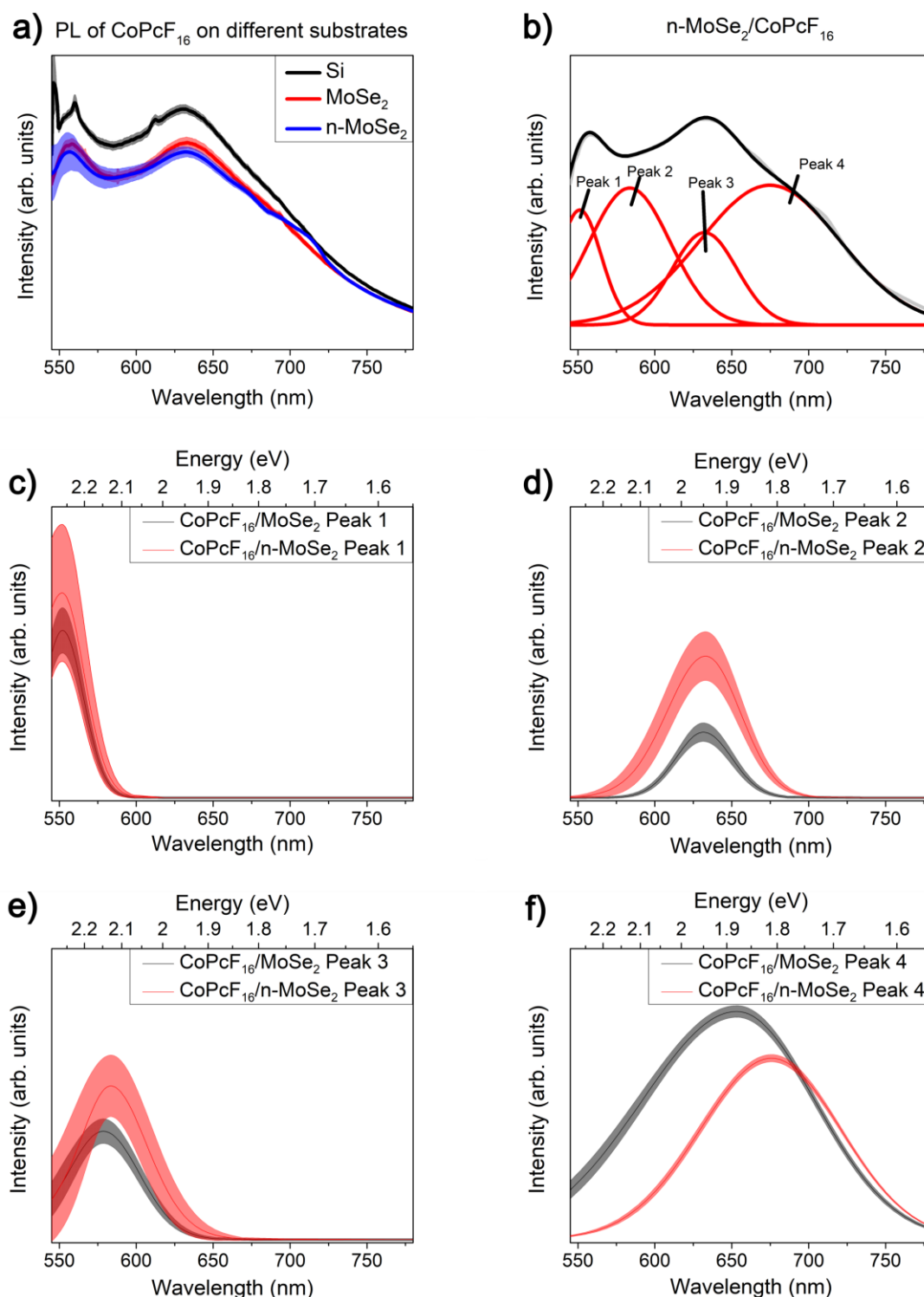


Figure 4.7: Photoluminescence spectra and fitted peaks (Gaussian function) for CoPcF₁₆ on various substrates: a) Comparison of doped and undoped MoSe₂ and Si substrates. b) Representative peak fitting for a CoPcF₁₆/MoSe₂ PL spectrum. c)–f) Comparison of the four subpeaks. The red and grey solid lines represent the averaged spectra obtained from 64 measurements acquired on CoPcF₁₆/n-MoSe₂ and CoPcF₁₆/MoSe₂, respectively. The shaded areas indicate the corresponding deviations calculated from spectra collected at different sample positions.

Three phenomena are observed in Figure 4.7a: 1) The spectral spreading for CoPcF₁₆/MoSe₂, and CoPcF₁₆/n-MoSe₂ is larger compared to CoPcF₁₆/Si, which may indicate heterogeneous interactions between the molecules and n-MoSe₂ and MoSe₂.^{230,231} 2) The spectral intensity is overall weaker on the TMDC substrates than it is on the Si substrate, though the CoPcF₁₆ layer thickness is the same. This might be related to an interfacial charge transfer, which can result in PL quenching, as observed for related molecule/TMDC interfaces.²¹⁰ 3) The PL spectral profiles of CoPcF₁₆/MoSe₂, and CoPcF₁₆/n-MoSe₂ show slight differences not only in the overall intensity, but also in the spectral shape.

To get insight into these observations, all collected spectra were spectrally fitted as exemplified for CoPcF₁₆/n-MoSe₂ in Figure 4.7b. Four subpeaks (red dash lines) are used to fit the original spectra (black solid line), and the cumulative fit is shown in grey. We first compare the maxima of the four subpeaks for CoPcF₁₆/MoSe₂, and CoPcF₁₆/n-MoSe₂ samples and the results are shown in Figure 4.7 c-d. The deviations derived from the 64 spectra taken from CoPcF₁₆/n-MoSe₂ are shown as red shadow, and the one for CoPcF₁₆/MoSe₂ is shown as grey shadow. For both types of samples, subpeak one appears at 552 nm, and subpeak three appears at 632 nm. Subpeak two appears at 579 nm for CoPcF₁₆/MoSe₂, which slightly shifts to 582 nm for CoPcF₁₆/n-MoSe₂. Subpeak 4 shows the largest shift, appearing at 650 nm for CoPcF₁₆/MoSe₂ and at 676 nm for CoPcF₁₆/n-MoSe₂. Furthermore, as shown in Table 7.17, the intensity ratio of subpeak 4 (calculated using the integrated peak area) to the total peak intensity is about 47% for CoPcF₁₆/n-MoSe₂, while it is 69% for CoPcF₁₆/MoSe₂. These changes indicate a complex interaction at molecule/substrate interface, depending on the strength of the interaction and/or the amount of charge transfer.

The changes in the PL peak position and intensity agree well with the results shown in Figure 4.6. With the doping of the MoSe₂ substrate, the energy level alignment of the molecule with the substrate varies as compared to the one without doping. Energetic

shifts of particular peaks and the PL quenching at the CoPcF₁₆/n-MoSe₂ interface may point to a partial occupation and/or the formation of new hybrid states at the interface accompanied by fast charge transfer.

4.1.5 Conclusion

In conclusion, we have shown that the formation of interface states at interfaces between MoSe₂ and cobalt phthalocyanines crucially depends on both the ionization potential of the molecule and the doping level of the substrate. A significant charge transfer from the substrate to the molecule is observed in the case of CoPcF₁₆, although no integer charge transfer might be expected from the relative position of the valence band of MoSe₂ with respect to the LUMO of CoPcF₁₆. Consequently, large interface dipoles can be formed. The interface states cannot be simply assigned to the occupation of formerly unoccupied molecular orbitals, since the charge is localized to a large extent at the Co atom of CoPcF₁₆. This underlines the pivotal role of the central metal atom of TMPcs for the tuning of electronic properties of TMDCs.

Interface properties between cobalt phthalocyanines and MoSe₂ are distinctly different to related MoS₂ interfaces, where hybrid interface states were presumed but could not be directly detected.²⁰ Thus, the reduced ionization potential and band gap of MoSe₂ compared to MoS₂ and/or nature of the topmost atoms enable stronger interactions at interfaces to molecules, which may be advantageous for the tuning of electronic properties for application in devices.

5. Outlook

In this chapter, further approaches continuing the work of this thesis are discussed. While many questions about altering the electronic structure could be answered, many more remain open. Every manuscript discussed in this thesis sets the foundation for future works by expanding the results found in previous studies to the large portfolio of possible heterostructures which can be created by different choices of metal contacts, TMPcs and especially TMDCs which can all be electronically altered by defect engineering and varying the layer number from bulk to single layers, yielding a nearly unlimited amount of options to achieve new heterostructured materials.

5.1 Future works on the $\text{MoSe}_2/\text{CoPcF}_{16}$ interface

Considering the significant findings at the (n-) $\text{MoSe}_2/\text{CoPcF}_{16}$ interface, discussed in 4.1, showing very intense signs of interaction between the (n-) MoSe_2 substrate and the Co atom of the TMPc, it is of high interest to investigate this interface even further to implement it into semiconducting devices in the future. From previous works on other TMDC photodetectors we know that multilayer TMDCs can have its advantages in photodetection due to lower defect concentrations when compared to single layers.⁴⁷ Therefore, the exfoliation of multilayer (n-) MoSe_2 flakes followed by a subsequent deposition of CoPcF_{16} might be promising for a new and highly effective photodetector assuming that the interactions between the TMPc and the TMDC described in 4.1 can be transposed to said device. From studies on multilayer flakes of MoS_2 , discussed in 3.2, we can assume that the orientation of the CoPcF_{16} molecule is most likely still flat-lying on (n-) MoSe_2 , yet further confirmation is desirable. In addition, a study on single layer $\text{MoSe}_2/\text{CoPcF}_{16}$ interfaces could be highly interesting as it is questionable if the results from 3.2 for single layer MoS_2 can be transposed to single layer MoSe_2 as easily, if there is a much stronger interaction between the substrate and the molecule. Even the latter is highly debatable considering the heavily altered electronic structure of the single layer MoSe_2 compared to its bulk counterpart.

Since MoSe_2 , that was n-type doped by foreign atoms, showed especially strong charge transfers between the TMDC and the CoPcF_{16} molecule, the comparison to other methods to achieve said doping would be of high interest as well. As shown in 3.1, the deposition of metal contacts onto MoS_2 was already sufficient to achieve severe n-type doped structures. Possibly, the desired doped MoSe_2 could therefore

already be achieved by contacting with e.g. gold electrodes which is needed for future device fabrication in any case.

5.2 Effects of metal contacts and sputtering on the electronic structure of further TMDCs

For many of the novel insights in engineering the electronic structure of TMDCs, molybdenum disulfide was used as its most common representative. The question remains how these results can be translated to other TMDCs and possible heterointerfaces. Therefore, it is of high interest to study how defect-rich TMDCs like WS₂, WSe₂ or MoSe₂ can be manufactured and if defect-engineering by Ar or Ne sputtering is possible to a similar extent as there is little to no work on this topic to this date. In future studies, one could investigate which type of defects are created after sputtering with different noble gases. Previous works show that intrinsic monosulfur vacancies (or chalcogen vacancies in general) are the predominant defects for monolayer WS₂ or MoSe₂/WSe₂.^{232,233} Similarly, it is expected that these defects are also the most prevalent for the bulk TMDCs, yet there have not been nearly as many studies as there are for bulk MoS₂. Therefore, for now it remains unclear how doping by sputtering is achieved and whether the resulting defects might be healed by the deposition of organic molecule like the TMPcs used in this thesis similar to thiol-based defect healing described for exfoliated WS₂ and WSe₂.²³³ In general, the tungsten dichalcogenides are of huge interest due to their seemingly superior optical and photoelectronic properties that allowed the manufacturing of some of the fastest TMDC based photodetectors with these materials.^{10,47} Therefore, optimization of its electronic properties and further defect healing might lead to the next step of ultrafast and highly responsive photodetectors.

The promising results on the (doped) MoS₂/CoPcF₁₆ interface show the huge potential of heterostructures consisting of defect-rich TMDCs and TMPcs. Examination of further heterostructures formed with different TMDCs, including Mo/WTe₂ and other TMPcs like MnPc or FePcF_x (x= 0, 4, 16) can lead to a vast portfolio of materials which can be well-suited for semiconducting devices. Also, the single or few-layer interfaces of these TMDCs must be studied further, since those are of special interest for the fabrication of photodetectors.

Since most experiments performed in this thesis are performed on large-scale single-layer crystals, direct implementation in electronic devices is challenging. A new approach called roll-to-roll fabrication (which will be further eluded in Chapter 5.4) allows large-area coverages of polycrystalline TMDC films which can then be contacted by microelectrode structures. By this technique, electronically altered heterostructures can be implemented relatively easily in devices.

5.3 Expanding the research to further TMDCs and TMPcs

Heterostructuring TMDCs with CoPcF₁₆ has now emerged as an interesting technique for several years including the MoS₂/CoPcF₁₆, WSe₂/CoPcF₁₆ and the MoSe₂/CoPcF₁₆ interface.^{20,27,88} The results on these experiments are vastly different, depending on the TMDC used. Therefore, it would be of high interest to expand the found results by other TMDCs like WS₂ or the peculiar Group VI ditellurides MoTe₂ and especially WTe₂. While both share a 2D structure that allows exfoliation down to single layers similar to the other TMDCs discussed before, their electronic properties are largely affected by the choice of the tellurium chalcogenide. This can be seen in the comparatively small band gap of the semiconducting MoTe₂ of about 0.943 eV²³⁴ (1315 nm), which lies directly in the second telecommunication window in the NIR (1000–1350 nm).²³⁵ The electronic structure of the heavier WTe₂ offers even more unique properties as it is considered a topological Type II Weyl semimetal.²³⁶ These materials offer notably different characteristics to other materials as they exhibit topological surface states called Fermi arcs. These materials show an extremely high charge-carrier mobility and anisotropic transport of charge carriers which makes them particularly interesting for novel photoelectronic devices.^{236,237}

To further elucidate the possibilities of feasible combinations of TMDCs and cobalt phthalocyanines it is advantageous to consult the energy alignment of the materials as depicted in Figure 5.1 using their ionization potentials and band gaps.

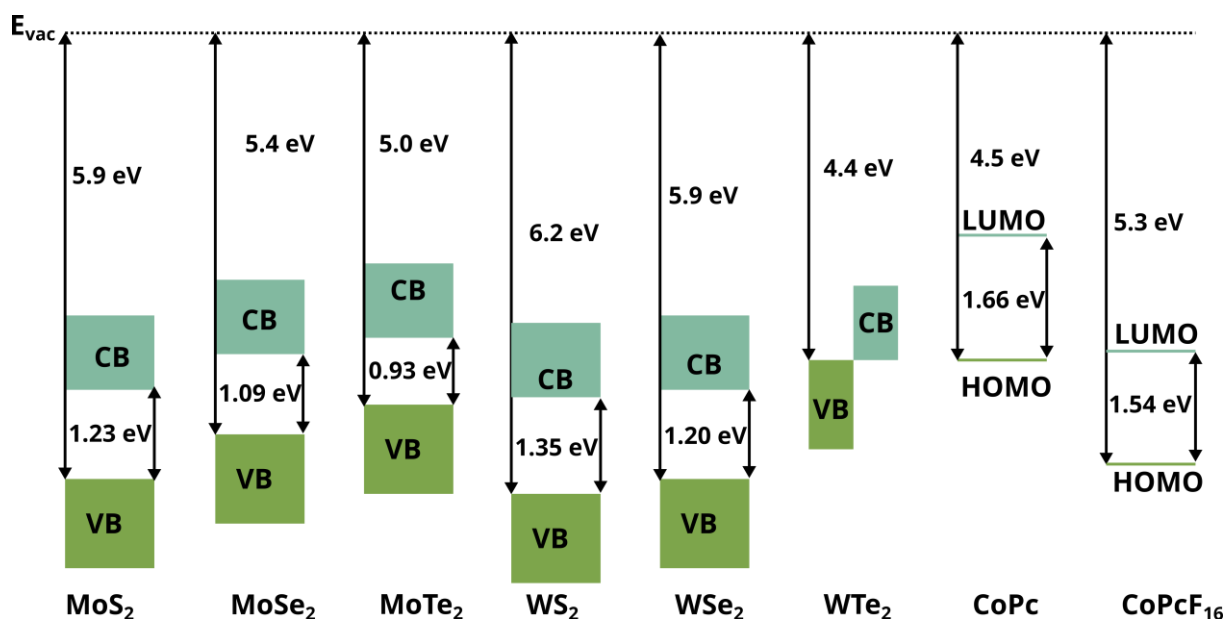


Figure 5.1: Band alignment with respect to the vacuum level of the group VI bulk TMDCs, CoPc and CoPcF₁₆ with their respective band gaps and ionization potentials.^{20,36,238–240}

By studying the depicted energy level alignments, predictions about possible paths for interaction between the substrate and the molecule can be made. In general, the location of the valence band of the TMDC and the HOMO and the location of the conduction band and the LUMO of the molecule can be compared to each other when aligned to the vacuum level. Considering the integer charge transfer (ICT) model, and assuming the ICT⁻ and ICT⁺ states (as the energy levels at which an electron is accepted and donated) are in proximity to the VBM/HOMO and CBM/LUMO, possible charge transfers can be anticipated. Since the Valence band maxima of MoTe₂ and WTe₂ lie rather close to the LUMO of CoPcF₁₆, a charge transfer of electrons from the TMDC to the molecule is expected. For the WTe₂/CoPc interface, a charge transfer of electrons from the HOMO of the molecule to the conduction band of the TMDC is also not unlikely to be observed. As the experiments for MoSe₂/CoPcF₁₆ depicted in Chapter 4.1 prove, the real path of charge transfers can be much more complex as, there, a CT was found experimentally even though the band alignment in Figure 5.1 would not suggest these types of interactions.

In the search for novel TMDC heterostructures, many more molecules besides the cobalt phthalocyanines studied in this thesis can be considered. Expanding the research to other TMPcs might therefore be a feasible option as well. In the studies

presented in this thesis, charge transfers towards the metallic central atom were commonly observed. As discussed in Chapter 2.2, the 3d orbitals of other TMPcs like FePc and especially MnPc lie in closer proximity to the Fermi level, heavily influencing the HOMO, which makes them also interesting for possible heterostructures, governing the interaction between the HOMO of the molecule and the electronic bands of the TMDC. Greulich et al.²² were already able to show the charge transfer between MoS₂ and two iron phthalocyanines (FePc, FePcF₄) showcasing the potential of these materials for TMDC heterostructures. This work could be expended by further expertise achieved through this thesis to other TMDCs with iron and manganese phthalocyanines.

5.4 Roll-to-roll TMDCs

In the pursuit of converting the findings from XPS experiments to device fabrication it is often challenging to translate the results discovered from large scale XPS experiments with sample sizes >1 cm² in the home laboratory or at least several mm² for highly focused synchrotron experiments to the miniaturized devices needed in many applications. The new technique of roll-to-roll TMDCs allows the fabrication of large sized polycrystalline samples with extremely high rates of exfoliation which are well-suited for home laboratory XPS experiments while the individual flakes are still in the micrometer regime making them feasible for application in photoelectronics.

To yield these polycrystalline samples a set-up based on two rolls with different diameters is built as depicted in Figure 5.2. To ensure maximum coverage, the diameters of the two rolls are set to two high prime numbers so the exact two spots only meet after a very large number of rotations. Onto the cylinders, double-sided tape is applied which is needed to mount Nitto tape, an adhesive tape made of polyvinylchloride (PVC) onto the rolls. Onto the tape of one roll, a cleaved bulk MoS₂ crystal is placed which is then pressed between the two rolls by rotation leading to a thin film of the desired TMDC.

These Nitto tapes can then be stored and used to transfer the sample to various substrates. Here the transfer to silicon wafers is shown. To transfer the sample the Nitto tape is simply placed on the wafer of choice and then heated to 110 °C on a heating plate for 5 minutes. This process can be repeated several times to increase the coverage on the wafer.²⁴¹

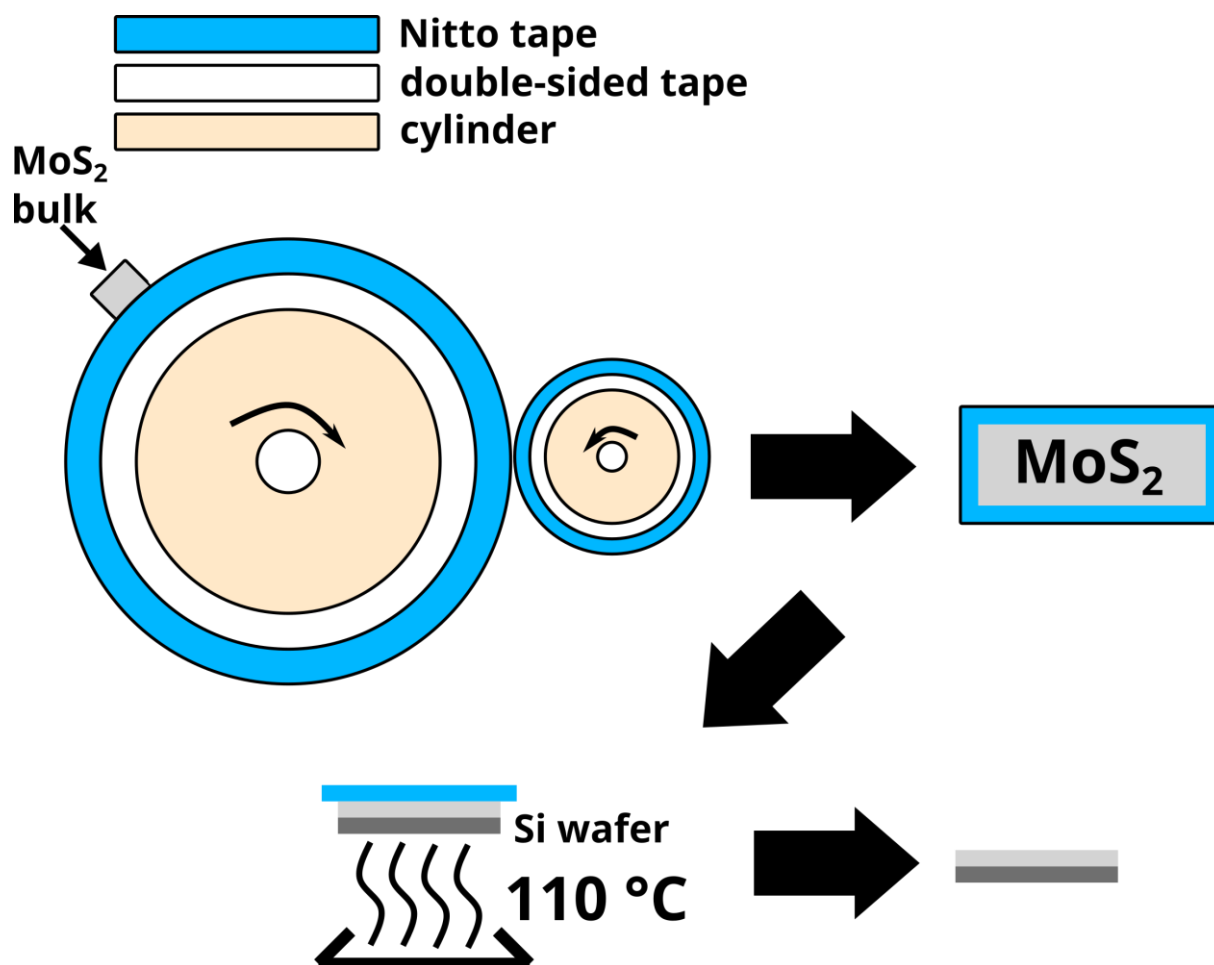


Figure 5.2: Roll-to-roll process to produce polycrystalline MoS₂ flakes on silicon wafers according to Sozen et al.

The resulting samples are then ready to be used in various experiments including X-ray photoemission spectroscopy. In a previous study, results for XPS experiments of roll-to-roll MoS₂ were already reported. To yield clean samples, the sample inside the UHV chamber was annealed leading to relatively low carbon coverage.²⁴²

With this novel way of producing polycrystalline TMDCs, whole new ways of investigating 2D semiconducting materials are possible. It would be of great interest to research if the results found for the monocrystalline bulk TMDCs can be translated to the polycrystalline counterparts or if there are differences between these two. The attempt to tune the electronic structure of polycrystalline TMDCs via methods like sputtering or heterostructuring is therefore of high interest since the yielded samples can then be easily contacted with electrodes to create semiconducting devices. This

can be seen as the final link between the studies performed in this thesis and device manufacturing.

6. Summary & Conclusion

This thesis serves to address the question on how the electronic properties of molybdenum dichalcogenides can be tuned. The results found in this work are summarized and concluded in this chapter.

The first approach to tune the electronic properties of MoS₂ crystals was the formation of heterostructures with the electrode materials gold, copper and titanium which are typically implemented in semiconducting devices. After depositing Au and Cu onto the MoS₂ substrate an n-type doping was observed which persists even after annealing to 250 °C. Since the degree of doping of the MoS₂ substrate does not seem to be affected by the annealing step, it can be expected that the Au and Cu atoms remain in the vicinity of the top-layer of the TMDC. Utilizing the charge transfer between the noble metals Au and Cu and the Co atom of the CoPcF₁₆ molecule as a probe, it was shown that gold only partially diffuses during the annealing step, while a full diffusion of copper atoms from the top-layer of the TMDC below the surface is occurring. These findings have been published in the journal *ACS Applied Electronic Materials*, 7, 14, 6484–6490 in 2025.

In the second work, discussed in Chapter 3.2, heterostructures between single- and multilayered MoS₂ and the organic molecules CoPc and CoPcF₁₆ were investigated. Using photoemission electron microscopy, coupled with X-ray absorption and X-ray photoemission spectroscopy, the behavior of the molecules on the TMDC substrates could be investigated. While no signs of strong interactions could be found between the different substrates and molecules, the X-ray absorption spectra showed a significant difference in orientation of the organic molecules on the TMDC flakes depending on their layer number. While a flat-lying geometry on thicker, bulk-like flakes was found, single and few-layer flakes exhibited a tilted geometry of the CoPc and CoPcF₁₆ molecules on the substrates. These findings are crucial for future studies on possible heterostructures as the orientation of the molecule and its orbitals dictate possible interaction paths. These results have been published in *The Journal of Physical Chemistry C*, 128, 5, 2107–2115 in 2024.

To achieve deeper understanding of the nature of surface defects in transition metal dichalcogenides, the ion bombardment of MoS₂ with the noble gases argon and neon was studied within the third publication discussed in Chapter 3.3 by using angle-

resolved photoemission, surface sensitive X-ray photoemission and X-ray absorption spectroscopy. After gentle sputtering with different doses of argon, a slightly p-type doped MoS₂ surface was yielded, while gentle sputtering with Ne results in a slightly n-type doped MoS₂. This can be explained by the formation of sulfur vacancies and metallic Mo as observed in the Mo 3d core level spectra. The results strongly suggest that the structure of the top layer of the MoS₂ crystal is significantly disturbed while the band structure of the second layer is intact as demonstrated by the band structures obtained from angle-resolved photoemission. By the deposition of CoPcF₁₆ a shift in Fermi level could be shown, especially for the Ne-sputtered MoS₂ crystal proving the possibility to even tune defect-rich MoS₂ surfaces. Additionally, a charge transfer between the defect-rich substrates and the Co atom of CoPcF₁₆ was found in the Co L_{2,3} edges and the Co 2p spectra obtained from X-ray absorption and photoemission spectroscopy. These results have been published in the *Beilstein Journal of Nanotechnology*, 17, 796–805 in 2026.

In Chapter 4, the interfaces between molybdenum diselenide and (perfluorinated) cobalt(II) phthalocyanine are discussed. By angle-resolved photoemission it was shown that interface states can form between the CoPcF₁₆ molecule and the MoSe₂ surface while those were not found for the MoSe₂/CoPc interface, highlighting the importance of the ionization potential of the used molecule. These interface states are accompanied by a total charge transfer from the MoSe₂ substrate to the Co atom of the CoPcF₁₆ molecule which can be derived from X-ray absorption and photoemission spectra. Additionally, it was shown that these effects also depend on the doping level of the MoSe₂ crystal as both, the intensity of the interface state and the charge transfer towards the Co atom could be amplified using n-type doped MoSe₂. By optical experiments a significant decrease in photoluminescence was found for the CoPcF₁₆ molecule at the (n-)MoSe₂ interface when compared to CoPcF₁₆ on silicon which can be attributed to photoluminescence quenching through the described charge transfer. The difference in spectral shape of the CoPcF₁₆ peaks between the MoSe₂/CoPcF₁₆ and the n-MoSe₂/CoPcF₁₆ interface, is likely due to the formation of hybrid states. The results are not peer-reviewed at the time this thesis is submitted.

Overall, this thesis embeds three publications that are published in scientific journals after peer review and one unpublished study. Combined, all works tackle the question of how to tune the electronic properties of molybdenum dichalcogenides in its own way

to achieve a more complete understanding about these semiconducting materials. The findings show that heterostructuring with both, metals and organic materials, can lead to doping of the TMDC substrate. While generally, strong charge transfers are not observed for the CoPc molecule, the cobalt atom of the CoPcF₁₆ molecule appears to be more active at the interface by forming reduced cobalt species when in contact with metal atoms like Au, Cu or Mo as well as (doped) MoSe₂. Via sputtering a targeted fabrication of n-type and p-type doped MoS₂ can be obtained. While Fermi level pinning must be considered for those highly defect-rich systems, the results show that heterostructuring can still lead to a change in doping, indicating defect healing. In this thesis, the significance of the layer number of the TMDCs is highlighted as it was shown that organic molecules can orientate differently on the MoS₂ surface when comparing single layer to multilayer structures. This indicates that the approach of tuning the electronic properties of MoS₂ with TMPcs to enhance its properties as a semiconducting device is mostly feasible for the bulk-like TMDC as only in this case the desired flat-lying orientation can be ensured. Considering the observed charge transfer between the MoSe₂ substrate and the CoPcF₁₆ molecule, it is unclear whether these results can be translated to other TMDCs as stronger interactions might make a flat-lying geometry more likely even for lower layer numbers. All in all, this thesis shows that various methods are feasible to achieve doped TMDC surfaces and that they can be tuned even further. The CoPc and especially the CoPcF₁₆ molecule used in this thesis are promising candidates for the formation of heterostructures to possibly create devices which are well-suited for future applications since successful doping, sometimes accompanied by charge transfers towards the reactive cobalt atom was achieved utilizing these materials.

7. Appendix

In this chapter the supporting information for the three publications discussed in 3.1–3.3 are depicted in the following chapters 7.1–7.3. Furthermore, the supporting information for the unpublished manuscript in 4.1 is presented in 7.4.

7.1 Supporting information: Effects of Annealing on Electrode/MoS₂ interfaces Studied by Photoelectron spectroscopy

Table 7.1: Peak fit parameters for Mo 3d and S 2s peak fits shown in Figure 3.1 a) (sub-) monolayer of Au, b) (sub-)monolayer of Cu, c) (sub-)monolayer of Ti.

a) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian [eV]	width	rel. area [%]
Mo 3d _{5/2}	229.05	0.55	0.10		45.0
Mo 3d _{3/2}	232.21	0.55	0.31		30.7
S 2s	226.21	0.69	1.36		23.1
Satellite	235.57	1.00	0.50		1.2
MoS₂+0.16 nm Au					
Mo 3d _{5/2}	229.31	0.55	0.10		44.7
Mo 3d _{3/2}	232.46	0.55	0.32		31.0
S 2s	226.47	0.70	1.35		23.1
Satellite	235.80	1.00	0.50		1.2
MoS₂+0.16 nm Au (annealed)					
Mo 3d _{5/2}	229.36	0.55	0.10		44.6
Mo 3d _{3/2}	232.52	0.55	0.32		30.8
S 2s	226.52	0.73	1.35		23.2
Satellite	235.87	1.00	0.50		1.4

7. Appendix

b) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian [eV]	width	rel. area [%]
Mo 3d _{5/2}	229.34	0.50	0.08		45.2
Mo 3d _{3/2}	232.49	0.50	0.25		30.0
S 2s	226.50	0.76	1.29		23.5
Satellite	235.82	1.00	0.50		1.3
MoS₂+0.32 nm Cu					
Mo 3d _{5/2}	229.82	0.50	0.09		44.2
Mo 3d _{3/2}	232.97	0.50	0.29		30.6
S 2s	226.98	0.61	1.41		23.3
Satellite	236.31	1.00	0.50		1.9
MoS₂+0.32 nm Cu (annealed)					
Mo 3d _{5/2}	229.87	0.55	0.10		44.9
Mo 3d _{3/2}	233.02	0.55	0.28		29.8
S 2s	227.03	0.70	1.37		23.6
Satellite	236.36	1.00	0.50		1.7
c) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian [eV]	width	rel. area [%]
Mo 3d _{5/2}	229.19	0.54	0.10		44.2
Mo 3d _{3/2}	232.35	0.54	0.31		30.0
S 2s	226.36	0.68	1.38		24.5
Satellite	235.75	1.00	0.50		1.2
MoS₂+0.33 nm Ti					
Mo 3d _{5/2}	229.26	0.51	0.15		38.8
Mo 3d _{3/2}	232.42	0.51	0.35		26.4
Mo 3d _{5/2} (interface)	228.23	0.70	0.10		6.7

Mo	3d _{3/2}	231.52	0.70	0.30	4.3
(interface)					
S 2s		226.45	0.83	1.40	23.2
Satellite		235.74	0.78	0.10	0.6

MoS₂+0.33					
nm Ti					
(annealed)					

Mo 3d _{5/2}		229.41	0.53	0.15	42.3
Mo 3d _{3/2}		232.57	0.53	0.35	28.6
Mo 3d _{5/2}		228.48	0.58	0.10	2.6
(interface)					
Mo 3d _{3/2}		231.90	0.58	0.32	1.8
(interface)					
S 2s		226.57	0.79	1.40	23.4
Satellite		235.88	0.63	0.50	1.4

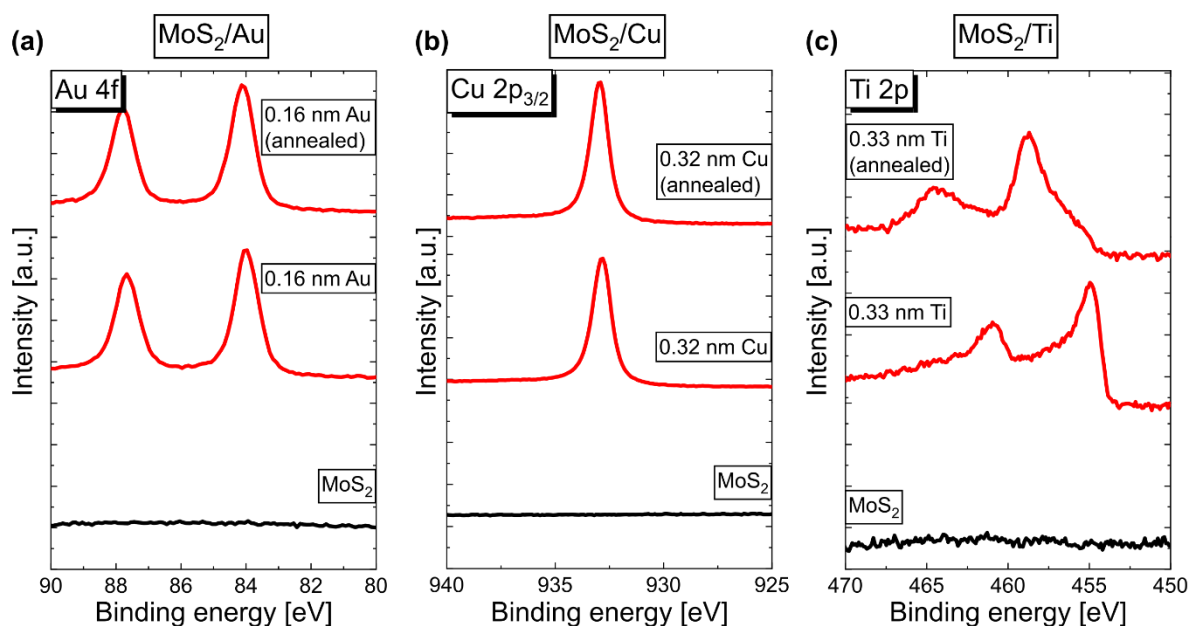


Figure 7.1: Core level spectra of the MoS₂/metal interface for (sub-)monolayer coverages of the metal depicting a) Au 4f, b) Cu 2p and c) Ti 2p.

It is notable that the Au 4f and Cu 2p_{3/2} do not change post-deposition. In contrast, after the deposition of Ti metal, depicted in Figure 7.1c, the Ti 2p peaks first show the binding energy of the peaks for Ti⁰. After annealing, the peak shifts towards higher binding

energies, indicating an oxidation of the Ti metal which most likely is the result of a reaction with remaining oxygen in the vacuum chamber at an elevated pressure of approximately $1 \cdot 10^{-7}$ mbar during the time of annealing.

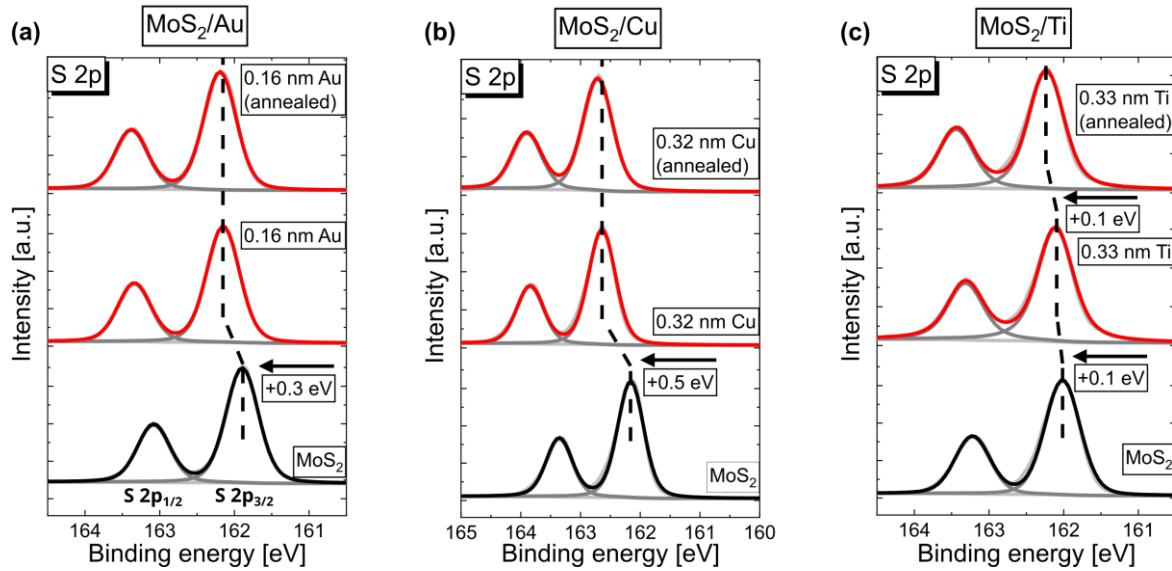


Figure 7.2: S 2p core level spectra of the MoS₂/metal interface for a (sub-)monolayer of a) gold, b) copper and c) titanium.

Table 7.2: Peak fit parameters for S 2p peak fits shown in Figure 7.2 a) (sub-)monolayer of Au, b) (sub-)monolayer of Cu, c) (sub-)monolayer of Ti.

a) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	161.89	0.45	0.12	66.7
S 2p _{1/2}	163.08	0.45	0.12	33.3
MoS₂+0.16 nm Au				
S 2p _{3/2}	162.15	0.46	0.11	66.7
S 2p _{1/2}	163.34	0.46	0.11	33.3
MoS₂+0.16 nm Au (annealed)				
S 2p _{3/2}	162.19	0.46	0.10	66.7
S 2p _{1/2}	163.38	0.46	0.10	33.3

b) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	162.16	0.44	0.13	66.7
S 2p _{1/2}	163.36	0.44	0.13	33.3
MoS₂+0.32 nm Cu				
S 2p _{3/2}	162.64	0.47	0.12	66.8
S 2p _{1/2}	163.84	0.47	0.12	33.2
MoS₂+0.32 nm Cu (annealed)				
S 2p _{3/2}	162.71	0.51	0.14	66.8
S 2p _{1/2}	163.90	0.51	0.14	33.2
c) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	162.01	0.50	0.10	66.7
S 2p _{1/2}	163.22	0.50	0.10	33.3
MoS₂+0.33 nm Ti				
S 2p _{3/2}	162.11	0.39	0.28	66.7
S 2p _{1/2}	163.31	0.39	0.28	33.3
MoS₂+0.33 nm Ti (annealed)				
S 2p _{3/2}	162.23	0.43	0.22	66.8
S 2p _{1/2}	163.44	0.43	0.22	33.2

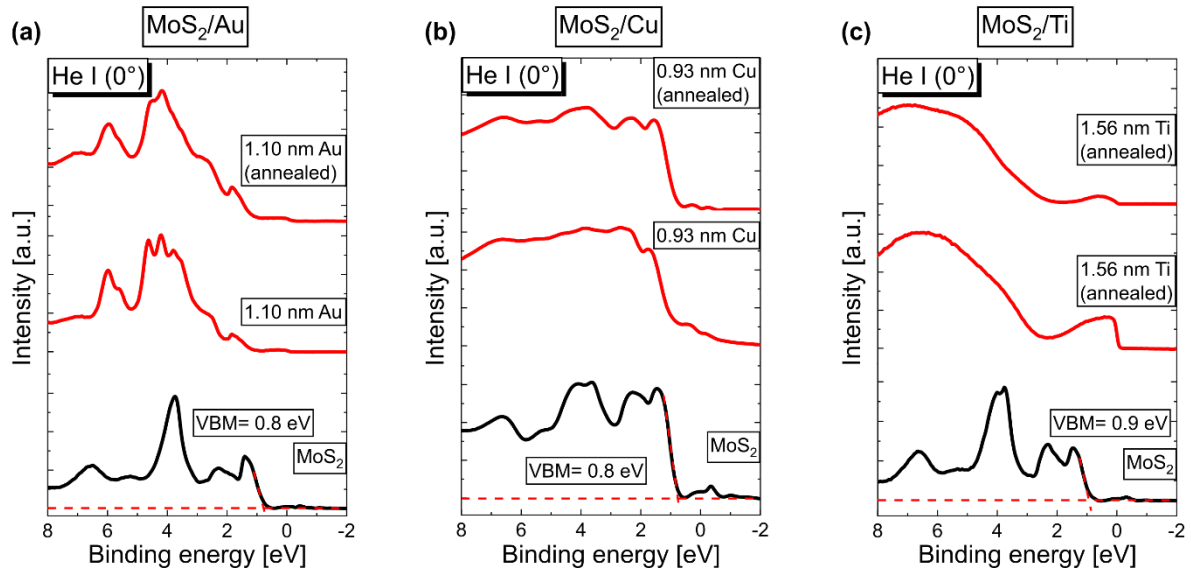


Figure 7.3: Valence band (He I excitation) spectra recorded at an angle of 0° towards the analyzer for a multilayer coverage of a) gold, b) copper and c) titanium.

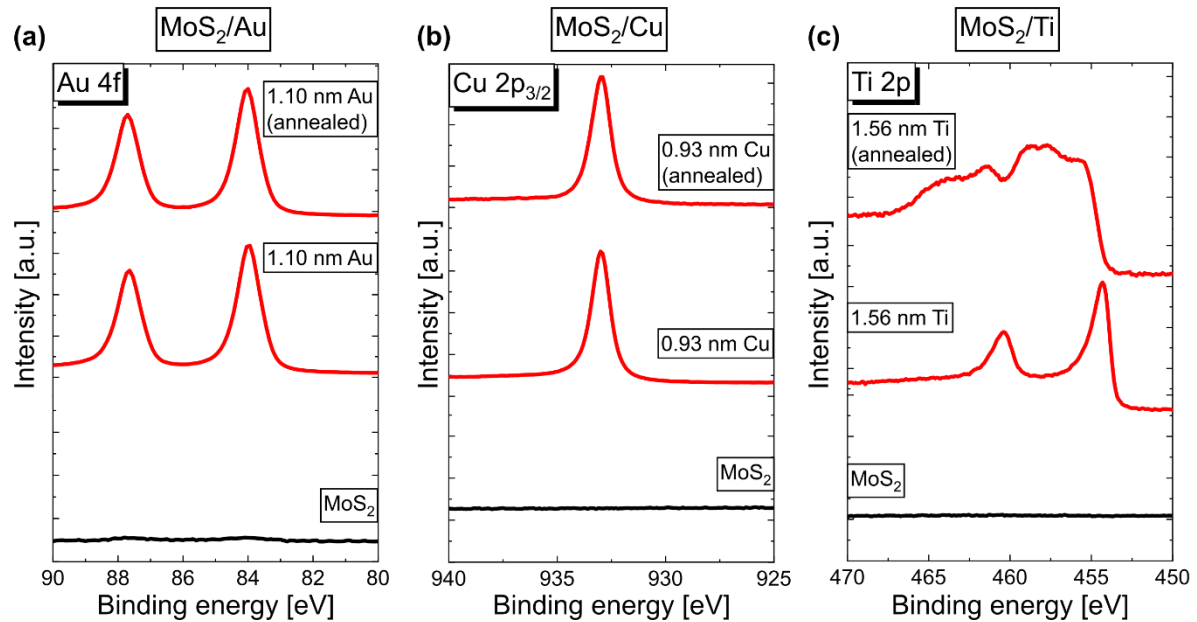


Figure 7.4: Core level spectra of the MoS₂/metal interface for multilayer coverages of the metal depicting a) Au 4f, b) Cu 2p and c) Ti 2p.

As already discussed for Figure 7.1, there is no change in peak shape between the Au 4f and Cu 2p_{3/2} peaks observable pre- and post-deposition. After the deposition of titanium, the obtained Ti 2p peaks resemble the peaks for Ti⁰ similar to the observed peaks in Figure 7.1c. After annealing a complex structure in peaks is shown which indicates a partial oxidation of titanium leading to various oxidation states as shown in the spectrum. Again, this oxidation might arise due to the reaction with the remaining

oxygen in the vacuum chamber at elevated pressure. Since the amount of oxygen is still low it is probable that not all the titanium atoms reacted.

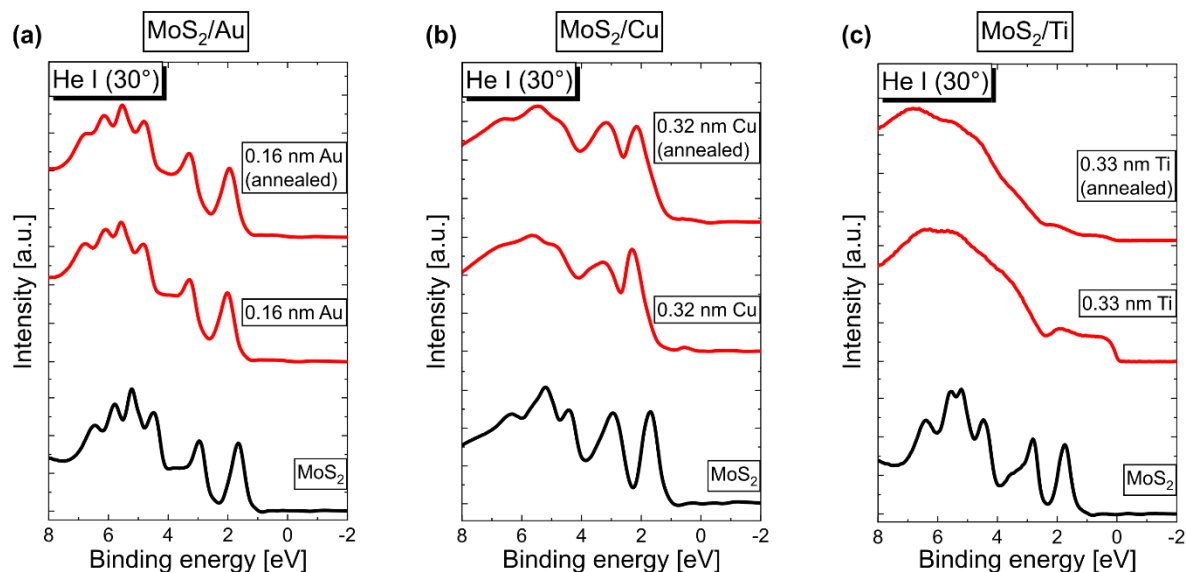


Figure 7.5: Valence band (He I excitation) spectra recorded at an angle of 30° towards the analyzer for a (sub-)monolayer coverage of a) gold, b) copper and c) titanium.

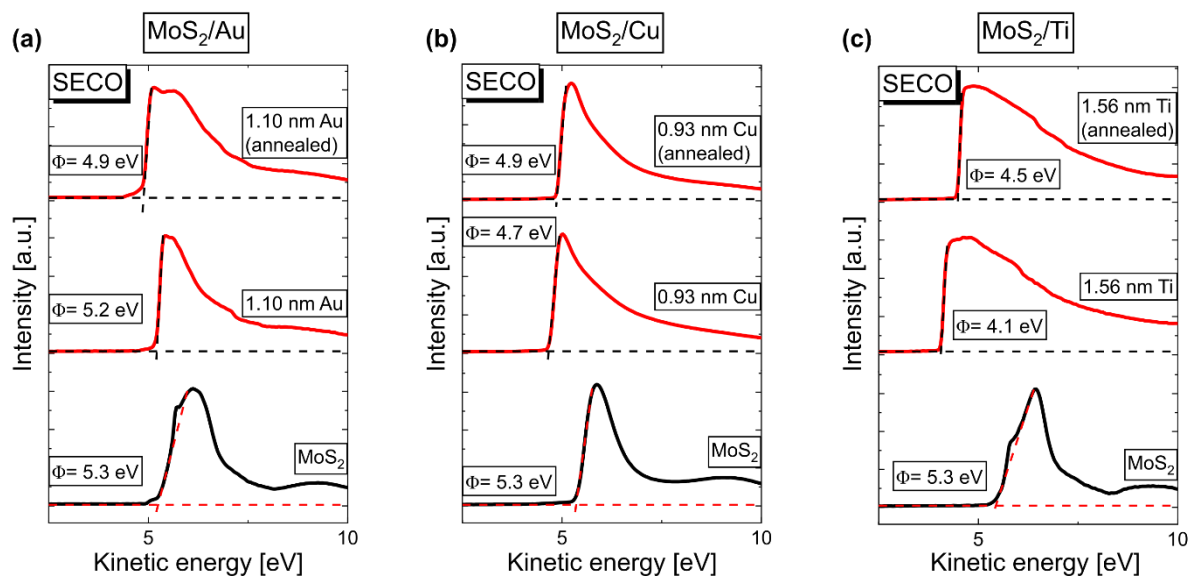


Figure 7.6: Secondary electron cut-off spectra of the MoS₂/metal interface for a multilayer coverage of a) gold, b) copper and c) titanium.

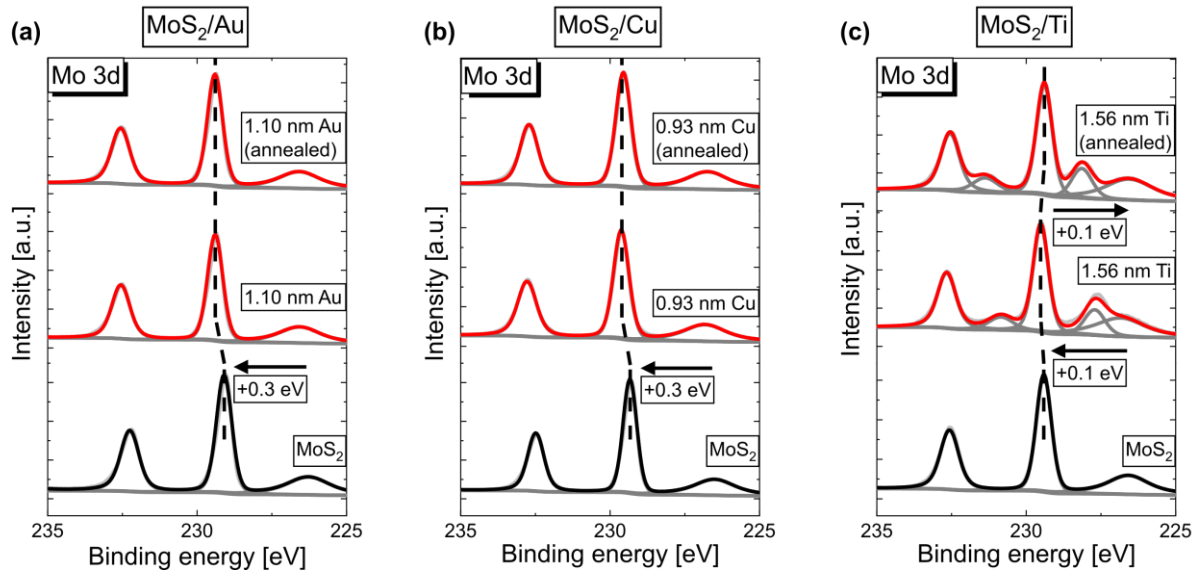


Figure 7.7: Mo 3d core level spectra of the MoS₂/metal interface for a multilayer of a) gold, b) copper and c) titanium.

Table 7.3: Peak fit parameters for Mo 3d and S 2s peak fits shown in Figure 7.7 a) multilayer of Au, b) multilayer of Cu, c) multilayer of Ti.

a) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo 3d _{5/2}	229.09	0.55	0.10	44.9
Mo 3d _{3/2}	232.25	0.55	0.30	30.4
S 2s	226.27	0.89	1.25	22.0
Satellite	235.73	1.00	1.00	2.7
MoS₂+1.10 nm Au				
Mo 3d _{5/2}	229.40	0.55	0.10	45.3
Mo 3d _{3/2}	232.55	0.55	0.30	30.3
S 2s	226.56	0.86	1.23	22.7
Satellite	235.86	0.00	1.00	1.6
MoS₂+1.10 nm Au (annealed)				
Mo 3d _{5/2}	229.40	0.55	0.10	45.8
Mo 3d _{3/2}	232.56	0.55	0.32	30.9
S 2s	226.58	0.81	1.26	22.7

Satellite	235.87	0.00	0.50	0.6
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b) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo 3d _{5/2}	229.34	0.50	0.08	45.2
Mo 3d _{3/2}	232.49	0.50	0.25	30.0
S 2s	226.50	0.76	1.29	23.5
Satellite	235.82	1.00	0.50	1.3

MoS₂+0.93
nm Cu

Mo 3d _{5/2}	229.63	0.55	0.12	44.9
Mo 3d _{3/2}	232.78	0.55	0.34	30.6
S 2s	226.82	0.74	1.40	23.3
Satellite	236.17	1.00	0.50	1.3

MoS₂+0.93
nm Cu
(annealed)

Mo 3d _{5/2}	229.56	0.55	0.10	44.5
Mo 3d _{3/2}	232.71	0.55	0.29	30.5
S 2s	226.73	0.70	1.39	23.3
Satellite	236.01	1.00	0.50	1.8

c) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo 3d _{5/2}	229.41	0.54	0.11	44.2
Mo 3d _{3/2}	232.57	0.54	0.33	30.4
S 2s	226.58	0.71	1.37	24.3
Satellite	235.94	1.00	0.50	1.2

MoS₂+1.56
nm Ti

Mo 3d _{5/2}	229.51	0.52	0.15	35.0
Mo 3d _{3/2}	232.66	0.52	0.35	23.7

Mo	3d _{5/2}	227.71	0.70	0.20	11.3
(interface)					
Mo	3d _{3/2}	230.85	0.70	0.44	7.4
(interface)					
S 2s		226.84	1.00	1.40	22.3
Satellite		236.04	0.50	0.10	0.5

MoS₂+1.56

nm	Ti				
(annealed)					

Mo 3d _{5/2}	229.40	0.54	0.15	34.0
Mo 3d _{3/2}	232.55	0.54	0.35	22.9
Mo 3d _{5/2}	228.14	0.70	0.20	12.0
(interface)				
Mo 3d _{3/2}	231.37	0.70	0.48	7.9
(interface)				
S 2s	226.55	1.00	1.40	22.8
Satellite	235.76	0.50	0.10	0.4

(a) MoS₂/Au

(b) MoS₂/Cu

(c) MoS₂/Ti

Figure 7.8: S 2p core level spectra of the MoS₂/metal interface for a multilayer of a) gold, b) copper and c) titanium.

Table 7.4: Peak fit parameters for S 2p peak fits shown in Figure 7.8 a) multilayer of Au, b) multilayer of Cu, c) multilayer of Ti.

a) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	161.89	0.37	0.16	66.6
S 2p _{1/2}	163.09	0.37	0.16	33.4
MoS₂+1.10 nm Au				
S 2p _{3/2}	162.19	0.42	0.15	66.7
S 2p _{1/2}	163.40	0.42	0.15	33.3
MoS₂+1.10 nm Au (annealed)				
S 2p _{3/2}	162.20	0.46	0.11	66.7
S 2p _{1/2}	163.41	0.46	0.11	33.3
b) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	162.16	0.44	0.13	66.7
S 2p _{1/2}	163.36	0.44	0.13	33.3
MoS₂+0.93 nm Cu				
S 2p _{3/2}	162.46	0.50	0.17	66.8
S 2p _{1/2}	163.66	0.50	0.17	33.2
MoS₂+0.93 nm Cu (annealed)				
S 2p _{3/2}	162.38	0.50	0.15	66.7
S 2p _{1/2}	163.58	0.50	0.15	33.3
c) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	162.25	0.49	0.11	66.7
S 2p _{1/2}	163.44	0.49	0.11	33.3

MoS₂+1.56**nm Ti**

S 2p _{3/2}	162.31	0.46	0.3	64.7
S 2p _{1/2}	163.46	0.46	0.3	35.3

MoS₂+1.56**nm Ti****(annealed)**

S 2p _{3/2}	162.28	0.50	0.30	66.5
S 2p _{1/2}	163.46	0.50	0.30	33.5

7.2 Supporting information: Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes

MoS₂ flake on native oxide silicon substrate

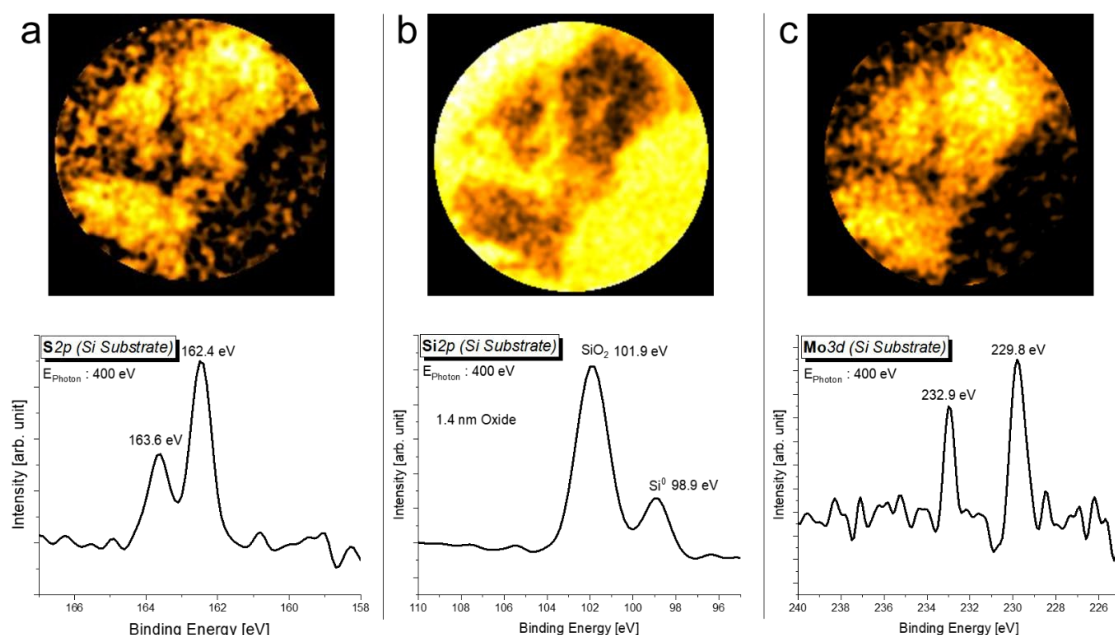


Figure 7.9: Micro-XPS measurements on a MoS₂ flake on native oxide silicon substrate, referred to as flake 1 in the main text. The intensity maps show the summed intensity measured over the S2p region (a), the Si2p region (b) and the Mo3d region (c). The bright pixels have an overall high intensity while the intensity in darker areas is low. Below each image the average spectra, integrated over the total detector area is shown.

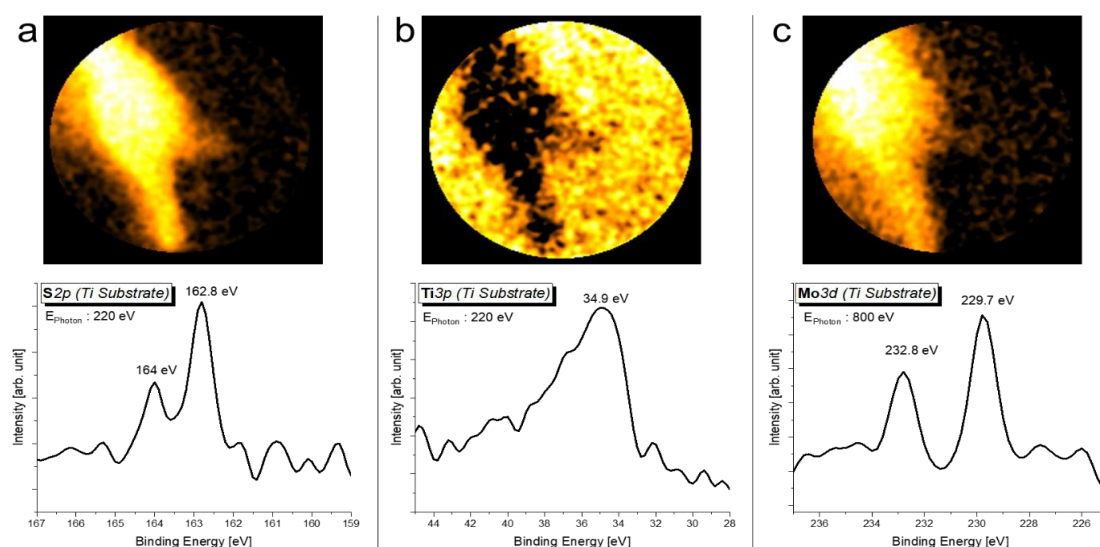
MoS₂ flake on titanium coated substrate

Figure 7.10: Micro-XPS measurements on a MoS₂ flake on a titanium coated substrate, referred to as flake 2 in the main text. The intensity maps show the summed intensity measured over the S2p region (a), the Ti3p region (b) and the Mo3d region (c). The bright pixels have an overall high intensity while the intensity in darker areas is low. Below each image the average spectra, integrated over the total detector area is shown.

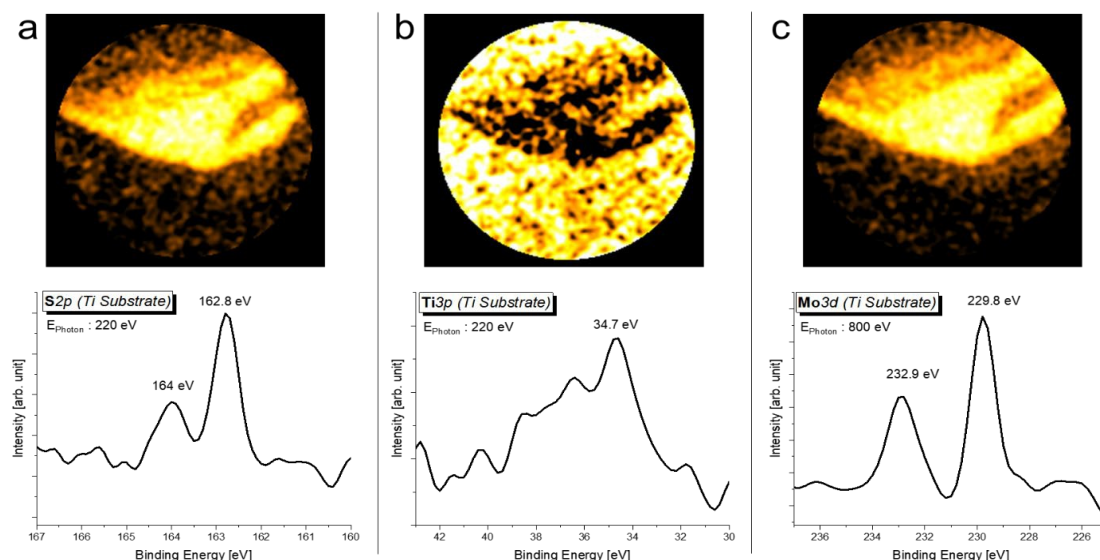
MoS₂ flake on titanium coated substrate

Figure 7.11: Micro-XPS measurements on a MoS₂ flake on a titanium coated substrate, referred to as flake 3 in the main text. The intensity maps show the summed intensity measured over the S2p region (a), the Ti3p region (b) and the Mo3d region (c). The bright pixels have an overall high intensity while the intensity in darker areas is low.

Below each image the average spectra, integrated over the total detector area is shown.

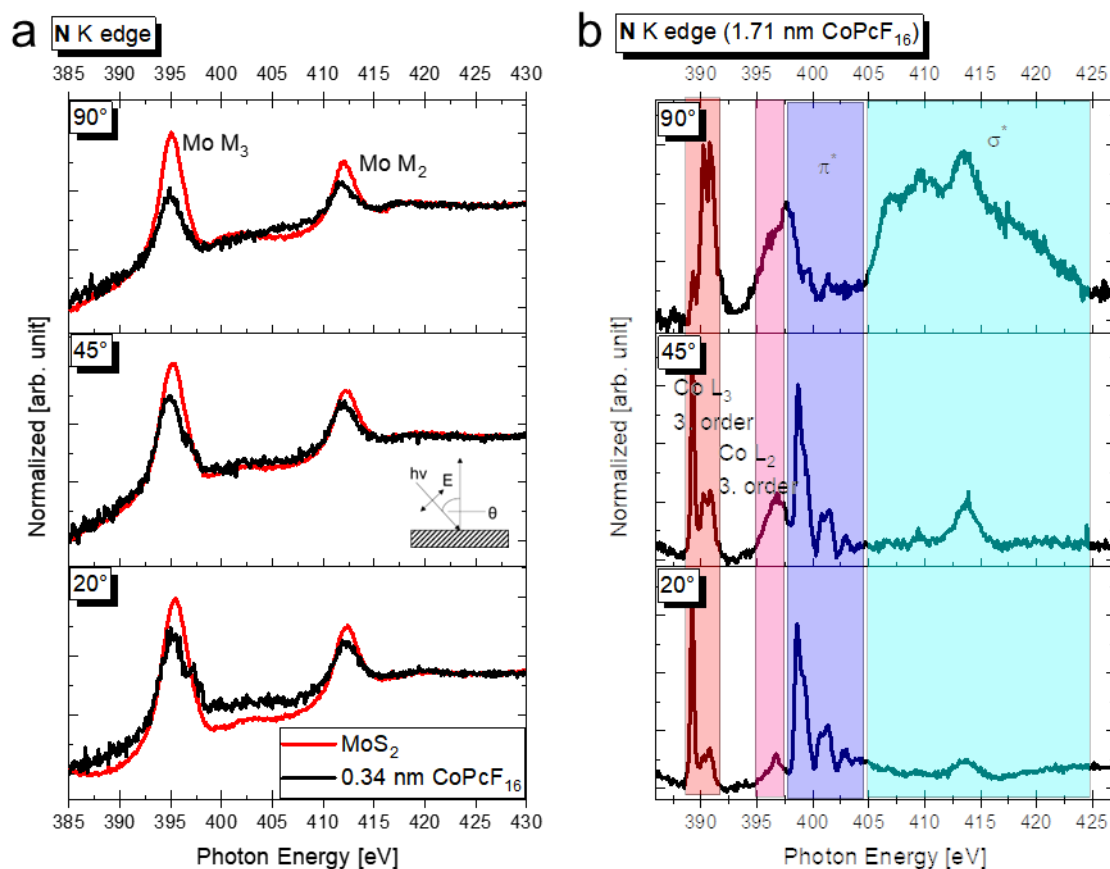


Figure 7.12: Angle dependent XAS measurements of (a) N K edge region of clean bulk MoS₂ (red) and bulk MoS₂ with an overlayer of CoPcF₁₆ (black). (b) N K edge region after the second deposition of CoPcF₁₆.

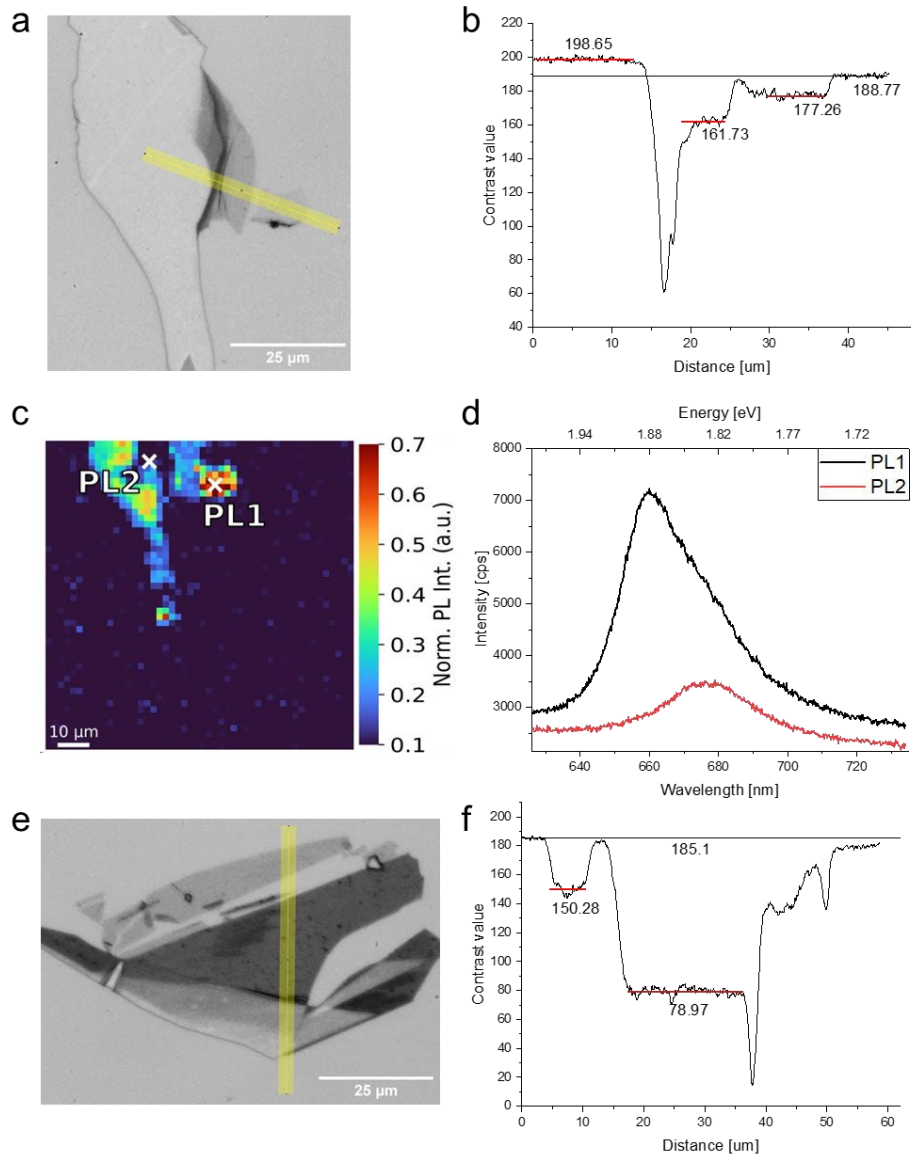


Figure 7.13: (a) and (e) display the red channel of the RGB optical microscope images of the samples referred to as flake 2 and 3 in the main text. The contrast profiles produced in (b) and (f) were generated using ImageJ and correspond to the values along the yellow line shown in (a) and (e). (c) presents a photoluminescence (PL) map of the flake shown in (a). Strong PL is observed in the monolayer areas, where direct band transitions occur. (d) shows the PL spectra of the monolayer (black) and the bulk (red) region. The peak maximum at an energy of 1.88 eV is typical for structures with two or less layers.¹⁷⁷ In addition, the increased photoluminescence in comparison to the bulk area is characteristic for such thin structures.¹⁷⁸

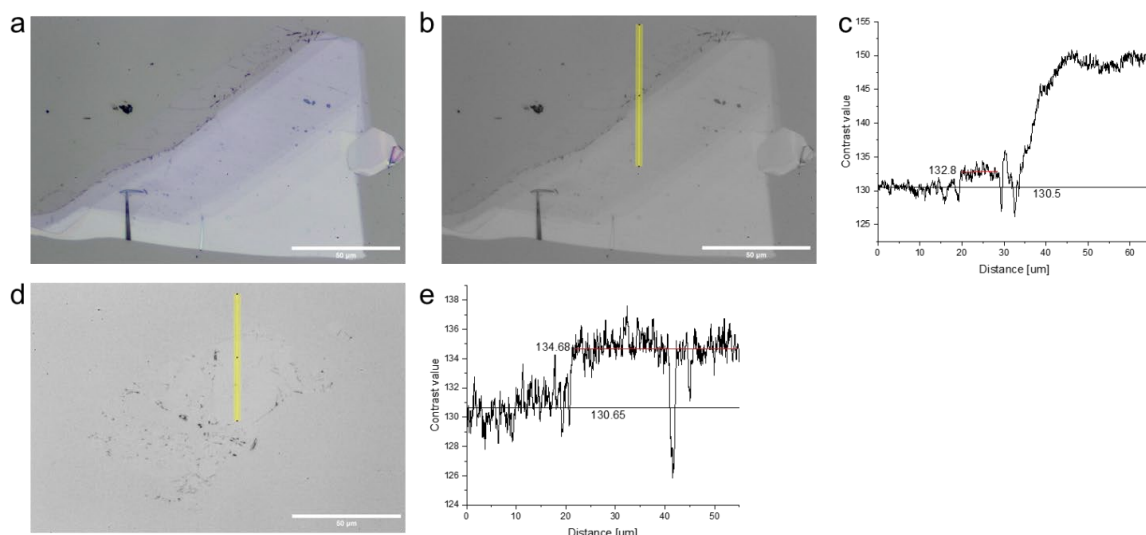


Figure 7.14: (a) displays the optical microscope image of an exfoliated flake on a silicon substrate with a native oxide layer. (b) and (d) show the red channel of the RGB optical microscope image of the flake presented in (a), as well as of flake 1 discussed in the main text. (c) and (e) depict the contrast values along the lines drawn in (b) and (d), which were generated using ImageJ.

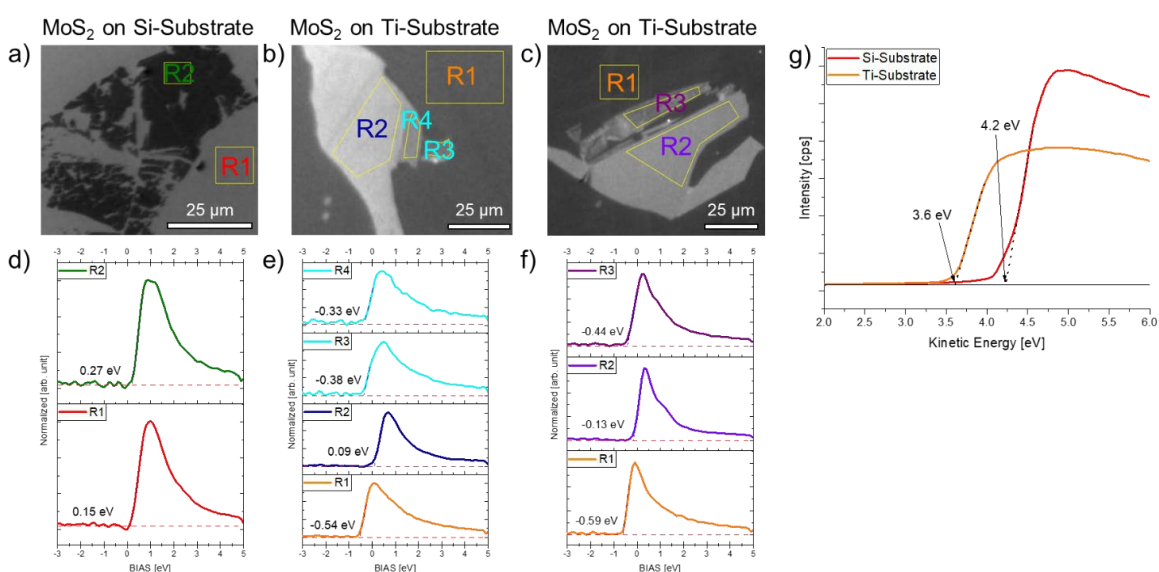


Figure 7.15: Measured BIAS voltages for flakes 1-3 (a–c) and the averaged spectra from the marked region of interest (d–f). (g) measured secondary electron cut-off for the clean substrates.

7.3 Supporting information: Tuning the electronic properties of defect-rich MoS₂

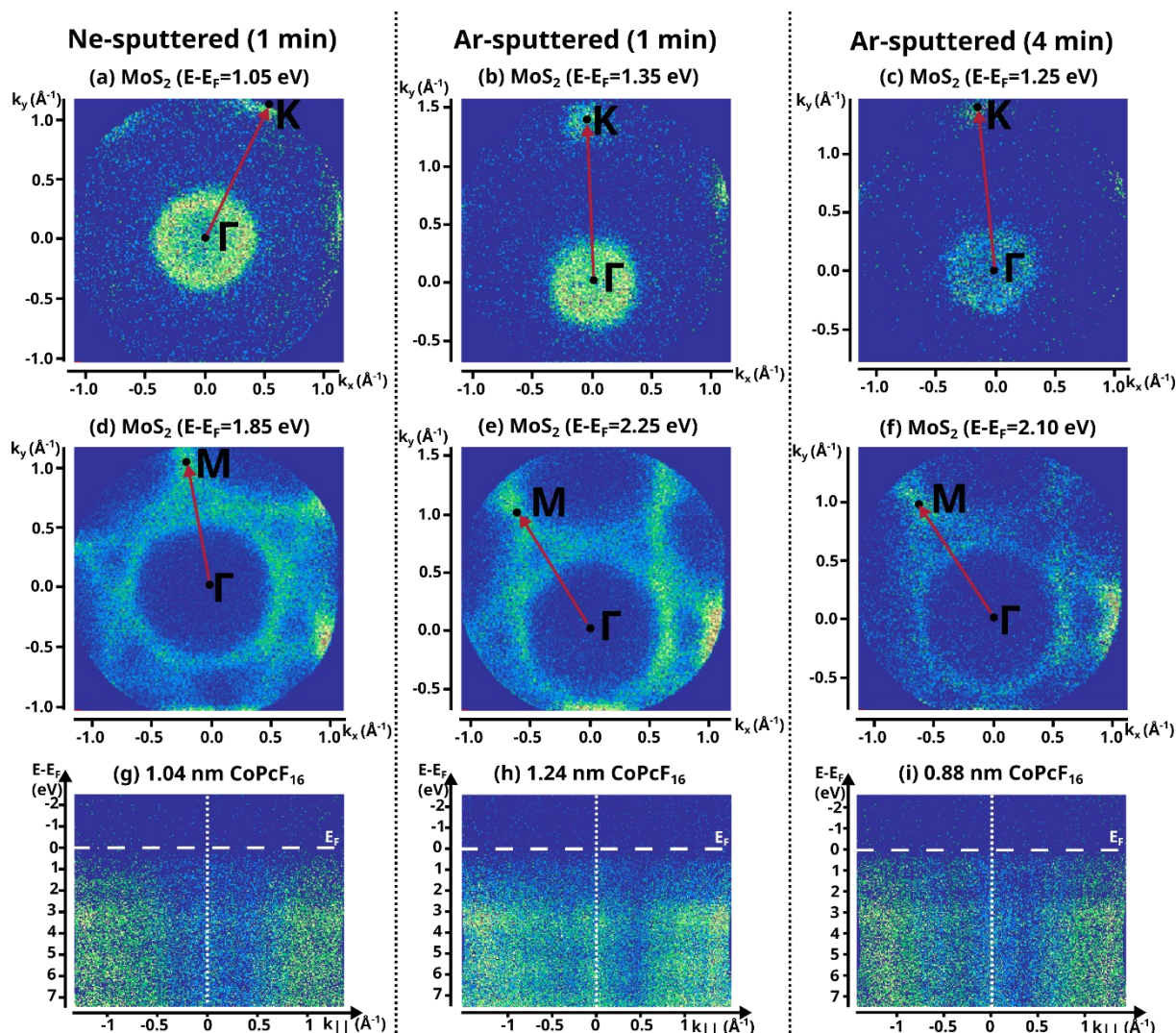


Figure 7.16: k_x - k_y -maps at selected energies showing K (a-c) and M (d-f) for the three pristine MoS₂ samples and ARPES band structures of the multilayer CoPcF₁₆ coverages (g-i) on given substrates.

The fitting of the C 1s and N 1s spectra shown in Figure 3.13 was performed using established models for perfluorinated phthalocyanines.¹¹⁶ The C 1s spectra consist of three individual carbon components, representing C-C (C1), C-N (C2) and C-F (C3) bonds, accompanied by satellite peaks (S1, S2, S3) at higher binding energies. The intensity ratio $C1+S1/C2+2/C3+S3$ is in good agreement with the stoichiometry of CoPcF₁₆ (see Table 7.5, supporting information). The N 1s spectra were fitted with a single main nitrogen peak (N) and an additional satellite (S) at higher binding energies

(see Table 7.6, supporting information). For all spectra, the fitting model was essentially independent of the film thickness and the underlying substrate. The different energetic shifts of the individual carbon components and the N 1s level, indicated by broken lines in Figure 3.13, may hint to a different electron distribution in the molecule at the interface compared to the bulk, but can also be explained by site-dependent screening effects.^{20,223}

Table 7.5: Fit parameters for the C 1s spectra shown in Figure 3.13.

a) Ne⁺ (1 min)	Position [eV]	Gaussian	Lorentzian	rel. area [%]
+ 0.39 nm		width [eV]	width [eV]	
CoPcF₁₆				
C1	284.40	0.55	0.15	26.6
S1	285.75	0.55	0.15	0.5
C2	285.53	0.54	0.30	21.7
S2	287.42	0.54	0.30	5.4
C3	286.67	0.56	0.14	36.1
S3	288.23	0.56	0.14	9.6
Ne⁺ (1 min) +				
1.04 nm				
CoPcF₁₆				
C1	284.80	0.80	0.30	22.8
S1	286.01	0.80	0.30	1.1
C2	285.97	0.81	0.30	17.1
S2	287.78	0.81	0.30	6.5
C3	286.89	0.76	0.30	44.0
S3	288.63	0.76	0.30	8.5

b) Ar⁺ (1 min) +	Position [eV]	Gaussian	Lorentzian	rel. area [%]
0.19 nm		width [eV]	width [eV]	
CoPcF₁₆				
C1	284.42	0.55	0.15	24.1
S1	285.63	0.55	0.15	0.5
C2	285.52	0.52	0.30	21.3
S2	288.06	0.52	0.30	7.5
C3	286.68	0.55	0.10	40.3
S3	288.76	0.55	0.10	6.3

Ar⁺ (1 min) +				
1.24 nm				
CoPcF₁₆				
C1	284.81	0.70	0.30	24.0
S1	286.01	0.70	0.30	0.5
C2	286.04	0.83	0.30	17.2
S2	288.27	0.83	0.30	6.5
C3	286.98	0.69	0.30	46.8
S3	289.09	0.69	0.30	5.0

c) Ar⁺ (4 min)	Position [eV]	Gaussian	Lorentzian	rel. area [%]
+ 0.36 nm		width [eV]	width [eV]	
CoPcF₁₆				
C1	284.40	0.65	0.15	26.0
S1	285.75	0.65	0.15	0.8
C2	285.53	0.75	0.30	22.3

S2	287.42	0.75	0.30	5.6
C3	286.67	0.65	0.18	35.9
S3	288.17	0.65	0.18	9.5

Ar⁺ (4 min) +

0.88 nm

CoPcF₁₆

C1	284.56	0.80	0.30	22.9
S1	286.16	0.80	0.30	0.7
C2	285.70	0.83	0.30	18.1
S2	287.70	0.83	0.30	8.1
C3	286.76	0.80	0.30	40.2
S3	288.56	0.80	0.30	10.1

Table 7.6: Fit parameters for the N 1s spectra shown in Figure 3.13.

d) Ne⁺ (1 min)+ 0.39 nm CoPcF₁₆

	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
--	---------------	---------------------	-----------------------	---------------

N	398.29	1.04	0.30	85.4
S	400.29	1.04	0.30	14.6

Ne⁺ (1 min) +

1.04 nm

CoPcF₁₆

N	398.75	1.16	0.30	90.6
S	400.85	1.16	0.30	9.4

e) Ar⁺ (1 min)	Position [eV]	Gaussian	Lorentzian	rel. area [%]
+ 0.19 nm		width [eV]	width [eV]	
CoPcF₁₆				
N	398.31	1.04	0.30	85.4
S	400.51	1.04	0.30	14.6
Ar⁺ (1 min) +				
1.24 nm				
CoPcF₁₆				
N	398.77	1.09	0.24	96.2
S	400.72	1.09	0.24	3.8
f) Ar⁺ (4 min)	Position [eV]	Gaussian	Lorentzian	rel. area [%]
+ 0.36 nm		width [eV]	width [eV]	
CoPcF₁₆				
N	398.34	1.02	0.26	86.2
S	400.35	1.02	0.26	13.8
Ar⁺ (4 min) +				
0.88 nm				
CoPcF₁₆				
N	398.72	1.26	1.26	91.2
S	400.74	0.10	0.10	8.8

Table 7.7: Fit parameters for the Mo 3d spectra measured with low surface sensitivity ($h\nu = 900$ eV) shown in Figure 3.14.

a) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo(IV) 3d _{5/2}	228.51	1.76	0.28	51.9
Mo(IV) 3d _{3/2}	231.72	1.76	0.43	35.0
S 2s	225.64	2.00	0.67	13.1
Ne⁺ (1 min)				
Mo(IV) 3d _{5/2}	228.62	1.76	0.29	51.3
Mo(IV) 3d _{3/2}	231.80	1.76	0.44	34.5
Mo(0) 3d _{5/2}	227.56	1.76	0.28	0.7
Mo(0) 3d _{3/2}	230.74	1.76	0.28	0.5
S 2s	225.79	2.00	0.68	13.0
0.39 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.63	1.76	0.29	51.7
Mo(IV) 3d _{3/2}	231.84	1.76	0.44	34.9
Mo(0) 3d _{5/2}	227.05	1.75	0.28	0.7
Mo(0) 3d _{3/2}	230.20	1.75	0.28	0.5
S 2s	225.76	2.00	0.62	12.1
1.04 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.69	2.20	0.29	52.9
Mo(IV) 3d _{3/2}	231.94	2.20	0.41	34.8
Mo(0) 3d _{5/2}	227.40	2.10	0.29	0.8
Mo(0) 3d _{3/2}	230.50	2.10	0.29	0.6
S 2s	225.63	2.00	0.68	10.9

b) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
Mo(IV) 3d _{5/2}	229.02	1.76	0.20	50.7
Mo(IV) 3d _{3/2}	232.21	1.76	0.30	34.6
S 2s	226.19	2.03	0.90	14.7

Ar⁺ (1 min)

Mo(IV) 3d _{5/2}	228.69	1.76	0.20	51.1
Mo(IV) 3d _{3/2}	231.90	1.76	0.30	34.7
S 2s	225.84	2.03	0.90	14.1

0.19 nm**CoPcF₁₆**

Mo(IV) 3d _{5/2}	228.71	1.76	0.20	50.5
Mo(IV) 3d _{3/2}	231.88	1.76	0.30	34.4
S 2s	225.99	2.03	0.90	15.1

1.24 nm**CoPcF₁₆**

Mo(IV) 3d _{5/2}	228.64	1.76	0.20	50.7
Mo(IV) 3d _{3/2}	231.79	1.76	0.30	34.2
S 2s	226.00	2.03	0.90	15.1

c) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
Mo(IV) 3d _{5/2}	228.56	1.95	0.25	51.4
Mo(IV) 3d _{3/2}	231.79	1.95	0.35	34.8

S 2s	225.65	1.50	1.29	13.8
Ar⁺ (4 min)				
Mo(IV) 3d _{5/2}	228.35	1.99	0.15	48.6
Mo(IV) 3d _{3/2}	231.56	1.99	0.30	32.6
Mo(0) 3d _{5/2}	227.53	2.00	0.15	2.8
Mo(0) 3d _{3/2}	230.73	2.00	0.15	1.9
S 2s	225.49	2.00	0.88	14.1
0.36 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.49	1.91	0.15	48.9
Mo(IV) 3d _{3/2}	231.74	1.91	0.30	33.0
Mo(0) 3d _{5/2}	227.30	2.00	0.15	3.3
Mo(0) 3d _{3/2}	230.50	2.00	0.15	2.2
S 2s	225.55	1.73	1.00	12.5
0.88 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.72	1.90	0.15	48.3
Mo(IV) 3d _{3/2}	231.90	1.90	0.30	32.5
Mo(0) 3d _{5/2}	227.28	2.00	0.15	3.6
Mo(0) 3d _{3/2}	230.38	2.00	0.15	2.4
S 2s	225.89	1.75	1.00	13.3

Table 7.8: Fit parameters for the Mo 3d spectra measured with high surface sensitivity (hν = 300 eV) shown in Figure 3.14.

7. Appendix

d) MoS₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo(IV) 3d _{5/2}	228.81	0.15	0.18	51.0
Mo(IV) 3d _{3/2}	231.97	0.15	0.41	31.8
S 2s	226.02	1.32	0.20	17.2
Ne⁺ (1 min)				
Mo(IV) 3d _{5/2}	228.86	0.32	0.20	45.7
Mo(IV) 3d _{3/2}	232.03	0.32	0.40	29.1
Mo(0) 3d _{5/2}	228.50	0.32	0.20	5.9
Mo(0) 3d _{3/2}	231.55	0.32	0.20	3.8
S 2s	226.03	1.53	0.12	15.6
0.39 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.93	0.32	0.20	47.6
Mo(IV) 3d _{3/2}	232.10	0.32	0.44	31.4
Mo(0) 3d _{5/2}	228.54	0.30	0.20	5.8
Mo(0) 3d _{3/2}	231.74	0.30	0.20	3.7
S 2s	226.20	1.30	0.44	11.6
1.04 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.87	0.31	0.20	45.8
Mo(IV) 3d _{3/2}	232.04	0.31	0.44	30.7
Mo(0) 3d _{5/2}	228.50	0.30	0.20	5.9
Mo(0) 3d _{3/2}	231.62	0.30	0.20	3.8
S 2s	225.97	1.30	0.54	13.7

e) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
Mo(IV) 3d _{5/2}	229.17	0.16	0.17	49.3
Mo(IV) 3d _{3/2}	232.32	0.16	0.48	32.9
S 2s	226.19	0.80	1.0	17.8
Ar⁺ (1 min)				
Mo(IV) 3d _{5/2}	229.00	0.27	0.17	44.2
Mo(IV) 3d _{3/2}	232.18	0.27	0.51	28.9
Mo(0) 3d _{5/2}	228.63	0.27	0.18	6.8
Mo(0) 3d _{3/2}	231.97	0.27	0.18	4.4
S 2s	226.14	0.80	1.00	15.7
0.19 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	228.97	0.27	0.17	45.0
Mo(IV) 3d _{3/2}	232.15	0.27	0.47	29.0
Mo(0) 3d _{5/2}	228.63	0.27	0.18	6.9
Mo(0) 3d _{3/2}	231.88	0.27	0.18	4.4
S 2s	226.11	0.80	1.00	14.7
1.24 nm				
CoPcF₁₆				
Mo(IV) 3d _{5/2}	229.03	0.27	0.17	44.2
Mo(IV) 3d _{3/2}	232.20	0.27	0.43	29.5
Mo(0) 3d _{5/2}	228.70	0.27	0.18	6.5
Mo(0) 3d _{3/2}	231.95	0.27	0.18	4.1

7. Appendix

S 2s	226.12	0.80	1.00	15.76
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f) MoS ₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
Mo(IV) 3d _{5/2}	228.95	0.22	0.14	50.9
Mo(IV) 3d _{3/2}	232.11	0.22	0.38	32.7
S 2s	225.96	0.69	0.75	16.3

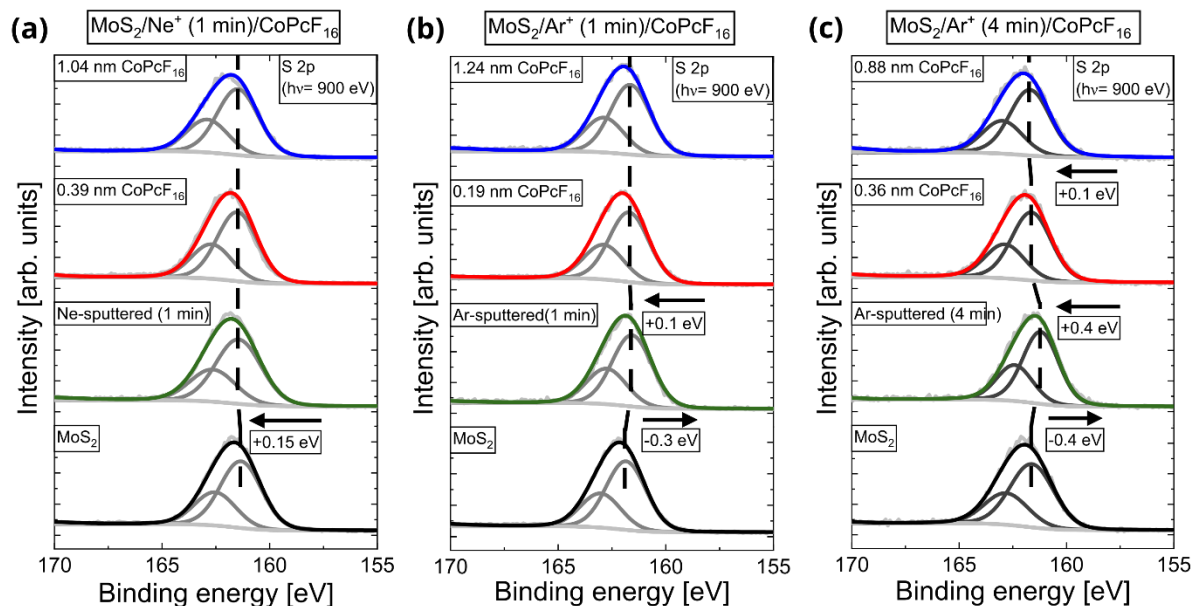
Ar ⁺ (4 min)				
Mo(IV) 3d _{5/2}	228.85	0.41	0.14	43.8
Mo(IV) 3d _{3/2}	232.02	0.41	0.38	28.4
Mo(0) 3d _{5/2}	228.42	0.40	0.14	9.8
Mo(0) 3d _{3/2}	231.61	0.40	0.14	6.5
S 2s	226.01	0.69	0.75	11.6

0.36 nm				
CoPcF ₁₆				
Mo(IV) 3d _{5/2}	228.83	0.41	0.14	43.4
Mo(IV) 3d _{3/2}	232.03	0.41	0.38	28.0
Mo(0) 3d _{5/2}	228.45	0.40	0.14	9.8
Mo(0) 3d _{3/2}	231.68	0.40	0.14	6.5
S 2s	225.84	0.69	0.75	12.4

0.88 nm				
CoPcF ₁₆				
Mo(IV) 3d _{5/2}	228.90	0.42	0.14	41.9
Mo(IV) 3d _{3/2}	232.12	0.42	0.39	27.3
Mo(0) 3d _{5/2}	228.55	0.41	0.14	10.0

Mo(0) 3d _{3/2}	231.77	0.41	0.14	6.5
S 2s	226.06	0.69	0.75	14.3

Low surface sensitivity ($\lambda \sim 2.6$ nm)



High surface sensitivity ($\lambda \sim 0.9$ nm)

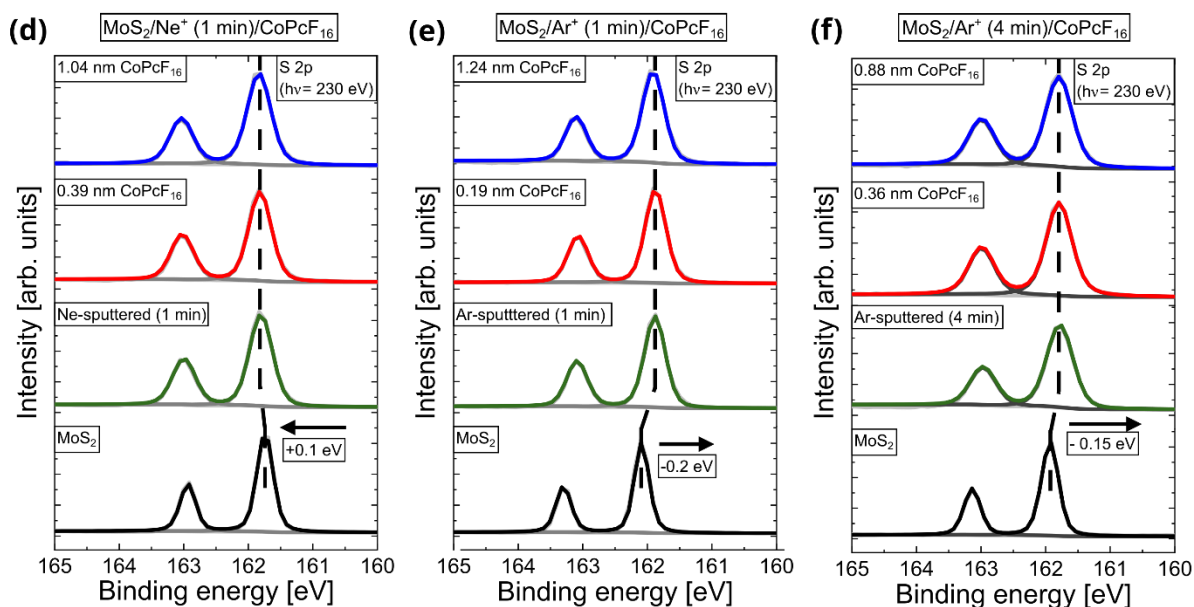


Figure 7.17: X-ray photoelectron spectroscopy (XPS) measurements of the S 2p core levels of MoS₂ following the sputtering with Ar and Ne and the deposition of CoPcF₁₆.

Table 7.9: Fit parameters for the S 2p spectra measured with low surface sensitivity ($h\nu = 900$ eV) shown in Figure 7.17.

a) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
S 2p _{3/2}	161.33	2.14	0.20	66.7
S 2p _{1/2}	162.53	2.14	0.20	33.3
Ne⁺ (1 min)				
S 2p _{3/2}	161.44	2.37	0.20	66.7
S 2p _{1/2}	162.64	2.37	0.20	33.3
0.39 nm				
CoPcF₁₆				
S 2p _{3/2}	161.50	2.10	0.20	66.7
S 2p _{1/2}	162.70	2.10	0.20	33.3
1.04 nm				
CoPcF₁₆				
S 2p _{3/2}	161.48	2.15	0.20	66.7
S 2p _{1/2}	162.68	2.15	0.20	33.3
b) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
S 2p _{3/2}	161.84	2.08	0.17	66.7
S 2p _{1/2}	163.02	2.08	0.17	33.3
Ar⁺ (1 min)				
S 2p _{3/2}	161.57	2.08	0.17	66.7
S 2p _{1/2}	162.75	2.08	0.17	33.3

0.19 nm				
CoPcF₁₆				
S 2p _{3/2}	161.71	2.08	0.17	66.7
S 2p _{1/2}	162.89	2.08	0.17	33.3
1.24 nm				
CoPcF₁₆				
S 2p _{3/2}	161.65	2.08	0.17	66.6
S 2p _{1/2}	162.87	2.08	0.17	33.4
c) MoS₂				
	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	161.61	2.26	0.24	66.7
S 2p _{1/2}	162.81	2.26	0.24	33.3
Ar⁺ (4 min)				
S 2p _{3/2}	161.20	1.80	0.30	66.7
S 2p _{1/2}	162.41	1.80	0.30	33.3
0.36 nm				
CoPcF₁₆				
S 2p _{3/2}	161.63	2.00	0.32	66.6
S 2p _{1/2}	162.87	2.00	0.32	33.4
0.88 nm				
CoPcF₁₆				
S 2p _{3/2}	161.70	2.00	0.41	66.7
S 2p _{1/2}	162.98	2.00	0.41	33.3

Table 7.10: Fit parameters for the S 2p spectra measured with high surface ($h\nu = 230$ eV) sensitivity shown in Figure 7.17.

d) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
S 2p _{3/2}	161.74	0.23	0.10	68.6
S 2p _{1/2}	162.94	0.23	0.10	31.4
Ne⁺ (1 min)				
S 2p _{3/2}	161.80	0.36	0.10	66.4
S 2p _{1/2}	163.00	0.36	0.10	33.6
0.39 nm				
CoPcF₁₆				
S 2p _{3/2}	161.81	0.36	0.10	65.8
S 2p _{1/2}	163.03	0.36	0.10	34.2
1.04 nm				
CoPcF₁₆				
S 2p _{3/2}	161.84	0.36	0.13	67.2
S 2p _{1/2}	163.04	0.36	0.13	32.8
e) MoS₂	Position [eV]	Gaussian	Lorentzian	rel. area [%]
		width [eV]	width [eV]	
S 2p _{3/2}	162.08	0.22	0.10	65.2
S 2p _{1/2}	163.29	0.22	0.10	34.8
Ar⁺ (1 min)				
S 2p _{3/2}	161.89	0.33	0.10	66.5
S 2p _{1/2}	163.08	0.33	0.10	33.5

0.19 nm				
CoPcF₁₆				
S 2p _{3/2}	161.87	0.31	0.10	66.9
S 2p _{1/2}	163.08	0.31	0.10	33.1
1.24 nm				
CoPcF₁₆				
S 2p _{3/2}	161.91	0.34	0.10	68.1
S 2p _{1/2}	163.11	0.34	0.10	31.9
f) MoS₂				
	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
S 2p _{3/2}	161.94	0.26	0.10	67.6
S 2p _{1/2}	163.13	0.26	0.10	32.4
Ar⁺ (4 min)				
S 2p _{3/2}	161.78	0.41	0.12	68.8
S 2p _{1/2}	162.96	0.41	0.12	31.2
0.36 nm				
CoPcF₁₆				
S 2p _{3/2}	161.79	0.36	0.19	66.3
S 2p _{1/2}	162.99	0.36	0.19	33.7
0.88 nm				
CoPcF₁₆				
S 2p _{3/2}	161.79	0.40	0.15	66.2
S 2p _{1/2}	162.99	0.40	0.15	33.8

To give further insights in the nature of defects produced by sputtering, the change in Mo/S-ratio can be considered. The ratio is calculated with the core level intensities given in Table 7.7 and 7.8 (supporting information) and the photoionization cross-sections σ provided by Yeh and Lindau¹¹⁷ via equation 7.1.

$$\text{Mo:S} = \frac{I_{\text{Mo } 3d} / \sigma_{\text{Mo } 3d}}{I_{\text{S } 2s} / \sigma_{\text{S } 2s}} \quad (7.1)$$

Table 7.11: Mo/S-ratio before and after sputtering for the experiments depicted in Figure 3.14.

Experiment	Mo:S (before sputtering)	Mo:S (after sputtering)	Relative change (%)
Ne ⁺ (1 min, hv= 900 eV)	1:1.56	1:1.55	-0.1
Ar ⁺ (1 min, hv= 900 eV)	1:1.79	1:1.70	-5.3
Ar ⁺ (4 min, hv= 900 eV)	1:1.66	1:1.70	+2.4
Ne ⁺ (1 min, hv= 300 eV)	1:2.89	1:2.57	-12.5
Ar ⁺ (1min, hv= 300 eV)	1:3.01	1:2.59	-16.2
Ar ⁺ (4min, hv= 300 eV)	1:2.71	1:1.83	-48.1

7.4 Supporting Information: Interfaces between Cobalt Phthalocyanines and MoSe₂: Conditions for charge transfer and the Nature of Gap States

Carolin Schüle^{1,#}, Eric Juriatti^{1,#}, Peter Nagel², Tim Parker¹, Michael Merz², Dai Zhang¹, Alfred J. Meixner¹, Thomas Chassé¹, Stefan Schuppler², Marcus Scheele^{1,*}, Heiko Peisert^{1,*}

1 Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

2 Institute for Quantum Materials and Technologies (IQMT), Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany, and Karlsruhe Nano and Micro Facility (KNMF), Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen, Germany

These authors contributed equally.

* Corresponding author, heiko.peisert@uni-tuebingen.de, Tel.: (+49) 07071 / 29-76931, Fax: (+49) 07071 / 29-5490 and marcus.scheele@uni-tuebingen.de

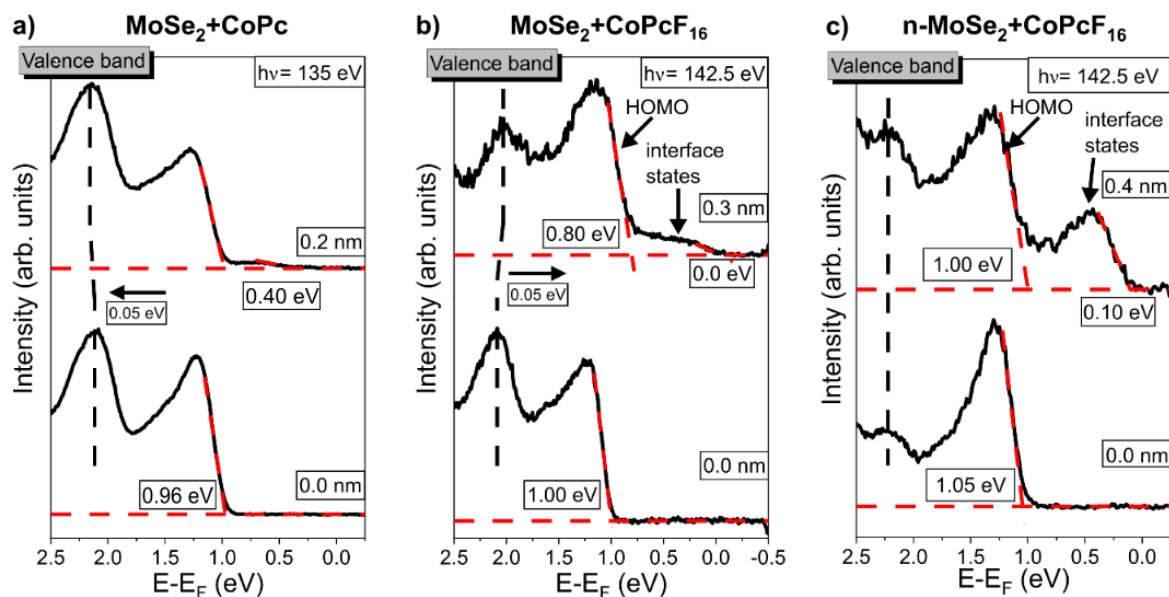


Figure 7.18: Valence band spectra derived from the ARPES experiments at normal emission ($\theta = 50^\circ$) for a) the $\text{MoSe}_2/\text{CoPc}$ interface, b) the $\text{MoSe}_2/\text{CoPcF}_{16}$ interface and c) the $n\text{-MoSe}_2/\text{CoPcF}_{16}$ interface. The horizontal black arrows highlight the shift in Valence band by 0.05 eV towards higher (lower) binding energies for the $\text{MoSe}_2/\text{CoPc}(\text{F}_{16})$ interfaces. The HOMO and interface states of the CoPcF_{16} molecule are marked by black arrows.

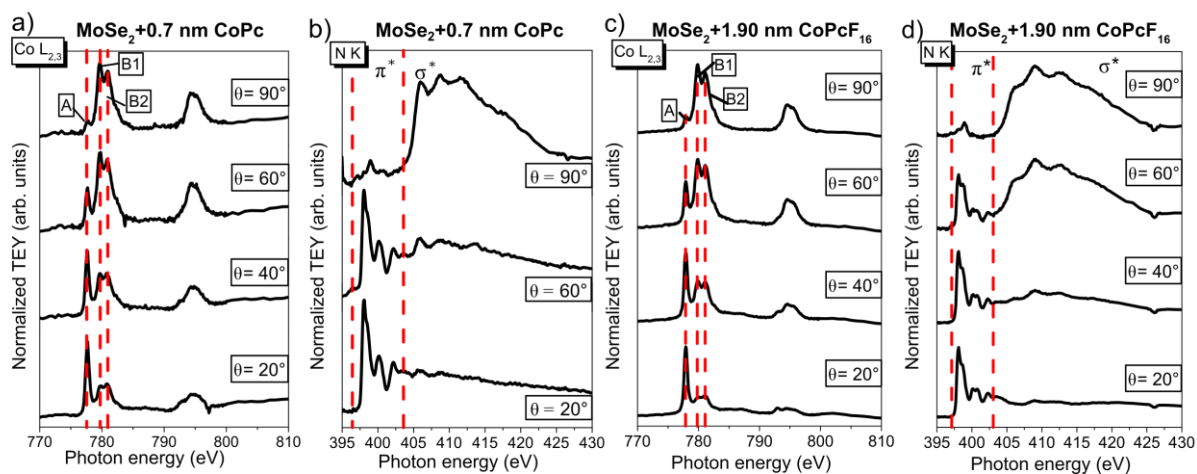


Figure 7.19: Angle-dependent XAS spectra of thicker films (about 2 nm) of CoPc and CoPcF_{16} on MoSe_2 .

Table 7.12: Fit parameters for the C 1s peaks depicted in Figure 4.5.

a) MoSe₂ + 0.2 nm CoPc	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
C-C	284.70	0.60	0.10	68.4
S C-C	286.21	0.60	0.10	6.8
C-N	285.56	0.60	0.10	20.5
S C-N	287.70	0.60	0.10	4.3
MoSe₂ + 0.7 nm CoPc				
C-C	284.56	0.50	0.14	68.4
S C-C	286.1	0.50	0.14	6.8
C-N	285.71	0.50	0.14	20.5
S C-N	287.81	0.50	0.14	4.3

b) MoSe₂ + 0.3 nm CoPcF₁₆	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
C-C	284.90	0.85	0.30	27.0
S C-C	285.90	0.85	0.30	1.1
C-N	285.90	0.82	0.30	18.2
S C-N	288.25	0.82	0.30	6.6
C-F	287.18	0.83	0.26	42.5
S C-F	288.80	0.83	0.26	4.7
n-MoSe₂ + 0.4 nm CoPcF₁₆				
C-C	284.56	0.44	0.30	22.3
S C-C	286.46	0.44	0.30	1.8
C-N	285.36	0.44	0.30	18.4
S C-N	287.50	0.44	0.30	6.9
C-F	286.83	0.44	0.30	28.0
S C-F	288.71	0.44	0.30	6.7

MoSe₂ + 1.9 nm CoPcF₁₆				
C-C	284.90	0.77	0.55	25.0
S C-C	286.70	0.77	0.55	1.3
C-N	285.93	0.77	0.55	17.0
S C-N	288.23	0.77	0.55	5.0
C-F	287.20	0.77	0.55	46.8
S C-F	288.63	0.77	0.55	5.0

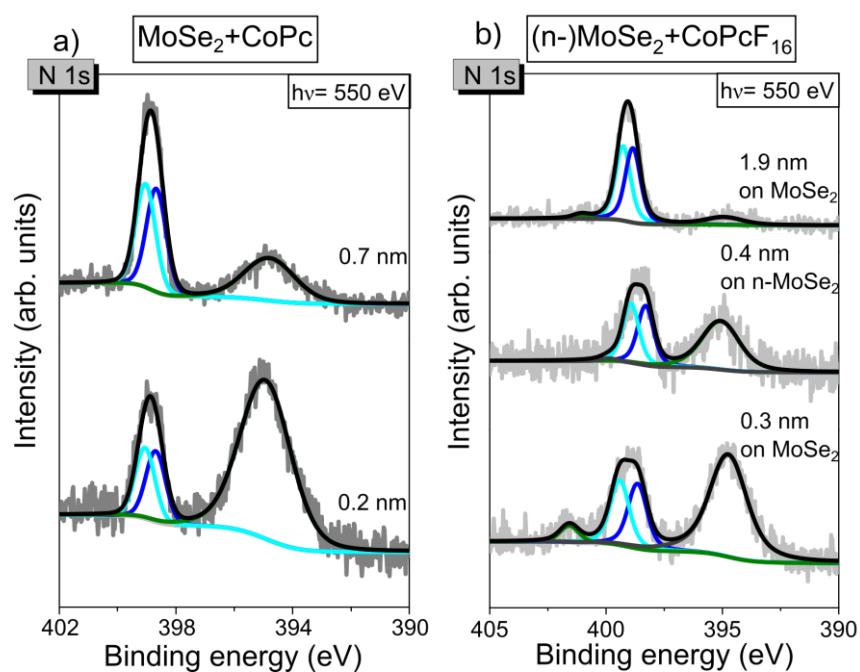


Figure 7.20: N1s core level spectra for a) CoPc/MoSe₂, b) CoPcF₁₆/(n-)MoSe₂, and c) CoPcF₁₆/n-MoSe₂. The two components are assigned to the two chemically different nitrogen atoms. The peak shape is similar in all cases, indicating the absence of strong interactions involving the N atom.

Table 7.13: Fit parameters for the N 1s peaks depicted in Figure 7.20.

a) MoSe₂ + 0.2 nm CoPc	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
N1	398.61	0.43	0.10	10.1
N2	399.03	0.43	0.10	10.1
S	399.32	0.43	0.10	2.7
Mo 3p _{3/2}	394.92	1.30	0.90	77.1
MoSe₂ + 0.7 nm CoPc				
N1	398.63	0.48	0.10	30.3
N2	399.06	0.48	0.10	30.3
S	399.41	0.48	0.10	1.9
Mo 3p _{3/2}	394.78	1.20	1.00	37.5
b) MoSe₂ + 0.3 nm CoPcF₁₆	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
N1	398.65	0.72	0.42	18.7
N2	399.41	0.72	0.42	18.7
S	401.58	0.72	0.42	4.8
Mo 3p _{3/2}	394.75	1.30	1.00	57.9
n-MoSe₂ + 0.4 nm CoPcF₁₆				
N1	398.93	0.62	0.35	25.7
N2	398.30	0.62	0.35	25.7
S	399.86	0.62	0.35	0.1
Mo 3p _{3/2}	395.08	1.30	0.81	47.4
MoSe₂ + 1.9 nm CoPcF₁₆				

N1	398.85	0.57	0.35	43.6
N2	399.27	0.57	0.35	43.6
S	401.08	0.57	0.35	0.2
Mo 3p _{3/2}	394.93	1.45	0.81	10.6

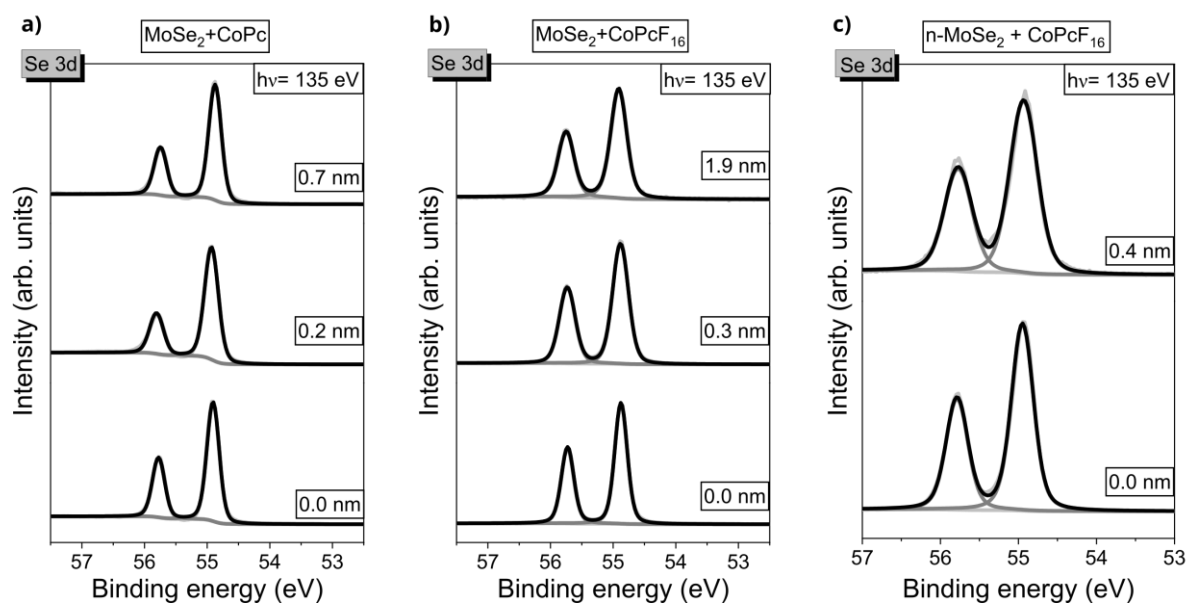


Figure 7.21: Surface sensitive Se 3d core level spectra for a) CoPc/MoSe₂, b) CoPcF₁₆/MoSe₂, and c) CoPcF₁₆/n-MoSe₂. Due to uncertainties in the calibration procedure, all binding energies are shifted to a reference value. In all cases, no interface peaks could be detected that would indicate a stronger interaction at this interface.

Table 7.14: Fit parameters for the Se 3d spectra obtained at an excitation energy of 135 eV.

a) MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Se 3d _{5/2}	54.91	0.21	0.05	66.6
Se 3d _{3/2}	55.78	0.21	0.05	33.4
MoSe₂ + 0.2 nm CoPc				
Se 3d _{5/2}	55.23	0.23	0.05	73.4
Se 3d _{3/2}	56.11	0.23	0.05	26.6
MoSe₂ + 0.7 nm CoPc				
Se 3d _{5/2}	55.07	0.21	0.05	70.6
Se 3d _{3/2}	55.95	0.21	0.05	29.4

b) MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Se 3d _{5/2}	54.87	0.20	0.07	61.4
Se 3d _{3/2}	55.72	0.20	0.07	38.6
MoSe₂ + 0.3 nm CoPcF₁₆				
Se 3d _{5/2}	54.82	0.26	0.07	61.4
Se 3d _{3/2}	55.67	0.26	0.07	38.7
MoSe₂ + 1.9 nm CoPcF₁₆				
Se 3d _{5/2}	54.54	0.24	0.10	62.8
Se 3d _{3/2}	55.37	0.24	0.10	37.3
c) n-MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]

7. Appendix

Se 3d _{5/2}	54.95	0.28	0.10	62.7
Se 3d _{3/2}	55.79	0.28	0.10	37.3
n-MoSe₂ + 0.4 nm CoPcF₁₆				
Se 3d _{5/2}	54.94	0.36	0.07	62.7
Se 3d _{3/2}	55.78	0.36	0.07	37.3

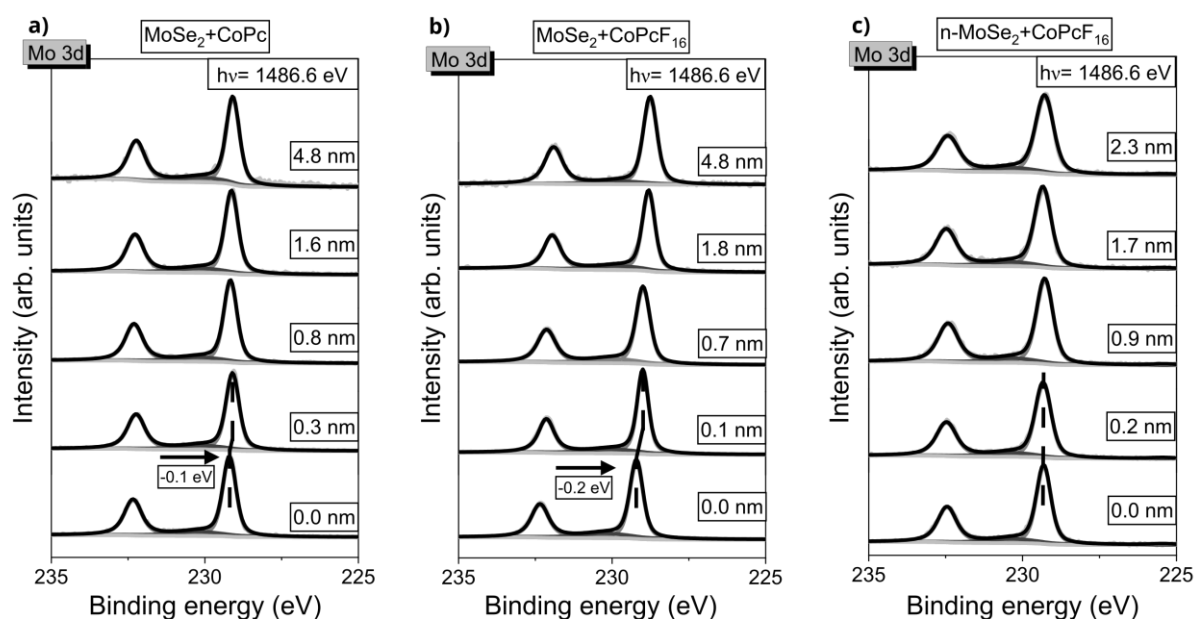


Figure 7.22: Mo 3d core level spectra acquired at an excitation energy of 1486.6 eV for a) the MoSe₂/CoPc, b) the MoSe₂/CoPcF₁₆ and c) the n-MoSe₂/CoPcF₁₆ interface.

Table 7.15: Fit parameters for the Mo 3d spectra depicted in Figure 7.22.

a) MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo 3d _{5/2}	299.18	0.38	0.23	52.3
Mo 3d _{3/2}	232.33	0.38	0.46	33.8
Se 3s	230.18	0.00	1.83	12.4
MoSe₂ + 0.3 nm CoPc				
Mo 3d _{5/2}	229.09	0.38	0.23	52.2
Mo 3d _{3/2}	232.22	0.38	0.46	33.9
Se 3s	230.09	0.00	1.83	12.4
MoSe₂ + 0.8 nm CoPc				
Mo 3d _{5/2}	299.16	0.38	0.23	52.2
Mo 3d _{3/2}	232.31	0.38	0.46	33.9
Se 3s	23.16	0.00	1.83	12.4
MoSe₂ + 1.6 nm CoPc				
Mo 3d _{5/2}	229.14	0.38	0.23	52.3
Mo 3d _{3/2}	232.29	0.38	0.46	33.8
Se 3s	230.14	0.00	1.83	10.4
MoSe₂ + 4.8 nm CoPc				
Mo 3d _{5/2}	229.09	0.38	0.23	52.2
Mo 3d _{3/2}	232.22	0.38	0.46	33.9
Se 3s	230.09	0.00	1.83	12.4

7. Appendix

b) MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo 3d _{5/2}	229.22	0.37	0.23	52.0
Mo 3d _{3/2}	232.37	0.37	0.46	33.2
Se 3s	230.22	0.00	1.97	14.9
MoSe₂ + 0.1 nm CoPcF₁₆				
Mo 3d _{5/2}	229.00	0.38	0.23	52.4
Mo 3d _{3/2}	232.15	0.38	0.46	31.8
Se 3s	230.00	0.00	1.97	13.9
MoSe₂ + 0.7 nm CoPcF₁₆				
Mo 3d _{5/2}	228.98	0.40	0.23	52.8
Mo 3d _{3/2}	232.13	0.40	0.46	31.8
Se 3s	229.98	0.00	1.97	13.9
MoSe₂ + 1.5 nm CoPcF₁₆				
Mo 3d _{5/2}	228.79	0.40	0.23	52.8
Mo 3d _{3/2}	231.93	0.40	0.46	32.4
Se 3s	229.79	0.00	1.97	13.1
MoSe₂ + 4.8 nm CoPcF₁₆				
Mo 3d _{5/2}	228.75	0.40	0.23	53.4
Mo 3d _{3/2}	231.89	0.40	0.46	32.6
Se 3s	229.75	0.00	1.97	14.0

c) n-MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Mo 3d _{5/2}	229.32	0.42	0.24	53.5
Mo 3d _{3/2}	232.45	0.42	0.47	34.1
Se 3s	230.32	0.00	1.81	11.3
n-MoSe₂ + 0.2 nm CoPcF₁₆				
Mo 3d _{5/2}	229.32	0.48	0.24	54.6
Mo 3d _{3/2}	232.45	0.48	0.47	33.8
Se 3s	230.32	0.00	1.81	10.7
n-MoSe₂ + 0.9 nm CoPcF₁₆				
Mo 3d _{5/2}	229.27	0.50	0.24	54.8
Mo 3d _{3/2}	232.40	0.50	0.47	33.7
Se 3s	230.27	0.00	1.81	10.5
n-MoSe₂ + 1.7 nm CoPcF₁₆				
Mo 3d _{5/2}	229.27	0.50	0.24	54.9
Mo 3d _{3/2}	232.40	0.50	0.47	33.7
Se 3s	230.27	0.00	1.81	10.4
n-MoSe₂ + 2.3 nm CoPcF₁₆				
Mo 3d _{5/2}	229.27	0.56	0.24	55.8
Mo 3d _{3/2}	232.40	0.56	0.47	33.4
Se 3s	230.27	0.00	1.81	9.8

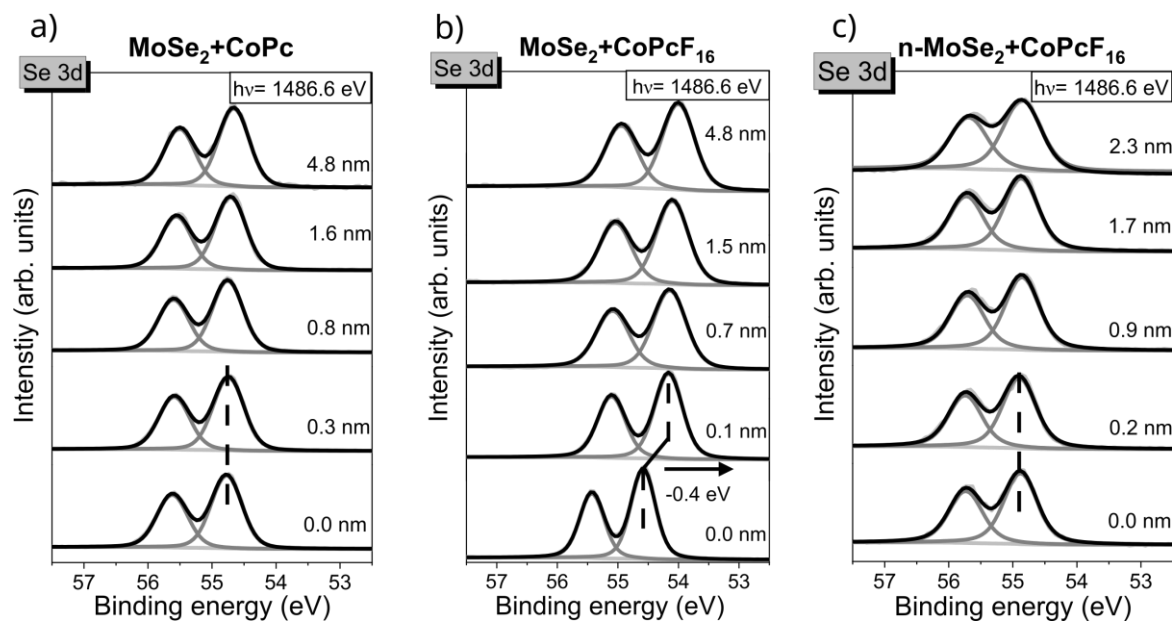


Figure 7.23: Substrate related core level spectra at an excitation energy of 1486.6 eV for a) CoPc/MoSe₂, b) CoPcF₁₆/MoSe₂, and c) CoPcF₁₆/n-MoSe₂. Shifts to lower binding energies with increasing film thickness in the case of CoPcF₁₆/MoSe₂ can be explained by a p-doping of the substrate.

Table 7.16: Fit parameters for the Se 3d spectra depicted in Figure 7.23.

a) MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Se 3d _{5/2}	54.77	0.51	0.10	58.1
Se 3d _{3/2}	55.62	0.51	0.10	41.9
MoSe₂ + 0.3 nm CoPc				
Se 3d _{5/2}	54.67	0.51	0.10	58.1
Se 3d _{3/2}	55.53	0.51	0.10	41.8
MoSe₂ + 0.8 nm CoPc				
Se 3d _{5/2}	54.78	0.51	0.10	58.1
Se 3d _{3/2}	55.61	0.51	0.10	41.9
MoSe₂ + 1.6 nm CoPc				
Se 3d _{5/2}	54.72	0.51	0.10	58.2
Se 3d _{3/2}	55.57	0.51	0.10	41.9
MoSe₂ + 4.8 nm CoPc				
Se 3d _{5/2}	54.67	0.51	0.10	58.2
Se 3d _{3/2}	55.52	0.51	0.10	41.9
b) MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Se 3d _{5/2}	54.38	0.40	0.13	58.1
Se 3d _{3/2}	55.23	0.40	0.13	41.9
MoSe₂ + 0.1 nm CoPcF₁₆				
Se 3d _{5/2}	54.26	0.42	0.13	58.1
Se 3d _{3/2}	55.11	0.42	0.13	41.9

7. Appendix

MoSe₂ + 0.7 nm CoPcF₁₆				
Se 3d _{5/2}	54.2	0.45	0.13	58.1
Se 3d _{3/2}	55.06	0.45	0.13	41.9
MoSe₂ + 1.5 nm CoPcF₁₆				
Se 3d _{5/2}	54.18	0.45	0.13	58.1
Se 3d _{3/2}	55.02	0.45	0.13	41.9
MoSe₂ + 4.8 nm CoPcF₁₆				
Se 3d _{5/2}	54.09	0.49	0.13	58.1
Se 3d _{3/2}	54.94	0.49	0.13	41.9
c) n-MoSe₂	Position [eV]	Gaussian width [eV]	Lorentzian width [eV]	rel. area [%]
Se 3d _{5/2}	54.84	0.48	0.24	57.8
Se 3d _{3/2}	55.70	0.48	0.24	42.2
n-MoSe₂ + 0.2 nm CoPcF₁₆				
Se 3d _{5/2}	54.85	0.48	0.24	57.8
Se 3d _{3/2}	55.71	0.48	0.24	42.2
n-MoSe₂ + 0.9 nm CoPcF₁₆				
Se 3d _{5/2}	54.74	0.49	0.24	57.7
Se 3d _{3/2}	55.70	0.49	0.24	42.3
n-MoSe₂ + 1.7 nm CoPcF₁₆				
Se 3d _{5/2}	54.85	0.49	0.24	57.8
Se 3d _{3/2}	55.71	0.49	0.24	42.3

n-MoSe₂ + 2.3 nm CoPcF₁₆				
Se 3d _{5/2}	54.81	0.56	0.24	57.8
Se 3d _{3/2}	55.66	0.56	0.24	42.3

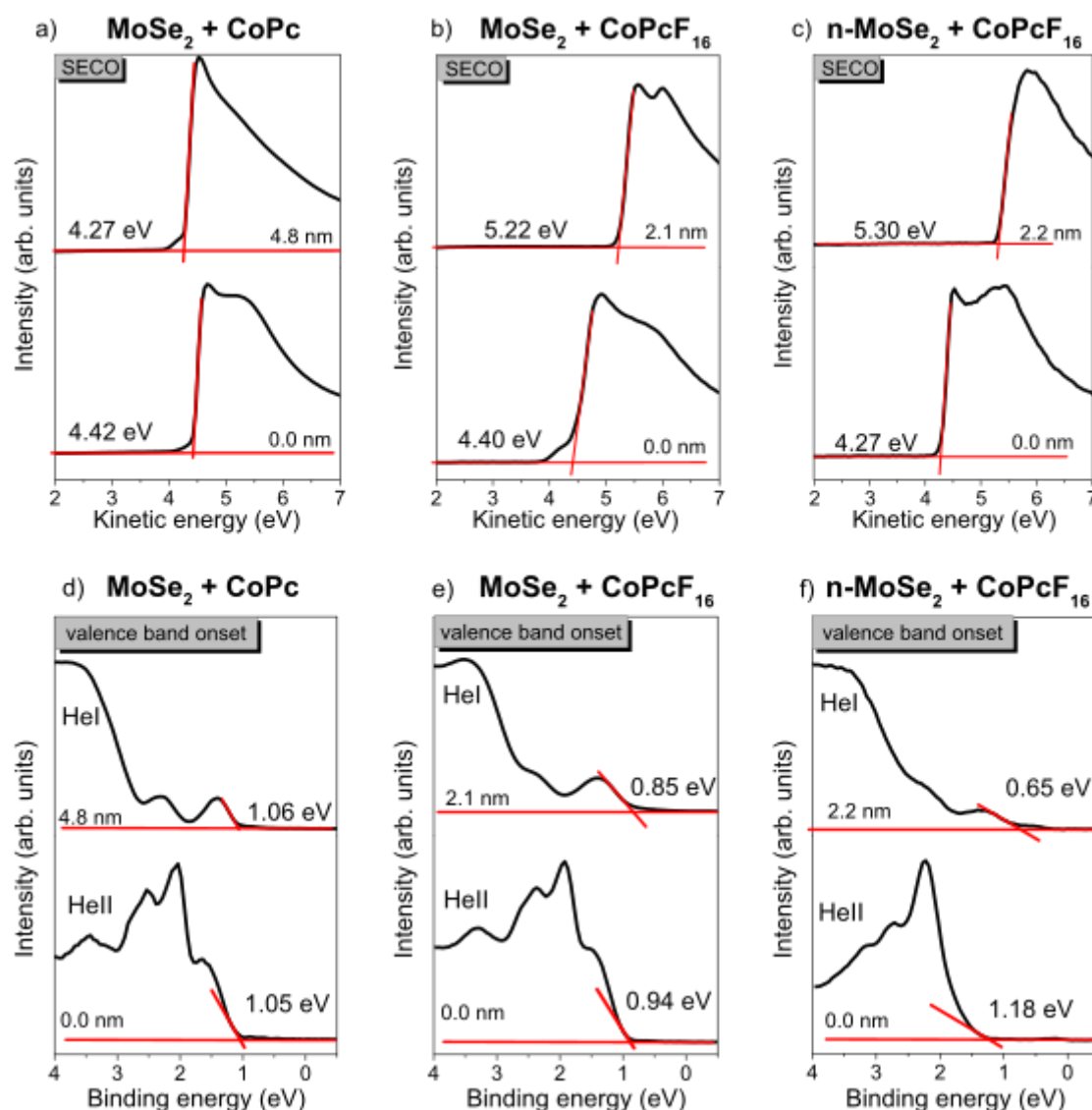


Figure 7.24: UPS valence band spectra measured at normal emission used for energy level alignment shown in Figure 7.25. a-c) Secondary electron cut-off (SECO), measured with He I excitation and a BIAS voltage of 10 or 15 V. d-f) Low binding energy region. Satellites were subtracted. To detect low-intensity features at Γ in the case of slightly tilted sample regions, He II excitation was employed for the pristine substrate, providing information over a broader $k_{\parallel}$ range. Instead, at higher coverages, He I excitation is used, which is advantageous due to the more favorable C 2p and C 2s cross-sections.

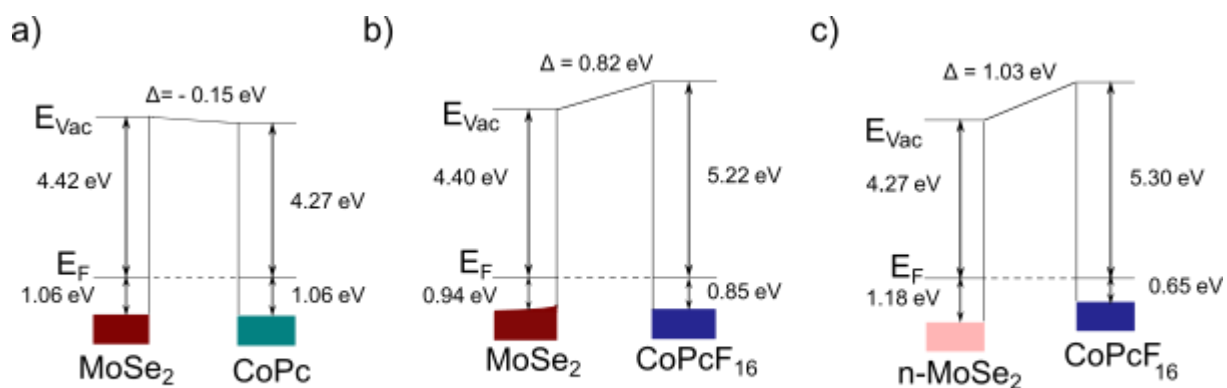


Figure 7.25: Energy level alignment for coverages $> 2\text{nm}$. a) CoPc/MoSe₂, b) CoPcF₁₆/MoSe₂, and c) CoPcF₁₆/n-MoSe₂.

Table 7.17: Fitting results for the peak position and peak area for the 64 luminescence spectra for both MoSe₂ and n-MoSe₂.

Peak	MoSe ₂		n-MoSe ₂		Wavelength Difference
	Peak Maximum	Peak area (%)	Peak Maximum	Peak area (%)	
1	552.1 nm	132119.1 (10)	551.8 nm	168587.5 (13)	0.3 nm
2	578.6 nm	92761.25 (7)	582.9 nm	263225.8 (20)	4.3 nm
3	631.4 nm	184279.7 (14)	633.0 nm	265702.3 (20)	1.6 nm
4	650.1 nm	916776.5 (69)	675.9 nm	624437.1 (47)	25.8 nm

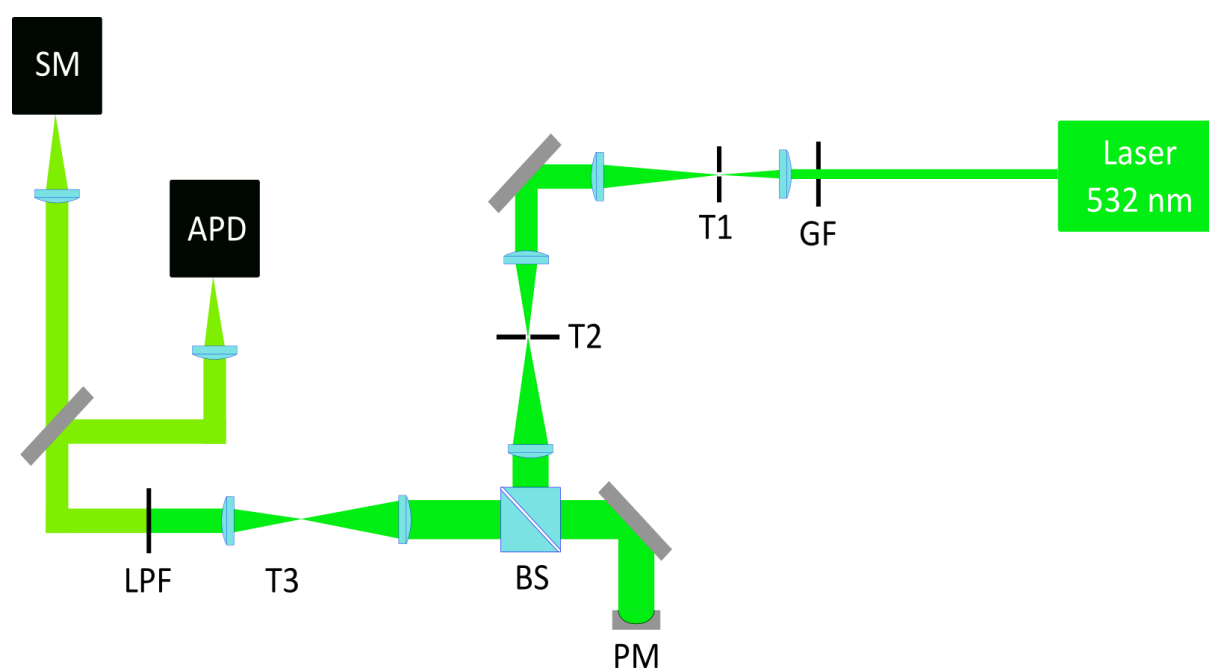


Figure 7.26: Home-built confocal microscope used for recording the luminescence spectra. GF = greyfilter; T1,2,3 = Telescopes 1,2 and 3 BS = beamsplitter; PM = parabolic mirror; LPF = longpass filter; APD = avalanche photodiode; SM = spectrometer.

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List of Abbreviations and Symbols

List of Symbols:

a	Monolayer thickness
α	Polar angle
a_1, a_2	primitive vector
$\vec{b}_1, \vec{b}_2$	Lattice vectors of the reciprocal space
d	Layer thickness
δ	Ionicity
Δ	Interface dipole
ΔE_c	Conduction band offset
ΔE_v	Valence band offset
E	Electric field vector
e	Unit vector in direction of the electric field vector
E_B	Binding energy
E_g	Band gap
E_{kin}	Kinetic energy
E_{vac}	Vacuum level
ε_i	Orbital energy of the initial state i
ε_r	Dielectric constant
γ	Polar angle
γ^{-1}	Angle of emittance of synchrotron radiation
ϕ_s	Work function of the spectrometer
ϕ_B	Schottky barrier height
ϕ	Work function
ϕ	Azimuthal angle
h	Planck constant: $h \approx 6.626 \times 10^{-34}$ Js
$\hbar$	Reduced Planck constant: $\hbar \approx 1.05 \cdot 10^{-34}$ Js
I	Intensity
j	Total angular momentum quantum number

k_x, k_y	Coordinates in reciprocal space
l	Azimuthal quantum number
λ	Inelastic mean free path
M	Molar mass
m_e	Electron mass: $m_e \approx 9.11 \cdot 10^{-31}$ kg
μ_B	Magnetic moment
n	Number of atoms in the molecule
N	Number of electrons
N	Avogadro's number: $N \approx 6.022 \times 10^{23}$ mol ⁻¹
ν	Frequency
O	Organic molecule
ω	Angular frequency
p	Momentum operator
P_{if}	Transition probability from initial to final state
q^P	Pauling charge
ρ	Density
$\rho_f(E)$	Energy density of final states
R_D	Dynamic relaxation energy
S	Pinning factor
S	Spin quantum number
σ_x	Sensitivity factor
t	Thickness
t	Time
θ	Angle between sample and analyzer
$\bar{V}$	Harmonic perturbation
x	Number of atoms in the chemical formula
χ	Electron affinity
χ	Electronegativity

List of Abbreviations:

2D	Two-dimensional
ARPES	Angle-resolved Photoemission spectroscopy
BESSY II	<i>Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung</i>
CB	Conduction band
CBM	Conduction band minimum
CCD	Charge-coupled device
CVD	Chemical vapor deposition
e.g.	<i>Exempli gratia</i> (for example)
ELA	Energy level alignment
EXAFS	Extended X-ray absorption fine structure
FET	Field-effect transistor
FWHM	Full width at half maximum
HOMO	Highest occupied molecular orbital
ICT	Integer charge transfer
IE	Ionization energy
IEF	Imaging energy filter
IF	Interface states
IP	Ionization potential
IS	Integrated sample stage
IMFP	Inelastic mean free path
KARA	Karlsruhe research accelerator
KPFM	Kelvin probe force microscopy
LUMO	Lowest unoccupied molecular orbital
MO	Molecular orbital
NADH	Nicotinamide adenine dinucleotide
NEXAFS	Near edge X-ray absorption fine structure
OFET	Organic field-effect transistor
OLED	Organic light-emitting diode
OPV	Organic photovoltaic
PDMS	Polydimethylsiloxane

PEEM	Photoemission electron microscopy
PES	Photoemission spectroscopy
PL	Photoluminescence
PTCDA	Perylene-3,4,9,10-tetracarboxylic dianhydride
PVC	Polyvinylchloride
QCM	Quartz crystal microbalance
QCMB	Quartz crystal microbalance
Ref	Reference
RGB	Red, green, blue
RoI	Region of interest
SC	Semiconductor
SECO	Secondary electron cutoff
SEM	Scanning electron microscopy
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
SXPS	Surface sensitive X-ray Photoelectron spectroscopy
TCNQ	7,7,8,8-tetracyanoquinodimethane
TMDC	Transition metal dichalcogenide
TMPc	Transition metal phthalocyanine
UHV	Ultrahigh vacuum
UPS	Ultraviolet photoemission spectroscopy
UV	Ultraviolet
V	Vacancy
VB	Valence band
VBM	Valence band maximum
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near edge structure
XPS	X-ray photoemission spectroscopy

List of Figures & Tables

List of Figures

Figure 2.1: Structure of 2H-TMDCs from a) y perspective, b) x perspective with the height between the sulfur plane and the molybdenum plane $h=1.58 \text{ \AA}$ for MoS_2 (MoSe_2 : $h=1.67 \text{ \AA}$) and c) z-perspective with added lattice parameter $a=3.16 \text{ \AA}$ (MoSe_2 : $a=3.29 \text{ \AA}$ ³⁵) and the Mo-S distance $a_0=a^2/3+h^2=2.41 \text{ \AA}$ (MoSe_2 : $a_0=2.54 \text{ \AA}$). ^{33,34}	6
Figure 2.2: Occupation of molecular orbitals in 2H-TMDCs. Own representation based on Kolobov et al. ³⁰	7
Figure 2.3: a) Hexagonal reciprocal lattice of MoS_2 and the schematic band structure of b) bulk MoS_2 and c) single layer MoS_2 . The symmetry and transitions for MoSe_2 are comparable. Own schematical representation based on the publication by Roldan et al. ^{30,38}	8
Figure 2.4: Standard procedure for mechanical exfoliation (scotch tape method): a) Removal of top layers of the TMDC from bulk MoS_2 , b) repeated stripping down to monolayer flakes with scotch tape, c) transfer to PDMS stamp and d) stamping of Monolayer flakes onto the desired substrate.	9
Figure 2.5: Chemical structure of transition metal phthalocyanines. a) ball-and-stick model of CoPc viewed in the z-direction, b) ball-and-stick model of CoPc viewed in the xy-direction, c) chemical formula of CoPc and d) chemical formula of CoPcF_{16} . C_1 represents carbon atoms bond to other carbon (C-C) or hydrogen (C-H) atoms, C_2 represents carbon atoms bond to nitrogen atoms (C-N) and C_3 represents carbon atoms bond to fluorine atoms (C-F). Bridging Nitrogen atoms are labeled as N_1 and Nitrogen atoms bond/coordinated to the cobalt atom are labeled as N_2	11
Figure 2.6: Most common vacancies in MoS_2 : a) depicts V_s highlighted by the red dotted line, b) depicts the MoS_2 defect with the missing two sulfur atoms highlighted by the red dotted line.	14
Figure 2.7: Electronic structure of a semiconductor substrate and a metal a) without contact and b) in contact under formation of an interface state (IF) and an interface dipole Δ and the resulting band bending.	16
Figure 2.8: Different types of semiconductor-organic band gap lineups. For Type I Straddling, the HOMO-LUMO gap of the organic molecule lies in between the band gap of the semiconductor. In the case of Type II, Staggered interface, the HOMO and LUMO of the organic molecule both lie below or above the respective bands of the	

semiconductor. For the Type III, Broken gap, both the HOMO and LUMO of the organic molecule lie below the VBM or above the CBM of the semiconductor. Own representation based on the publication by Xu et al. ⁸⁰	18
Figure 2.9: Electronic structure of a semiconductor substrate and an organic molecule a) without contact and b) in contact under formation of an interface state (IF), an interface dipole Δ and band bending. Own representation based on Ishii et al. ⁸¹	19
Figure 2.10: Formation of synchrotron radiation at an electron storage ring. The electrons, which have been accelerated to relativistic velocities by a linear accelerator or booster, are injected into the storage ring where they interact with a magnetic field to keep their circular trajectory under emission of synchrotron radiation as depicted.	22
Figure 2.11 :Photoionization and detection of photoelectrons at the sample and the analyzer. Own representation based on Henzler et al. ⁸⁹	23
Figure 2.12: a) Formation of photoelectrons in UPS and b) inelastic mean free path (IMFP) at $E_B=0$ eV for common light sources (He I, He II, Al $K\alpha$, Mg $K\alpha$). Own representation using the formula given by Seah and Dench for inorganic molecules. ⁹³	28
Figure 2.13: Helium discharge lines including satellites for a) Helium I excitation and b) Helium II excitation, c) summarizes the resulting excitation energies, and relative shifts and intensities for the different transitions (values taken from ref ⁹⁴).	29
Figure 2.14: a) Geometry of an ARPES experiment with either a movable detector or a movable sample. b) Geometry of k_x - k_y momentum maps of a hexagonal system with the most important points of high symmetry.	30
Figure 2.15: Schematic composition of a PEEM set-up with an imaging energy filter (IEF). The emitted photoelectrons are extracted and magnified via the objective lens. Via the aperture stray electrons are filtered out. The octupole stigmator corrects astigmatism. The projection lenses further magnify the image. The electron beam is focused via the entrance lense. The imaging electron filter filters high energy electrons to reduce chromatic aberration. The multichannel plate increases the photoelectron signal. A phosphorous screen transforms the electronic signal into an optical signal which is then detected by the charge-coupled device (CCD) camera.	32
Figure 2.16: Scheme of X-ray absorption: a) Attenuation of the inciting intensity of the X-rays according to Beer's law and b) Observed transition of a photoelectron from a core level to an excited state.	34

Figure 2.17: Geometry of orbitals with respect to a) the molecular plane, b) π^* and σ^* orbitals, c) d_{z^2} orbital and d) $d_{x^2-y^2}$ orbitals.	35
Figure 2.18: Geometry at the molecular plane according to Stöhr. ¹⁰² With θ as the angle of incident which is equal to the polar angle of $E^{\parallel}$ and the azimuthal angle ϕ . a) depicts the vector final state (green arrow) in the direction O characterized by ϕ and the polar angle α . δ describes the angle between O and $E^{\parallel}$. For the plane final state (white plane) depicted in b) its direction is given by N characterized by ϕ and the polar angle γ . The angle between N and $E^{\parallel}$ is given as ϵ	36
Figure 2.19: Geometry of the electric field vector in comparison to the molecular plane with exemplary d_{z^2} orbital for a) $\theta = 45^\circ$ incidence, b) normal incidence ($\theta = 90^\circ$) and c) grazing incidence ($\theta = 10^\circ$).	38
Figure 3.1: Mo 3d core level spectra for the MoS ₂ /metal interface for (sub-)monolayer coverage of (a) gold, (b) copper and (c) titanium. Interface peaks are observed after deposition of titanium (arrows in Fig. 3.1c), indicating a chemical interaction.	46
Figure 3.2: Valence band (He I excitation) spectra recorded at an angle of 30° with respect to the analyzer for a multilayer coverage of a) gold, b) copper and c) titanium.	47
Figure 3.3: Energy level alignment (ELA) diagrams of the MoS ₂ /metal interfaces for coverages of a) 1.10 nm Au, b) 0.93 nm Cu and c) 1.56 nm Ti.	49
Figure 3.4: SEM images for a) pristine MoS ₂ , b) MoS ₂ +1.5 nm Au, c) MoS ₂ +0.4 nm Au (annealed at 250 °C), d) MoS ₂ +0.9 nm Cu, e) MoS ₂ +0.8 nm Cu (annealed at 250 °C) f) MoS ₂ +0.4 nm Ti.	50
Figure 3.5: Co 2p _{3/2} spectra of MoS ₂ /Au/CoPcF ₁₆ interfaces for a) (sub-)monolayer coverage of Au (not annealed); b) (sub-)monolayer coverage of Au (annealed); c) multilayer coverage of Au (annealed).	51
Figure 3.6: Co 2p _{3/2} spectra of MoS ₂ /Cu/CoPcF ₁₆ interfaces for a) (sub-)monolayer coverage of Cu (not annealed); b) (sub-)monolayer coverage of Cu (annealed); and c) multilayer coverage of Cu (annealed).	52
Figure 3.7: Angle-dependent XAS measurements in the Co L ₃ region show intensity differences of features A and the two B features depending on the orientation of the electric field with respect to the sample for CoPcF ₁₆ shown in (a) and CoPc shown in (b) on bulk MoS ₂ , with the respective structural formula below each spectrum.	62
Figure 3.8: (a – c) Optical microscope images of MoS ₂ flakes on SiO _x (a, flake 1) and on TiO _x substrates (b) and (c), flake 2 and flake 3 respectively. Averaged images of the	

work function contrast sequence for the samples containing flake 1, flake 2 and flake 3 are shown in (d), (e) and (f) respectively. The grayscale is arbitrary to maximize contrast. (g – i) μ -PES spectra of the secondary electron cutoff and the calculated work functions.	64
Figure 3.9: PEEM XAS measurements at an incident angle of 25° in the region of the Co L edge. (a – c) show average intensity images with an arbitrarily chosen grayscale to maximize contrast. Intensity differences are mostly based on secondary electron counts and to a lesser extent on spectral features. Selected regions of interests in these images are like those chosen for work function contrast measurements shown in Figure 3.8. (d – f) show the normalized spectra of the respective RoI for the flakes 1–3 above.....	67
Figure 3.10: ARPES band structure of MoS ₂ before (a, b, c) and after sputtering (d, e, f) and the subsequent deposition of a monolayer film of CoPcF ₁₆ (g, h, i) and the integrated valence band structures (j, k, l) measured at an excitation energy of $h\nu=75$ eV.	76
Figure 3.11: Co L _{2,3} -XAS spectra of CoPcF ₁₆ coverages in the mono- or multilayer range on Ne ⁺ or Ar ⁺ sputtered MoS ₂	79
Figure 3.12: Co 2p XPS spectra before and after the deposition of mono- and multilayer films of CoPcF ₁₆ after a) 2.5 min Ne sputtering b) 2.5 min Ar sputtering c) 10 min Ne-sputtering and d) 10 min Ar sputtering.	81
Figure 3.13: Molecule-related C 1s (a,b,c) and N 1s (d,e,f) core level spectra on differently sputtered MoS ₂ surfaces. The absence of additional interface peaks indicates the absence of strong, local interactions.	82
Figure 3.14: X-ray photoelectron spectroscopy (XPS) measurements of the Mo 3d core levels of MoS ₂ following the sputtering with Ar ⁺ and Ne ⁺ and the deposition of CoPcF ₁₆ measured at excitation energies of 900 and 300 eV, resulting in different inelastic mean free paths λ of the detected photoelectrons and thus a different surface sensitivity. Additional peaks after sputtering (dark grey lines) are attributed to Mo ⁰ species. Shifts towards higher(lower) binding energies are indicated by black arrows.....	84
Figure 4.1: Position of important energy levels of the MoSe ₂ substrate and the molecules CoPc and CoPcF ₁₆ with respect to the vacuum level E_v as obtained from ultraviolet photoemission spectroscopy (UPS). The CoPc or CoPcF ₁₆ film thickness on MoSe ₂ was > 1.8 nm. The indirect band gap ($E_{VBM} - E_{CBM}$) for MoSe ₂ and the optical	

gaps of the molecules E(HOMO)-E(LUMO)) were taken from the literature (rounded to a half tenth of an eV). ^{20,216,217}	90
Figure 4.2: Comparison of ARPES band structures before and after deposition of CoPc or CoPcF ₁₆ : a-c) pristine substrates, d-f) coverages in the monolayer range. The same crystal was used for a) and b), the slight energy shift is ascribed to inhomogeneities of the crystal. For the n-doped crystal (c), intensity at the doping level can be seen in vicinity to the K point.....	93
Figure 4.3: Angle-dependent Co L _{2,3} edge XAS spectra for coverages in the monolayer range a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /MoSe ₂ , c) CoPcF ₁₆ /n-type MoSe ₂ . Only for CoPc/MoSe ₂ the spectral shape is very similar to the bulk indicating the absence of charge transfer across the interface involving the Co atom of CoPc.	95
Figure 4.4: Co 2p _{3/2} core level spectra (hν = 1486.6 eV) of a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /MoSe ₂ , and c) CoPcF ₁₆ /n-MoSe ₂ for thicknesses ranging from (sub-)monolayer to several multilayers. The additional interface peak for CoPcF ₁₆ /n-MoSe ₂ indicates a charge transfer to the Co ion of CoPcF ₁₆	96
Figure 4.5: Molecule related C 1s core level spectra. a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /(n-)MoSe ₂ . The spectral shape is very similar to the bulk indicating the absence of strong interactions involving the carbon atoms of the macrocycle of the molecules.....	97
Figure 4.6: Energy level alignment for coverages in the monolayer range: a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /MoSe ₂ , c) CoPcF ₁₆ /n-type MoSe ₂	98
Figure 4.7: Photoluminescence spectra and fitted peaks (Gaussian function) for CoPcF ₁₆ on various substrates: a) Comparison of doped and undoped MoSe ₂ and Si substrates. b) Representative peak fitting for a CoPcF ₁₆ /MoSe ₂ PL spectrum. c)–f) Comparison of the four subpeaks. The red and grey solid lines represent the averaged spectra obtained from 64 measurements acquired on CoPcF ₁₆ /n-MoSe ₂ and CoPcF ₁₆ /MoSe ₂ , respectively. The shaded areas indicate the corresponding deviations calculated from spectra collected at different sample positions.	101
Figure 5.1: Band alignment with respect to the vacuum level of the group VI bulk TMDCs, CoPc and CoPcF ₁₆ with their respective band gaps and ionization potentials. ^{20,36,237–239}	106
Figure 5.2: Roll-to-roll process to produce polycrystalline MoS ₂ flakes on silicon wafers according to Sozen et al.	108
Figure 7.1: Core level spectra of the MoS ₂ /metal interface for (sub-)monolayer coverages of the metal depicting a) Au 4f, b) Cu 2p and c) Ti 2p.	115

Figure 7.2: S 2p core level spectra of the MoS ₂ /metal interface for a (sub-)monolayer of a) gold, b) copper and c) titanium.	116
Figure 7.3: Valence band (He I excitation) spectra recorded at an angle of 0° towards the analyzer for a multilayer coverage of a) gold, b) copper and c) titanium.	118
Figure 7.4: Core level spectra of the MoS ₂ /metal interface for multilayer coverages of the metal depicting a) Au 4f, b) Cu 2p and c) Ti 2p.	118
Figure 7.5: Valence band (He I excitation) spectra recorded at an angle of 30° towards the analyzer for a (sub-)monolayer coverage of a) gold, b) copper and c) titanium.	119
Figure 7.6: Secondary electron cut-off spectra of the MoS ₂ /metal interface for a multilayer coverage of a) gold, b) copper and c) titanium.	119
Figure 7.7: Mo 3d core level spectra of the MoS ₂ /metal interface for a multilayer of a) gold, b) copper and c) titanium.	120
Figure 7.8: S 2p core level spectra of the MoS ₂ /metal interface for a multilayer of a) gold, b) copper and c) titanium.	122
Figure 7.9: Micro-XPS measurements on a MoS ₂ flake on native oxide silicon substrate, referred to as flake 1 in the main text. The intensity maps show the summed intensity measured over the S2p region (a), the Si2p region (b) and the Mo3d region (c). The bright pixels have an overall high intensity while the intensity in darker areas is low. Below each image the average spectra, integrated over the total detector area is shown.	125
Figure 7.10: Micro-XPS measurements on a MoS ₂ flake on a titanium coated substrate, referred to as flake 2 in the main text. The intensity maps show the summed intensity measured over the S2p region (a), the Ti3p region (b) and the Mo3d region (c). The bright pixels have an overall high intensity while the intensity in darker areas is low. Below each image the average spectra, integrated over the total detector area is shown.	126
Figure 7.11: Micro-XPS measurements on a MoS ₂ flake on a titanium coated substrate, referred to as flake 3 in the main text. The intensity maps show the summed intensity measured over the S2p region (a), the Ti3p region (b) and the Mo3d region (c). The bright pixels have an overall high intensity while the intensity in darker areas is low. Below each image the average spectra, integrated over the total detector area is shown.	126

Figure 7.12: Angle dependent XAS measurements of (a) N K edge region of clean bulk MoS ₂ (red) and bulk MoS ₂ with an overlayer of CoPcF ₁₆ (black). (b) N K edge region after the second deposition of CoPcF ₁₆	127
Figure 7.13: (a) and (e) display the red channel of the RGB optical microscope images of the samples referred to as flake 2 and 3 in the main text. The contrast profiles produced in (b) and (f) were generated using ImageJ and correspond to the values along the yellow line shown in (a) and (e). (c) presents a photoluminescence (PL) map of the flake shown in (a). Strong PL is observed in the monolayer areas, where direct band transitions occur. (d) shows the PL spectra of the monolayer (black) and the bulk (red) region. The peak maximum at an energy of 1.88 eV is typical for structures with two or less layers. ¹⁷⁶ In addition, the increased photoluminescence in comparison to the bulk area is characteristic for such thin structures. ¹⁷⁷	128
Figure 7.14: (a) displays the optical microscope image of an exfoliated flake on a silicon substrate with a native oxide layer. (b) and (d) show the red channel of the RGB optical microscope image of the flake presented in (a), as well as of flake 1 discussed in the main text. (c) and (e) depict the contrast values along the lines drawn in (b) and (d), which were generated using ImageJ.	129
Figure 7.15: Measured BIAS voltages for flakes 1-3 (a–c) and the averaged spectra from the marked region of interest (d–f). (g) measured secondary electron cut-off for the clean substrates.	129
Figure 7.16: kx-ky-maps at selected energies showing K (a-c) and M (d-f) for the three pristine MoS ₂ samples and ARPES band structures of the multilayer CoPcF ₁₆ coverages (g-i) on given substrates.....	130
Figure 7.17: X-ray photoelectron spectroscopy (XPS) measurements of the S 2p core levels of MoS ₂ following the sputtering with Ar and Ne and the deposition of CoPcF ₁₆	141
Figure 7.18: Valence band spectra derived from the ARPES experiments at normal emission ($\theta = 50^\circ$) for a) the MoSe ₂ /CoPc interface, b) the MoSe ₂ /CoPcF ₁₆ interface and c) the n-MoSe ₂ /CoPcF ₁₆ interface. The horizontal black arrows highlight the shift in Valence band by 0.05 eV towards higher (lower) binding energies for the MoSe ₂ /CoPc(F ₁₆) interfaces. The HOMO and interface states of the CoPcF ₁₆ molecule are marked by black arrows.....	148
Figure 7.19: Angle-dependent XAS spectra of thicker films (about 2 nm) of CoPc and CoPcF ₁₆ on MoSe ₂	148

Figure 7.20: N1s core level spectra for a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /(n-)MoSe ₂ , and c) CoPcF ₁₆ /n-MoSe ₂ . The two components are assigned to the two chemically different nitrogen atoms. The peak shape is similar in all cases, indicating the absence of strong interactions involving the N atom.....	150
Figure 7.21: Surface sensitive Se 3d core level spectra for a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /MoSe ₂ , and c) CoPcF ₁₆ /n-MoSe ₂ . Due to uncertainties in the calibration procedure, all binding energies are shifted to a reference value. In all cases, no interface peaks could be detected that would indicate a stronger interaction at this interface.....	152
Figure 7.22: Mo 3d core level spectra acquired at an excitation energy of 1486.6 eV for a) the MoSe ₂ /CoPc, b) the MoSe ₂ /CoPcF ₁₆ and c) the n-MoSe ₂ /CoPcF ₁₆ interface.	154
Figure 7.23: Substrate related core level spectra at an excitation energy of 1486.6 eV for a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /MoSe ₂ , and c) CoPcF ₁₆ /n-MoSe ₂ . Shifts to lower binding energies with increasing film thickness in the case of CoPcF ₁₆ /MoSe ₂ can be explained by a p-doping of the substrate.	158
Figure 7.24: UPS valence band spectra measured at normal emission used for energy level alignment shown in Figure 7.25. a-c) Secondary electron cut-off (SECO), measured with He I excitation and a BIAS voltage of 10 or 15 V. d-f) Low binding energy region. Satellites were subtracted. To detect low-intensity features at Γ in the case of slightly tilted sample regions, He II excitation was employed for the pristine substrate, providing information over a broader $k_{ }$ range. Instead, at higher coverages, He I excitation is used, which is advantageous due to the more favorable C 2p and C 2s cross-sections.....	162
Figure 7.25: Energy level alignment for coverages > 2nm. a) CoPc/MoSe ₂ , b) CoPcF ₁₆ /MoSe ₂ , and c) CoPcF ₁₆ /n-MoSe ₂	163
Figure 7.26: Home-built confocal microscope used for recording the luminescence spectra. GF = greyfilter; T1,2,3 = Telescopes 1,2 and 3 BS = beamsplitter; PM = parabolic mirror; LPF = longpass filter; APD = avalanche photodiode; SM = spectrometer.....	164

List of Tables

Table 2.1: Spin-orbit splitting and density of states for p,d and f orbitals.	25
Table 2.2: Calculated distances Γ M and Γ K for MoS ₂ and MoSe ₂	31
Table 7.1: Peak fit parameters for Mo 3d and S 2s peak fits shown in Figure 3.1 a) (sub-) monolayer of Au, b) (sub-)monolayer of Cu, c) (sub-)monolayer of Ti.	113
Table 7.2: Peak fit parameters for S 2p peak fits shown in Figure 7.2 a) (sub-) monolayer of Au, b) (sub-)monolayer of Cu, c) (sub-)monolayer of Ti.	116
Table 7.3: Peak fit parameters for Mo 3d and S 2s peak fits shown in Figure 7.7 a) multilayer of Au, b) multilayer of Cu, c) multilayer of Ti.	120
Table 7.4: Peak fit parameters for S 2p peak fits shown in Figure 7.8 a) multilayer of Au, b) multilayer of Cu, c) multilayer of Ti.	122
Table 7.5: Fit parameters for the C 1s spectra shown in Figure 3.13.	131
Table 7.6: Fit parameters for the N 1s spectra shown in Figure 3.13.	133
Table 7.7: Fit parameters for the Mo 3d spectra measured with low surface sensitivity (hv= 900 eV) shown in Figure 3.14.	134
Table 7.8: Fit parameters for the Mo 3d spectra measured with high surface sensitivity (hv =300 eV) shown in Figure 3.14.	137
Table 7.9: Fit parameters for the S 2p spectra measured with low surface sensitivity (hv= 900 eV) shown in Figure 7.17.	142
Table 7.10: Fit parameters for the S 2p spectra measured with high surface (hv= 230 eV) sensitivity shown in Figure 7.17.	144
Table 7.11: Mo/S-ratio before and after sputtering for the experiments depicted in Figure 3.14.	146
Table 7.12: Fit parameters for the C 1s peaks depicted in Figure 4.5.	149
Table 7.13: Fit parameters for the N 1s peaks depicted in Figure 7.20.	151
Table 7.14: Fit parameters for the Se 3d spectra obtained at an excitation energy of 135 eV.	153
Table 7.15: Fit parameters for the Mo 3d spectra depicted in Figure 7.22.	155
Table 7.16: Fit parameters for the Se 3d spectra depicted in Figure 7.23.	159
Table 7.17: Fitting results for the peak position and peak area for the 64 luminescence spectra for both MoSe ₂ and n-MoSe ₂	163

List of Publications and Scientific contributions

Peer-reviewed publications as a first author:

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3. **Eric Juriatti**, Martina Binniger, Carolin Schüle, Maren Zirwick, Katarina Margetic, Erika Giangrisostomi, Marcus Scheele & Heiko Peisert.
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2. Kevin Woern, Claudio Schrenk, **Eric Juriatti** & Andreas Schnepf.
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Small Science, 5, 10, 2500276, (2025).
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4. Fabian Grahlow, Jan Beitzberger, Mario Martin, **Eric Juriatti**, Heiko Peisert, Marcus Scheele, Markus Ströbele, Carl P. Romao & Hans-Jürgen Meyer.
Structural modifications of $M_5O_4I_{11}$ (M = Nb, Ta) cluster networks from heterogeneous solid-state reactions.
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5. Felix Schneider, Tim Parker, Liangxuan Wang, Michel Rebmann, Yang Zhao, **Eric Juriatti**, Heiko Peisert, Alfred J. Meixner, Johannes Gierschner, Lingyan Meng & Dai Zhang.
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1. Martina Binninger, internship, Chemistry M.Ed. (2023)
“*Untersuchung des Einflusses von Argon und Neon-Sputtering auf die Wechselwirkungen der Grenzfläche von Hexadecafluorophthalocyanin und Molybdändisulfid mit XPS und UPS*“
2. Christoph Späth, Bachelor thesis, Nano-Science (2024)
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1. Dr. Philipp Haizmann, PhD thesis
2. Dr. Fabian Grahlow, PhD thesis
3. Carolin Schüle, PhD thesis
4. Kevin Woern, PhD thesis
5. Felix Schneider, PhD thesis
6. Tim Parker, PhD thesis
7. Keno Kraut, Master thesis

Declaration of Contribution

This chapter serves to give an estimated amount of the authors contribution to the publications which were discussed in 3.1–3.3 and the non-peer-reviewed results depicted in 4.1.

1. 'Effects of Annealing on Electrode/MoS₂ Interfaces Studied by Photoelectron Spectroscopy" published in *ACS Applied Electronic Materials*.'

All experiments were planned by me. The investigations on the MoS₂/Cu interface were part of the bachelor thesis of Christoph Späth and therefore the experiments and data evaluation were executed jointly. All other XPS and UPS experiments were performed and evaluated by me. The SEM measurements were performed by Elke Nadler. All Figures were designed by me, and the manuscript was written by me. Heiko Peisert and Marcus Scheele critically reviewed the manuscript and gave important recommendations.

Estimated contribution of myself: 75 %.

2. 'Orientation of Cobalt-Phthalocyanines on Molybdenum Disulfide: Distinguishing between Single Crystals and Small Flakes' published in the *Journal of Physical Chemistry C*.

The experiments at the KARA Synchrotron facility (PEEM, μ XAS, μ PES) were planned and performed jointly by Philipp Haizmann and me with help from Heiko Peisert and the staff of the WERA beamline (Peter Nagel, Michael Merz, Stefan Schuppler, Amir Ghiami). The prior characterization of monolayer flakes by photoluminescence spectroscopy was performed by me. The manuscript was written by Philipp Haizmann and me. Heiko Peisert and Marcus Scheele critically reviewed the manuscript and gave important recommendations.

Estimated contribution of myself: 40 %.

3. 'Tuning the electronic properties of defect-rich MoS₂' published in the *Beilstein Journal of Nanotechnology*

All experiments were planned and carried out by me. For conducting the synchrotron experiments (ARPES, SXPS, XAS) I was supported by Heiko Peisert, Carolin Schüle, Maren Zirwick, Katarina Margetic and the staff of the PM4 beamline at BESSY II (Erika

Giangrisostomi). The PES experiments in the home laboratory were part of the internship of Martina Binniger and conducted jointly with me. The manuscript was written by me and critically reviewed by Marcus Scheele and Heiko Peisert. The table of contents figure was designed collaboratively with Mario Martin.

Estimated contribution of myself: 75 %.

4. 'Interfaces between Cobalt Phthalocyanines and MoSe₂: Conditions for charge transfer and the Nature of Gap States', not published at the time this thesis is submitted.

All synchrotron experiments (ARPES, SXPS, XAS) were planned and carried out jointly by Carolin Schüle and me supported by the staff of the WERA beamline at KARA (Peter Nagel, Stefan Schuppler, Michael Merz). The data evaluation was performed jointly by Carolin Schüle and me. Specifically, I performed all evaluation on the synchrotron data of the MoSe₂/CoPc and the MoSe₂/CoPcF₁₆ interface beside the experiments for the thick layer of the molecule. Tim Parker and Dai Zhang performed the photoluminescence experiments. All figures were designed by me. The manuscript was written by Heiko Peisert and me under critical review by Marcus Scheele.

Estimated contribution of myself: 40 %.

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