In Vacuo Fabrication and Electronic Structure Characterization of Atomic Layer Deposition Thin Films

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In Vacuo Fabrication and Electronic Structure Characterization of Atomic Layer Deposition Thin Films

by

Michael Schaefer

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy Department of Physics College of Arts and Sciences University of South Florida

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Keywords: XPS, UPS, IPES, dipole layer, nanoparticles, in vacuo

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DEDICATION

I would like to dedicate this dissertation first and foremost to my parents, Armin Schaefer and Marion Schaefer, as well as to the extended parts of my family in Germany. Without their liberal way of nurturing and supporting me as long as I can remember and their encouragement for science and research as a child, I would not be where I am today. I want to further dedicate this dissertation to my wonderful partner, Janine Field. Without her support, help and patience over the last three years, especially in the last 3 month while I was finishing up my thesis, I could not have finished this dissertation.
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ABSTRACT

Improvement of novel electronic devices is possible by tailor-designing the electronic structure at device interfaces. Common problems observed at interfaces are related to unwanted band alignment caused by the chemical diversity of interface partners, influencing device performance negatively. One way to address this problem is by introducing ultra-thin interfacial dipole layers, steering the band alignment in a desired direction. The requirements are strict in terms of thickness, conformity and low density of defects, making sophisticated deposition techniques necessary. Atomic layer deposition (ALD) with its Ångstrom-precise thickness control can fulfill those requirements.

The work presented here encompasses the implementation of an ALD reactor into an UHV photoemission characterization system to enable in-situ experimentation while avoiding ambient contamination. With this setup, the study of the electronic structure of two prototypical heterojunction systems – Ru(O\textsubscript{x})|Au and In\textsubscript{2}O\textsubscript{3}|TiO\textsubscript{2} is presented with a focus on interface dipole modulation and growth behavior. In addition, this work presents a proof-of-concept integration of a nanoparticle injector system into the ALD reactor.

The implementation of the ALD reactor was demonstrated successfully. The study of the Ru(O\textsubscript{x})|Au and In\textsubscript{2}O\textsubscript{3}|TiO\textsubscript{2} heterojunctions yielded insight into the interface dipole formation depending on ALD parameters, substrate conformation and preparation method. It was further shown that micro-plasma nanoparticle synthesis can be adapted to high vacuum environments.
This established a direct path to the application of surface sensitive vacuum based techniques for the characterization of such nanoparticles and experiments with co-deposited ALD structures.
CHAPTER 1: INTRODUCTION

1.1: Motivation and Outline of this Dissertation

We are moving head-on towards a paradigm shift in electronic device manufacturing as device sizes approach the physical limitations of miniaturization. For many years following Moore’s law was a driving factor to the semiconductor manufacturing industry on the path of ever increasing transistor integration.

In order to advance technology further, the International Technology Roadmap for Semiconductors (ITRS) suggests the investigation of alternative means that lead to further device improvement, i.e. performance, reliability, durability, etc., decoupled from miniaturization efforts. Modern devices crucially depend on the electronic structure of interfaces involving an increasing number of materials. Common problems observed at such heterojunctions are related to unwanted band alignment phenomena as a consequence of the chemical variety of the interface partners. This can influence device performance negatively and needs to be addressed. A viable path to approach that problem has been found in trying to tailor-design the electronic structure at heterojunction interfaces by introducing ultra-thin interfacial dipole layers that can steer band alignment in desired direction. To achieve the desired improvements, the band tuning possibilities at novel heterojunction interfaces need to be investigated first. For that purpose, sophisticated thin film deposition methods in conjunction with integrated electronic structure characterization systems are necessary. Fabricating dipole layers remains challenging as
requirements are strict in terms of thickness, conformity and density of defects. In some instances these layers do not exceed 1 nm thickness. Atomic layer deposition (ALD) is a relatively novel gas-phase based deposition technique that makes use of special organometallic precursor gasses that allow building the material structure layer-by-layer. This technique offers superior control in terms of thin film thickness reaching Ångstrom-precise resolution, while maintaining very high conformity of the deposited thin films. In order to enable the systematic investigation of electronic structure phenomena, the deposition method needs to be coupled with appropriate analytical techniques. Photoemission spectroscopy (PES) offers a way of investigating the electronic structure of interfaces due to its high surface sensitivity, thus allowing detecting miniscule changes made to material surfaces. The successful utilization of PES requires in-situ deposition to be able to achieve accurate results by keeping ambient contamination to a minimum.

The work presented here is based on this theme and is focused on studying the band tuning capabilities, specifically the interface dipole formation and growth behavior, of ALD thin films fabricated in a home-built ALD reactor integrated with a photoemission spectroscopy system via an in-situ sample transfer system. Once in place this system was used to study two prototypical model heterojunctions – Ru(Oₓ)|Au and In₂O₃|TiO₂. In an expansion of this work the adaptation of a microplasma based nanoparticle injector system into the ALD reactor was explored with the goal to enable the investigation of ALD layer encapsulated nanoparticle systems.

This dissertation begins with a topical introduction followed by an introduction to the employed methodology (Chapter 1 and Chapter 2). Subsequently, the conceptualization, construction and integration of a stop-flow type thermal ALD reactor with the pre-existing multi-
chamber photoemission system is discussed. In addition, the construction and integration of a nanoparticle injector system is described with the purpose of indicating how the initially built system can be expanded upon and how this attachment can lead to interesting future research projects (Chapter 3). Chapter 4 and Chapter 5 are dedicated towards elaborating on the results and observations made while investigating heterojunction interfaces. The final chapter discusses the proof-of-concept adaptation of an ambient DC microplasma based nanoparticle injector system for vacuum operation. This system was tested and characterized by synthesizing iron oxide nanoparticles from a ferrocene precursor directly in vacuum (Chapter 6). The work concludes by summarizing the findings of the presented studies in the context of tailoring the electronic structure of heterojunctions (Chapter 7).

1.2: Impact and Relevance of ALD Thin Films as Interfacial Layers

Major parts of this dissertation are focused around the investigation of the electronic structure of ALD thin films and thin film interfaces. Their capability as interfacial dipole layers was explored, which enables band line-up tuning at heterojunctions. This chapter talks about the concepts of the chemical dipole and the dipole formation at interfaces and relates this information to the impact of the band alignment at heterojunctions. In addition, this chapter is setting a foundation for later reported studies (compare p. 97 and p. 116), detailing the benefits of using ALD thin films as interfacial dipole layers.
1.2.1: The Chemical Dipole

Chemical dipoles can form when elements of different electronegativity are brought together to form a chemical bond. The electronegativity of an element is defined by its electron affinity, or in other words, its strength with which it attracts electrons. The electronegativity scale, also referred to as Pauling scale, is a relative scale based on the bond energy referenced to the element with the highest attraction potential – fluorine, with an electronegativity of 3.98. In the periodic system of the elements, the electronegativity increases within groups from left to right and within periods from bottom to top. The atomic radii decrease with the same trend, which is no coincidence. A smaller atomic radius means that valence electrons, those mainly partaking in chemical bonds, are closer to the nucleus, thus experiencing stronger attraction or electronegativity.

The simplest representation of a dipole in a chemical sense is a polar covalent bond joining two elements of different electronegativity. By default, those elements have a different electron affinity, which means that electrons in between the atoms that stabilize the bond are shifted towards the element with higher electronegativity. This causes one side of the bond to be “oversaturated” with electrons, thus leaving it with a partial electronegative charge ($\delta^-$), while the bonding partner is left with less electronic density, causing a partial electropositive charge ($\delta^+$). The resulting dipole moment $\vec{\mu}_D$ is a vector pointing from negative ($\delta^-$) to positive charge ($\delta^+$) (analog to the standard definition of the electric dipole moment) and can be expressed by:

$$\vec{\mu}_D = \delta \vec{d},$$ (1)
with the distance between the atoms $\vec{d}$ and the charge $\delta$. Because of the unpracticality of the dipole moment’s SI unit ($C \cdot m$), i.e. atoms are on the scale of Ångstroms not meters, another unit with a historic origin is used called Debye (D). A Debye relates directly to the size of atoms and is therefore a much better fit [132]. A Debye is equal to $3.335 \times 10^{-30}$ Cm. Common dipole moments range from $0.5$ – $11$ D [5]. The magnitude of the dipole moment in units of Debye can also be roughly related to the electronegativity of the individual elements and quantified according to Pauling’s equation:

$$\mu_D[D] \approx \chi_B - \chi_A \approx \Delta \chi,$$

(2)

with the electronegativity $\chi_A$ and $\chi_B$ for element A and B respectively. More complex systems, i.e. molecules, can include multiple polar bonds in which partial charges at each atom have to be taken into account to calculate the total dipole moment. For larger molecules or crystalized systems, this problem becomes quickly non-trivial. In those cases it is unpractical to solve the problem mathematically. Instead it makes more sense to measure the macroscopic effect of that permanent dipole for instance in photoemission experiments (compare p. 7). However, in a brute force approach, the dipole moment of a larger system can be calculated by taking into account that the dipole moment is a vector, so its magnitude $\mu_D^{total}$ can be expressed as:

$$\mu_D^{total} = \sqrt{(\mu_x)^2 + (\mu_y)^2 + (\mu_z)^2},$$

(3)
with the individual contributions to the dipole moment in each dimension \( \mu_x \), \( \mu_y \) and \( \mu_z \) respectively. The dipole moment in each direction is defined as sum of all partial charges \( q_j \) located at the N atoms multiplied by their relative x, y or z coordinate in reference to an arbitrary point in the molecule. The expression for the x component is as follows (and is the same for each dimension):

\[
\mu_x = \sum_{j=1}^{N} q_j x_j.
\] (4)

The potential energy \( U \) of a permanent dipole is related to the dipole moment \( \mu \) and the electric field \( E \) that is created as a consequence of the charge separation. For a single polar bond the electric field \( E \) can be expressed as:

\[
E = \frac{2\mu}{4\pi\varepsilon_0 r^3},
\] (5)

with the vacuum permittivity \( \varepsilon_0 \) and the distance between charges \( r \). The potential energy of a permanent dipole also referred to as dipole strength is a better suited parameter than the dipole moment to explain band alignment phenomena at heterojunctions, because usually an energy scale referenced to the Fermi energy is used to align the bands in respective energy diagrams. The potential energy \( U \) is defined as:

\[
U = -\mu E.
\] (6)
Due to the nature of the dipole moment being vectorial, interesting aspects related to the system’s symmetry can be derived. Knowing the symmetry of a molecule or larger structure is a good indication towards answering the question if it is exerting a permanent non-zero dipole or not. In nature most molecules are asymmetric, resulting in a non-zero net dipole moment. This is the reason for so many polar molecules in nature that enable many possible chemical reactions. However, there are some exceptions. For example, the molecule CO$_2$ has two polar double bonds that connect the oxygen molecules to the center carbon. CO$_2$ is symmetric along its main axis, combining its net dipole to zero. A molecule like water on the other hand has an H-O-H bonding angle of 104.5 °, resulting in a non-zero net dipole moment. For even more complex systems made from thousands of atoms, i.e. thin films, thin film heterojunctions, crystals, etc., it is clear that the probability for the existence of simple symmetries that cancel the net dipole to zero is practically not existent. This effect can be used advantageously, i.e. thin films of less than 1 nm thickness can be used to modify a material’s surface with a permanent dipole, thus altering its surface characteristics. The advantages are discussed in detail on p. 14 following [5, 68, 117, 120, 132, 133].

1.2.2: Band Alignment and Dipole Formation at Heterojunctions

Within the presented work, metal-metal, metal-semiconductor and semiconductor-semiconductor heterojunctions were investigated. This chapter introduces the effects and consequences of band alignment phenomena at those heterojunctions.

Metals are usually defined by their work function, conduction band minimum and location of the Fermi-level with respect to the conduction band minimum. If two metals of
different work function are brought in contact, the Fermi-levels align. Due to the work function differences, equilibrium can only be achieved if charge flows from the metal with lower work function to the metal with higher work function. The spatial redistribution of charge carriers, i.e. electrons, causes an interface dipole to arise which leaves the initial metal with positive cores and the second metal with additional electrons. Due to the high charge density in the conduction band of metals, this charge imbalance is screened within the first couple atomic layers of each respective metal. Therefore, the structure beyond that point is practically unperturbed. The dipole potential at such heterojunctions is also referred to as contact potential, which is ideally just the difference between both metal work functions.

Metal-semiconductor and semiconductor-semiconductor interfaces play a large role in the modern electronic device industry. Understanding the band alignment phenomena at the interface region is the key for novel applications [105]. Figure 1 illustrates the band alignment effects that occur for various metal-semiconductor interfaces. In thermal equilibrium, the chemical potential or Fermi-energy needs to be equivalent on both sides of the interfaces, i.e. causing the Fermi-levels to align. Due to the differences of the metal work function and the electron affinity of the semiconductor, charge to flow from one side to the other, causing band bending at the interface. A dipole potential $\Delta$ forms at the interface as a consequence of this charge separation. Four cases can be distinguished depending on the materials brought in contact.

If for instance an n-type semiconductor is brought in contact with a high work function metal, upwards band bending occurs at the interface and electrons flow from the semiconductor to the metal causing a depletion region, i.e. a region of low electron density, to form in the surface of the semiconductor. In this scenario, the excess electrons in the metal are screened (shielded by the electron cloud in the metal) within a couple Ångstroms of the metal’s surface.
Figure 1: Band Alignment at metal-semiconductor interfaces before and after contact. Four cases can be distinguished: a) and b) show high and low work function material in contact with an n-type semiconductor; c) and d) relate both work functions to a p-type semiconductor. Depending on the material combination either a depletion or accumulation area is created once the heterojunction is formed. Reproduced with permission. © Springer-Verlag Berlin Heidelberg 2010. All rights reserved.¹

Therefore, the excess charge has practically no influence into the electronic structure of the metal beyond that point. However, due to the much lower charge carrier concentration in the

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semiconducting material, screening effects are strongly reduced, which causes the space charge to extend much further into the material ($\leq 50$ nm). If that same n-type semiconductor is brought in contact with a low work function metal, it has the opposite effect. Charge flows from the metal into the semiconductor, causing an accumulation region, i.e. an area of higher electronic density, to form in the surface of the semiconductor. The same arguments about the screening effects are applicable, which means that the excess electronic space charge extends deep into the semiconductor. Similar charge separation effects are observed for p-type semiconductors in contact with metals of different work function (compare Figure 1).

When upwards band bending occurs as consequence of Fermi-level alignment, a potential barrier arises, also referred to as Schottky barrier [159]. It describes a potential that has to be overcome by an electron that is excited from the metal into the semiconductor. Its magnitude $e\phi_{SB}$ is dependent on the maximum band bending at the interface $eV_B$ which in terms is correlated to Poisson’s equation (Ch. 7 in [105]). In an ideal scenario, the magnitude of the Schottky barrier $\phi_{SB}$ can be estimated if the electron affinity of the semiconductor $\chi_{SC}$ and the work function of the metal $\psi_M$ are known according to following expression:

$$\phi_{SB} = \psi_M - \chi_{SC}. \quad (7)$$

In reality however, interfaces are much more complicated, making it hard to evaluate the exact electron affinity at the heterojunction interface, thus rendering this approach challenging. In addition to the discussed effects above, real material interfaces form chemical covalent bonds with suitable elements across the interface. Those bonds are mostly polar, which causes the formation of a dipole layer $\Delta$ in atomistic dimensions. The net dipole strength at the interface and
its direction can be evaluated by comparing the work functions and electron affinities of the interface partners. In shall be noted that in reality the dipole strength is extrapolated in photoemission spectroscopy experiments by comparing the work function of the pristine substrate with the one after a surface modification took place, i.e. annealing, oxidation, UV induced surface reactions, thin film deposition, etc. Due to this dipole being caused by chemical bonds, its extension at the interface is strongly limited (~ 1 – 2 Å). Exemplarily, the interface of an n-type semiconductor in contact with a high work function metal is shown in Figure 2 again.

Figure 2: Band alignment of a metal-semiconductor interface, specifically taking the interface dipole region into account. The formation of a Schottky barrier of magnitude $e\Phi_{SB}^0$ is displayed as a consequence of band bending that is caused by the Fermi-level alignment. An interface dipole $\Delta$ arises from the formation of polar bonds at the interface. Reproduced with permission. © Springer-Verlag Berlin Heidelberg 2010. All rights reserved.²

² See Appendix A: Permissions for permission.
However, this time emphasizing the interface dipole region and explicitly showing the magnitude of the dipole $\Delta$ in relation to the metal work function and the semiconductor electron affinity. The dipole potential further causes interface states to appear that pin the Fermi-level. The evaluation of the total dipole potential in real heterojunction interfaces remains challenging because of the presence of atomistic dipoles that occur right at the heterojunction interface as a consequence of polar covalent bonds and semi-macroscopic space charge related effects, i.e. band bending, causing a charge separation at the interface with effects extending much deeper into the structure.

The situation gets more complicated at semiconductor-semiconductor interfaces. Figure 3 for example shows the band alignment effects that occur when two semiconductors of different doping level and different band gaps are brought in contact. In part a), the band structure of the individual semiconductors is shown. This is followed by part b), a scenario in which both interface partners are brought in contact but thermal equilibrium has not yet been established. This case is fictional as band alignment happens immediately after both partners are brought in contact. However, it illustrates that both valence bands and conduction bands at the interface are offset against each other. In thermal equilibrium (Figure 3 c)), i.e. chemical potential on both sides is now equalized and therefore Fermi-levels are aligned, band bending occurs on both sides. For the moderately doped semiconductor (I) downward band bending occurs, while upwards band bending occurs for the heavily doped semiconductor (II).

It can be seen that in thermal equilibrium the bands at the interface remained at a distinct offset. This offset relates to one of the most important parameters for semiconductor heterojunctions – the band offset at the valence band maxima $\Delta E_V$ and conduction band minima $\Delta E_C$ respectively.
Figure 3: Band alignment in n-type semiconductor-semiconductor heterojunctions. Both materials have different doping levels. a) depicts the band structure of the isolated materials, b) when brought in contact but not yet in thermal equilibrium, c) shows an ideal interface in thermal equilibrium and d) a realistic imperfect interface in which defect interface states are formed that pin the Fermi-level at the interface. Reproduced with permission. © Springer-Verlag Berlin Heidelberg 2010. All rights reserved.

3 See Appendix A: Permissions for permission.
Both are equal as band bending effects happen uniformly across all bands. For ideal interfaces this offset can be expressed as difference of the electron affinities of the individual interface partners to:

\[ \Delta E_V = \Delta E_C = \chi_I - \chi_H. \]  

(8)

Due to the inadvertent formation of interface dipoles in real interfaces however, this approach is unpractical.

A more promising approach includes determination of the maximum band bending with the theories of space charge layer formation (Chapter 7 in [105]), which ultimately leads to the band offset \( \Delta E_{C/V} \). It shall be mentioned that the ideal semiconductor heterojunction interface shown in Figure 3 c) is only limited applicably for real world interfaces. Under realistic condition the interfaces are never pristine and perfect. Surface contaminations, impurities, surface defects, dangling bonds, etc. can impact the band alignment at the junctions, thus giving rise to the formation of interface or defect states at the junction. These states can pin the Fermi level at the interface which causes a completely different band alignment, band bending, band offset, etc. to occur (compare Figure 3 d)) [73, 105, 120, 160].

1.2.3: Tailor-Designing Heterojunction Interfaces

Novel micro-electronic devices are conceptualized and manufactured in large quantities nowadays. The foundations of those devices are electronic junctions mostly made up from putting different materials together. The resulting heterojunction causes a constantly reoccurring
problem. Due to the different chemical nature of the materials put in contact, effects like band bending, formation of interface dipoles, defect states, etc. (compare p. 7) are formed that have the potential of decreasing device performance or blocking device operation completely. One prominent problem arises from putting metals and semiconductors in contact. In certain configurations the occurring band bending causes a potential barrier (Schottky barrier) to establish that hinders electron flow. In devices including transistors, solar cells, field-effect transistors, etc. this can cause severe problems. The formation of a Schottky barrier is illustrated in Figure 4 a).

Figure 4: Formation of a Schottky barrier at a metal-semiconductor interface as a consequence of band bending that occurs when a high work function metal and an n-type semiconductor are brought in contact (a), and b) alleviation of this problem by introducing a thin film in between the interface acting as dipole layer, thus helping with the band alignment. Reproduced with permission. All rights reserved.\footnote{See Appendix A: Permissions for permission.}
The contact shown is poorly conductive. The upwards band bending in the semiconductor hinders the electrons to flow from the conduction band of the semiconductor to the metal. Vice versa, the potential barrier hinders electrons from the metal to get injected into the semiconductor. This unfavorable situation can be alleviated with a method of adjusting the bands on one side of the interface relative to the other. One way to achieve that is by introducing a defined dipole potential in form of a very thin film in between the interface. The result is depicted in Figure 4 b).

If the thin film is deposited on top of the metal, the electronic band line-up is altered. When in a subsequent step, the altered metal is put in contact with the semiconductor; the bands align perfectly and allow electron transport. By choosing deposition materials carefully, i.e. the dipole strength has to have a similar magnitude as the expected Schottky barrier, this effect can be exploited and the interface dipole strength can be tailor-designed, giving access to a wide range of surface/interface modifications that can help with band alignment problems.

Thin films suitable for this application need to be as perfect as possible in terms of defectiveness and conformity to allow precise tailor-designing of material interfaces. Atomic layer deposition (ALD), a modern thin film deposition technique, with its sequential injection of organo-metallic precursor gasses allows bottom-up fabrication of thin films with Ångstrom thickness precision and is therefore a perfect candidate. When this technique is operated in stop-flow mode (compare p. 58), it can produce excellent highly conformal, defect-free thin films [81].

The thickness of the thin films is of particular importance. They need to be thin enough to form a stable permanent dipole potential normal to the material surface in order to cause the desired band alignment effect [52, 123]. In thicker layers, the formation of electric fields negates
this effect [158]. In addition, in thicker thin films bulk effects can occur, i.e. accumulation of counter charge in surface states or surface recombination, in order to stabilize the thin film surface, thus compensating the dipole field [118].

![Diagram of metal induced gap states (MIGS)](image)

**Figure 5**: Formation of metal induced gap states (MIGS) at the metal semiconductor interface, effectively pinning the Fermi-level at the interface in conjunction with band bending and the formation of a thermionic potential barrier (a), and alleviating this problem by introducing a thin interfacial dipole layer (b). © 2004 IEEE. Reprinted, with permission, from [30].

If the interfacial layer is insulating, additional considerations have to be taken into account related to the layer thickness. Metal induced gap states (MIGS) form when metals come

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5 See Appendix A: Permissions for permission.
in contact with semiconductors, effectively pinning the Fermi-level at the interface and creating a thermionic potential barrier that hinders electrons from passing through the interface. The introduction of an interfacial insulating layer can “de-pin” the Fermi-level from its position and reduce the thermionic barrier (compare Figure 5) [30].

![Diagram](image)

**Figure 6**: Tunneling effects through the interfacial dipole layer (a). It can be seen that energetically deeper lying MIGS are attenuated faster (smaller arrow), effectively blocking them from penetrating through the insulating layer, thus causing Fermi-level pinning. Free charge carrier states at the surface however can penetrate the insulator layer freely. The insulator thickness is of major importance as shown on the right. If the layer is too small, gap states penetrate through it, and if the layer is too thick, all states including the free carrier states are blocked, hindering them from tunneling through the insulator causing the interface to have an unwanted high resistance. The optimal thickness is found in the middle between both extrema. © 2004 IEEE. Reprinted, with permission, from [30].

The goal is to tailor-design the layer thickness to values that on one hand deep energy MIGS are attenuated fast to prevent Fermi-level pinning. On the other hand, free charge carrier

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6 See Appendix A: Permissions for permission.
states need to be able to penetrate the tunneling barrier in order to cross the interface. The “sweet spot” achieving the lowest resistance lies in the middle between both extrema. The attenuation effect is illustrated in Figure 6.

![Figure 7: Band gap as a function of dielectric constant for a selection of possible materials that can be used as interfacial dipole layers. The graph indicates that a wide variety of band gap and dielectric is available. S and p orbital dominant compounds like SiO$_2$ and Al$_2$O$_3$ have high band gaps while compounds with d-orbitals have lower band gap which can originate from additional gap states introduced by the additional orbitals. Reproduced with permission. © Springer. All rights reserved.](image)

ALD offers a wide selection of dipole layers that can be deposited with crystalline orientation on a selection of substrates including amorphous, single- and polycrystalline materials [50, 86, 97, 138]. In addition to the stability and growth capabilities of ALD thin films, the band gap and dielectric constant of the dipole material is important for fine-tuning band

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7 See Appendix A: Permissions for permission.
alignment efforts. A selection of possible materials with different band gaps and dielectric constants is shown in Figure 7. It shall be noted that s- and p-orbital dominant compounds have higher band gaps than compounds with d-orbitals which can introduce additional gap states, thus lowering the overall band gap.

1.2.4: Applications that Benefit from Interfacial ALD Layers

This chapter is focused on representative studies and reports that make use of ALD thin films as interfacial dipole layers in order to improve electronic devices. This is done in order to correlate the importance and relevance of these studies with the contributions presented in later chapters of this dissertation (compare p. 97 and p. 116).

According to the 2013 International Technology Roadmap for Semiconductors (ITRS) it is unavoidable to explore other means that lead to device performance improvements as we approach the physical limitations of device miniaturization [31]. A major hurdle is the so called parasitic resistance or contact resistance that arises from the formation of potential barriers at heterojunction interfaces (compare p. 7). In that light, alleviating this situation by using interfacial ALD dipole layers for band alignment and band tuning purposes is one possible solution. In fact, the successful incorporation of precisely tuned dipole structures into micro- and nanoelectronic devices like CMOS/MOSFET’s, thin film transistors (TFT’s), capacitors, solar cells, and others is considered to set the path for further device improvement. It is therefore of great importance to study and understand the electronic structure and band alignment phenomena.

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8 Available online at: http://www.public.itrs.net
that occur at heterojunctions of novel interfaces. Selected highlight studies will be present in the following chapters.

1.2.4.1: Interfacial Dipole Layers in MOSFET’s

MOSFET’s like any other complex electronic device that consists of many different materials including metals, semiconductors and insulators suffers from the problematic of parasitic resistance that occurs when materials of different nature are brought together to form a heterojunction, i.e. formation of a Schottky barrier as the consequence of band alignment (band bending). In fact, ITRS in 2007 suggested that Schottky barrier heights below 0.1 eV are necessary to achieve effective advancement of the MOSFET technology [31]. The problem can be tackled by using ultra-thin ALD thin films, mostly semiconductors and insulators, which can be inserted in between particular heterojunctions to aid in band alignment. It has been shown that this technique can be added to large batch production systems without overcomplicating the work flow too much, i.e. adding too many extra process steps, making this approach a viable option [31].

L. Lin et al. used simulations to report a topical introduction into the effects of Schottky barrier height (SBH) modulation in MOSFET’s based on the example of Al₂O₃ and SiNx interfacial dipole layers [99]. A research group around D. Connelly expanded further on this topic by reporting an effective Fermi-level de-pinning at metal source/drain structures (Al/Er/Yb/Ti|n-Si) by introducing ultra-thin insulating ALD SiNx tunneling layers in between the metal semiconductor heterojunction [30]. The thickness of the insulating tunneling layer was subject to optimization in order to achieve effective de-pinning by also keeping the contact at
low resistance, i.e. allow electrons to tunnel through the barrier. A concept drawing in shown in Figure 8.

Another study by B. E. Coss et al. reported a reduction of the SBH at source/drain contacts in p- and n-doped Si|SiO$_2$|TaN MOSFET’s by incorporating ultra-thin (approx. 10 – 20 Å) dielectric ALD AlO$_x$ and PVD LaO$_x$ layers into the SiO$_2$|TaN junction [31]. Both dielectrics cause dipole layers with opposite directions, thus allowing convenient SBH modulation at p as well as n-doped interfaces. The band alignment is illustrated in Figure 9. Reported modulation ranges reached up to +0.5 eV in p-Si|SiO$_2$|AlO$_x$|TaN structures and up to -0.3 eV in n-Si|SiO$_2$|LaO$_x$|TaN structures. This resulted in SBH’s of ≤ 0.1 eV at the conduction band edge and ≤ 0.2 eV at the valence band edge respectively [31].

**Figure 8:** Metal/insulator/n-type heterojunction for a potential zero barrier source/drain field effect transistor using ultra-thin ALD SiNx insulating layers in between the metal contacts to prevent Fermi-level pinning caused by MIGS at the heterojunction. All contacts are metals. Current flows from anode (A) to cathode (C). Current flow is measured with a distant tap (T). © 2004 IEEE. Reprinted, with permission, from [30].

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9 See Appendix A: Permissions for permission.
Figure 9: Band alignment at the p-Si|SiO$_2$|AlO$_x$|TaN heterojunction on the left and at the n-Si|SiO$_2$|LaO$_x$|TaN heterojunction on the right. The direction of the dipole in LaO$_x$ is opposite to the one in AlO$_x$, thus allowing the convenient SBH modulation at p- and n-doped interfaces. © 2009 IEEE. Reprinted, with permission, from [31].

The reported margins were coincident with suggestions made by ITRS 2007. The same group reported similar effects on multi-gate MOSFET’s [32]. One last example for single dipole layer insertion was reported by a team around W. J. Maeng that used plasma-enhanced ALD to fabricate different stack combinations of ultra-thin interfacial HfO$_2$ and La$_2$O$_3$ layers in between a Ru|p-Si heterojunction to create interfacial dipoles that can potentially be used to modulate the flat band voltage (difference between metal and semiconductor work function at metal|semiconductor heterojunction assumed that no interface charge is present) on the metal electrode side at MOSFET gates [109]. The band alignment based on the Ru|HfO$_2$|La$_2$O$_3$|HfO$_2$|p-Si heterostructure is shown in Figure 10. The reported dipole originated from the diffusion of La atoms into the HfO$_2$ overlayer in a post annealing process step, causing polar covalent Hf-O-La bonds to form at the HfO$_2$|p-Si heterojunction.

Interfacial ALD dipole layers for SBH modulation in MOSFET like heterostructures can also consist of multiple individually stacked dipole layers. In fact, the use of multilayer dipole
layers consisting of ALD Al$_2$O$_3$ and TiO$_2$ in between the Al|n-GaAs heterojunction has been reported by J. Hu et al. [69]. Figure 11 exemplarily shows the band alignment at this junction.

In the light of the presented studies it can be concluded that tailor-designing heterojunction interfaces in MOSFET like structures with ALD dipole layers presents a capable and practical way to achieve further device improvement. It is therefore important to study band alignment phenomena at novel interface combinations via electronic structure characterizations to continue this improvement path.

\textbf{Figure 10:} Band alignment at the Ru|HfO$_2$|La$_2$O$_3$|HfO$_2$|p-Si heterostructure. In one of the fabrication processes (annealing), La atoms diffuse into the space region between p-Si and HfO$_2$. They form polar covalent Hf-O-La bonds that cause a permanent dipole, thus modulating the effective work function of the metal electrode. Reproduced with permission from [109]. Copyright 2010, AIP Publishing LLC.  

\textsuperscript{11} See Appendix A: Permissions for permission.
Figure 11: Band alignment at formation of the Al|Al₂O₃|TiO₂|n-GaAs heterostructure (a-c), and correlation of the insulator thickness to the contact resistance in terms of SBH and tunneling resistance (d). If the layer is too thin, Fermi-level pinning occurs at the interface causing a high Schottky barrier to form. Reproduced with permission from [69]. Copyright 2011, AIP Publishing LLC.¹²

1.2.4.2: Recombination Barriers and CB Modulation in Solid-State DSSC’s

Solid-state dye-sensitized solar cells (DSSC’s) based on the original Grätzel cell (an electrolyte/dye/metal oxide based photoelectrochemical system) are subject to active research for commercial photovoltaic systems because of their low cost, easy design and high modularity. High performance DSSC’s have reached conversion efficiency levels in the last decade exceeding 8 %. However, to be competitive with established amorphous silicon based solar cells, the efficiency needs to be increased beyond 10 % [53]. A common problem among DSSC’s is the reduction in conversion efficiency caused by high charge recombination rate that occurs when electrons injected by the dye molecule either recombine with oxidized dye molecules or holes in the hole transport material [17]. A possible solution to this problem is the insertion of ultra-thin interfacial ALD layers in between the photo anode metal oxide and the dye. Three main advantages can be derived from this concept: First, the interfacial layers passivate the metal oxide surface, thus reducing defect states that can serve as recombination centers, second, the

¹² See Appendix A: Permissions for permission.
layers can be used as an insulating potential barrier between photo anode and oxidized dyes or hole transport material effectively reducing recombination rates at the interface, and third, the interfacial layers cause an interface dipole to occur at the photo anode that can modulate its conduction band [125]. Those effects are not exclusive and can work in conjunction to raise the short circuit current and open circuit voltage of a DSSC. However, the dominance of the individual effects is material dependent [17].

T. P. Brennan et al. for instance reported a successful conduction band modulation of the photo anode leading to an increase in open circuit voltage in TiO$_2$|WN1|spiro-OMeTAD solid-state dye sensitized solar cells by 100 mV after inserting ALD In$_2$O$_3$ recombination barriers into the TiO$_2$|WN1 heterojunction [17]. An illustration of the band alignment for different In$_2$O$_3$ layers thicknesses is shown in Figure 12. Extreme cases reached open circuit voltage improvements of up to 1 V. Best device performance was achieved with recombination barrier layer thicknesses of approx. 2 Å, thus emphasizing the importance of the deposition method (ALD), because only ALD can achieve conformal films at these levels of thickness. The group also reported on observing the inverse effect, i.e. a significant open voltage drop, for ALD layer thicknesses exceeding 4 Å, further emphasizing the importance of the interfacial ALD layer thickness in terms of device improvement. The same group reports on using ALD Al$_2$O$_3$ recombination barrier layers with the same success in terms of lowering charge recombination rates. However, due to the insulating nature of Al$_2$O$_3$, reported device performances were strongly reduced mainly due to the reduction in open circuit current [16]. T.-C. Tien and co-workers elaborated further on using ALD Al$_2$O$_3$ as interfacial dipole layer in their TiO$_2$ based DSSC’s that increased the cell performance by up to 14 % [155]. They suggested the formation of a dipole $\Delta \Phi_{A-T}$ of 0.4 eV caused by polar covalent Ti-O-Al(OH)$_2$ bonds at the TiO$_2$|Al$_2$O$_3$
Due to this interface dipole, their energy diagram shown in Figure 13 suggested the formation of a charge recombination barrier of 0.1 eV at the TiO$_2$|Al$_2$O$_3$ interface (in reference to the conduction band of TiO$_2$ and Al$_2$O$_3$) and an interface barrier at the Al$_2$O$_3$|dye interface. Increasing the Al$_2$O$_3$ layer showed similar effects in accordance with other groups. Another more general approach was pursued by a team around G. Dingemans. They studied charge accumulation and recombination effects at Si|SiO$_x$|Al$_2$O$_3$ interfaces for Si based solar cell applications by intentionally growing ALD SiO$_2$ interlayers on H-terminated (100) Si substrates and studying the interlayer thickness related charge distribution [37].

![Figure 12: Band alignment at the TiO$_2$|WN1|spiro-OMeTAD interface before (left) and after insertion of an ALD In$_2$O$_3$ recombination barrier (middle and right). In case no recombination barrier is inserted, the device is dominated by charge recombination of injected electrons with oxidized dyes or holes in the hole transport material, thus reducing the overall device performance. After insertion of the ALD In$_2$O$_3$, a recombination barrier is established and the photo anode conduction band is raised which reduces the overall charge recombination rate. However, if the layer’s thickness is increased beyond a certain thickness, inverse effects occur shifting the conduction band of the photo anode closer to the energetic level of the hole transport material, promoting charge recombination. Reprinted with permission from [17]. Copyright 2013 American Chemical Society.](image)

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13 See Appendix A: Permissions for permission.
In conclusion it can be said that interfacial ALD layers are suitable for achieving device performance boosts especially as recombination barriers and photo anode band modulators in the field of DSSC’s but also for Si based solar cells.

1.3: DC Microplasmas for Nanoparticle Fabrication

The studies conducted in this dissertation include the fabrication of Fe$_2$O$_3$ nanoparticles using a DC microplasma reactor system that allows the decomposition of organo-metallic precursor materials in the gas-phase to homogeneously nucleate nanoparticles.

![Diagram](image)

**Figure 13:** Band alignment at the TiO$_2$|Al$_2$O$_3$|N719 (dye) interface. It is suggested that a recombination barrier $\varepsilon_{RB}$ of 0.1 eV forms between the CBM of TiO$_2$ and Al$_2$O$_3$. Another interface barrier $\varepsilon_{IB}$ forms at the interface of Al$_2$O$_3$ and the dye molecule. Due to the differences in work function between TiO$_2$ and Al$_2$O$_3$, an interface dipole $\Delta\Phi_{A-T}$ of 0.4 eV forms that is caused by polar covalent Ti-O-Al(OH)$_2$ bonds at the interface. From [155]. © IOP Publishing. Reproduced with permission. All rights reserved.\(^{14}\)

\(^{14}\) See Appendix A: Permissions for permission.
This chapter shall therefore be dedicated to talk about the general scope and influence of nanoparticles and nanostructures related to materials science and it shall further be dedicated to elaborate on the specifics of DC microplasma reactor systems and reference highlight applications relevant to iron containing nanoparticles.

1.3.1: Influence of Nanostructures in Material Science

In the 1930’s, technological breakthroughs in the field of electron microscopy made it possible to observe our world on a never before reached scale – the nanoscale (1 nm can be compared to $\frac{1}{100000}$ of the thickness of a human hair). A sketch relating the size of nanoparticles with every day macroscopic objects visible to our eyes is shown in Figure 14. With the ability to observe this new nanoscale world, scientists developed a desire to mimic, manipulate and exploit it in anticipation of finding new phenomena and novel applications [60, 119, 143, 144].

Ever since then, fascinating research has been reported, describing the efforts that were undertaken to manipulate this nano-world on always smaller getting structures. For example, it was reported that atomic force microscopy (AFM) can be used for controlled arrangement manipulations of nanometer-sized particles [78, 127], sometimes with the effect of enhancing material properties like fluorescence [13] or with the goal of building nanometer-sized devices, i.e. nano-mechanical switches [79]. Other reports state that a technique called scanning tunneling microscopy (STM) can be used for manipulations of single atoms [9, 108]. Phenomenological observations made in nanometer-sized structures, i.e. giant magnetoresistance [19, 89, 106] and coulomb blockade [18, 114] further increased the popularity of nanoscience.
Figure 14: Correlation of various differently sized objects in relation to the size of nanoparticles. Different observation techniques are mentioned that can be used to investigate those objects.

Nowadays, nanoparticles play an ever increasing role in the scientific world. In fact nanoscience has already penetrated many fields of science including materials science, molecular biology, solid-state physics, and others [143].

The contributions mentioned earlier are just examples demonstrating the capabilities of modern probing techniques that allow precise manipulations of nanostructures. However, a major challenge lies in the reliable fabrication, growth and size control of nanoparticles. Many fabrication techniques have been reported to date. They are usually separated into top-down and bottom-up methods. Top-down methods describe the fabrication of nanoscale materials from
larger structures whereas bottom-up methods relate to a fabrication process of nanoscale structures from even smaller particulates, i.e. atoms, molecules, molecular precursors, etc. Historically, top-down methods were developed and used first because of their relative simplicity and availability of the necessary equipment. These methods are mainly based on attrition and milling procedures of larger particles grinded down to achieve desired nanoparticle sizes [7, 36]. However, most of these methods are outdated due to their limited dispersity and size control. Bottom-up methods on the other hand offer much finer control over particle dispersity, size and shape. This concept is therefore booming with new variations being reported frequently [60, 119, 143, 144]. Bottom-up variations can be grouped into solution based and gas-phase based techniques. Solution based techniques include sol-gel chemistry, solvothermal reactions and the use of micellar structured precursors, while gas-phase techniques are mainly either based on precursor pyrolysis, vapor condensation or a combination of both methods [103, 126]. For example, one of the most prominent representatives is called spray-pyrolysis, combining the production of super-fine precursor droplets from an aerosol that is then sprayed into a hot oven or furnace, causing a pyrolytic formation of nanoparticles which can be either precipitated to form thin films or isolated nanoparticles [131, 136]. However, although ample methods have been reported fabricating isolated nanometer-sized structures, building more complex or even interacting nano-structures, i.e. nano-machines, is very challenging and subject to active research. The associated field referred to as nano-engineering, describing the fabrication and control of complex nanometer sized machines, is still in its rudimentary stages [143]. One of the factors driving the advancement in the field of nanoparticle fabrication is the potential to replace bulk structures in existing and new applications, allowing improvement and further miniaturization [60, 119, 143, 144]. Nowadays, it is well understood that nanoparticles have the
potential to exceed their bulk equivalents by far in terms of their material properties. The question is:

What makes nanoparticles superior over bulk materials?

To answer this question adequately, the definition of nanoparticles needs to be established first. A nanoparticle is defined as an aggregation of atoms usually with sizes less than 100 nm, or in other words, with spatial dimensions less than 100 molecular diameters \[143\]. By default, this size-confinement leads to a vastly increased surface-to-volume ratio. The repercussions of this statement can be demonstrated with a simple thought experiment of a solid cube of length 1 cm that is successively filled with smaller cubes while the initial volume is kept constant (compare Figure 15). The initial cube has a surface area of 6 cm\(^2\), comparable to a piece of gum. If the initial cube is filled with cubes of length 1 mm, the total surface area increases to 60 cm\(^2\), comparable to one side of a post card. For cubes of length 1 \(\mu\)m, the surface area increases to 60,000 cm\(^2\) which is comparable to the surface area of a small bathroom. Cubes of length 1 nm would increase the surface area to 60,000,000 cm\(^2\), which is 6000 m\(^2\) or approx. 64584 ft\(^2\). This surface area is larger than a football field. Note that the initial cube just had a surface area of 6 cm\(^2\), which means that in this thought experiment the surface area of the nanocubes was increased by a factor of 10,000,000 while the initial volume was kept constant. Scientifically speaking, the size confinement, structural isolation and increased surface-to-volume ratio promotes the dominance of quantum effects over bulk properties on one hand and enhances surface related material properties by large factors \[60\]. Some examples of enhanced
material properties include catalytic properties [51], optical properties [151], magnetic properties [45], electronic properties [44], gas transport properties through membranes [116], and others.

Even though we are not yet capable of building complex nanoscale machines, simpler nanoparticles and nano-structured compositions have long arrived in our daily life. Improved progress in sizing, shaping and composition as a result of active research has opened up a market with plentiful applications ranging from using nanostructured cavities for advanced drug delivery in modern pharmaceuticals [35], cancer treatments [29], paints [74], flame retardant additives [88], printing [33] to ink-jet printed MEMS [48] and more.

**Figure 15:** Sketch relating the cube length with the surface area. The picture shows how the surface area increases dramatically when the initial cube is filled with smaller cubes while the volume is kept constant.
The future for nanoparticle and nanostructure applications is bright and with ultra-fast emerging technologies that have the potential to be “game changers” including 3D printing, fuel cells, neuromorphic microchips, solar cells, and many more, we sit on the cusp exploring the possibilities.

1.3.2: Characteristics of Microplasmas

Relevant to this dissertation is a division of nanoscience that focuses on the fabrication of nanoparticles by non-solution based methods, i.e. gas-phase based methods. This chapter is therefore dedicated to introduce the specifics of microplasmas that can be used in microplasma reactor systems to fabricate nanoparticles.

Microplasma are defined as plasmas with small expansion in at least one dimension, for example its length. Typical microplasma expansions can range from a few micrometers to thousands of micrometers. However, length limitations are usually found within the single digit millimeter range (< 10 mm) [112]. Microplasmas are operated under atmospheric conditions, making them easy to control and maintain. When they are used to fabricate nanoscale particulates, the size is mainly modulated by the pressure and length of the plasma – the so called pD-scaling (p for pressure and D for distance) [112]. Typically reported nanoparticle sizes range from 2 nm to 6 nm [28, 100]. By adjusting the electrode distances, the plasma length can be altered, which in terms defines the nucleation time for particulates.

The plasma confinement in typical microplasma reactor arrangements causes unique properties to appear. For instance, microplasmas are operated under non-thermal equilibrium conditions [92]. Figure 16 relates thermal and non-thermal operation regimes, for plasma with
set gas-flow, electrode geometry, gas mixture, etc., with the properties for pressure (p) and physical length (D).

Changing these parameters can shift the thermal equilibrium curve, indicated by the red arrows in Figure 16. In addition, effects like electrode cooling [98, 102], gas mixture selection [104] and pulsed power [21] can cause a similar shift, allowing for additional control of the non-equilibrium regime. If the electrodes are actively cooled, i.e. water cooling, more heat can be transferred away from the plasma, resulting in an upward shift of the thermal equilibrium curve to higher pressures [112].

**Figure 16:** Plasma operation regimes of a plasma with set gas-flow, gas-mixture, electrode geometry, etc. as a function of pressure (p) and plasma length (D). Microplasmas are operated in a non-thermal equilibrium in which the plasma gas temperature ($T_g$) is at least 10 times smaller than the effective electron temperature ($T_e$), indicating a low energy regime. The thermal equilibrium curve can be shifted by effects like electrode cooling, gas selection, pulsing, etc. From [112]. © IOP Publishing. Reproduced with permission. All rights reserved.\(^{15}\)

\(^{15}\) See Appendix A: Permissions for permission. Link to full text: [http://dx.doi.org/10.1088/0022-3727/43/32/323001](http://dx.doi.org/10.1088/0022-3727/43/32/323001)
Operating microplasmas under non-equilibrium conditions means that the plasma gas temperature $T_g$ is at least 10 times smaller than the effective electron temperature $T_e$ (compare Figure 16). As a consequence, microplasmas are much colder in comparison to plasmas operated at thermal equilibrium ($T_g = T_e$), i.e. large volume bulk plasmas. The increased electron temperature $T_e$ is a consequence of the plasma confinement that causes stronger electric fields and higher electron densities [111, 134]. It further increases the probability for electrons to collide inelastically with themselves or with neutral and ionic gas molecules. This allows for energy to be transferred between electrons but also to be passed onto injected precursor materials, i.e. electron heating [47].

At first glance, previously described plasma conditions sound unfavorable for material processing, i.e. the ability to decompose organo-metallic precursors effectively. On the contrary, non-equilibrium thermodynamics are in fact more desirable for the microplasma-assisted fabrication of nanoparticles because these conditions have the potential to open up new non-thermal reaction pathways. In addition, the “softer” plasma conditions allow the use of more sensitive precursor materials [92, 112]. Reactions in the plasma are promoted by electrons which allow avoiding high plasma temperatures that have the potential of causing unwanted particle coagulation [101]. This effect is further supported by assumed ionic nature of nucleating nanoparticles in the plasma [49, 75]. A detailed discourse of further microplasma characteristics can be found in a topical review a by D. Mariotti and R. M. Sankaran [112].
1.3.3: Basics of Microplasma Reactor Systems

The fabrication method is the key concept that dictates a nanoparticle’s size, shape and dispersity. Understanding, controlling and evolving the fabrication process is therefore very important to achieve better nanoparticle properties. In the last decade, a non-solution method has emerged that is capable of fabricating highly monodisperse nanoparticles, one of the most desired properties besides the actual size. The technique describes the use of DC microplasmas to homogeneously and continuously nucleate nanoparticles directly from the gas-phase by injecting volatile organo-metallic precursor materials into the plasma gas stream [28, 100, 101, 112, 113]. A simplified graphic of a microplasma reactor system is shown in Figure 17.

![Figure 17: Simplified sketch of a DC microplasma used to fabricate nanoparticles. The plasma is encapsulated in quartz insulation. Typical plasma lengths are in the millimeter range. Nanoparticles are produced by applying an electric field across cathode and anode. Passing inert gas, i.e. Ar, is ignited and injected precursor material is decomposed by the plasma. The length between cathode and anode determines the nucleation time and therefore the size of the nanoparticles. A resistor is used as ballast to limit the current after plasma ignition.](image-url)
In this setup, a hollow cathode (e.g. stainless steel capillary) and anode (e.g. stainless steel mesh) are encapsulated in a quartz tube. A high voltage is applied by a DC power supply connected across cathode and anode. Passing an inert gas, e.g. Ar, through the tubing ionizes the gas. Free electrons created that way are accelerated in the applied electric field and collide mainly inelastically with themselves or ionic and neutral gas molecules, thus transferring energy to the gas which at some point ignites the plasma. Once these conditions are reached, the plasma acts similar to a jumper wire connecting cathode and anode electrically which causes a current to flow. This current flow is usually reduced by a ballast resistor in series with power supply and anode.

To produce nanoparticles, an organo-metallic precursor is injected into the plasma gas stream causing its decomposition in the plasma. The precursor is usually kept in a reservoir in line with the plasma gas tubing. The flow rate of gas is controlled by mass-flow controllers. More advanced systems have multiple injection lines which allow intermixing just before the plasma to either inject multiple different organo-metallic species into the plasma or to dilute the plasma gas stream. Typical precursors that have been reported to work well with this process are volatile and easy to sublimate substances like ferrocene and nickelocene [28], copper acetylacetonate [100], platinum acetylacetonate [101], and other similar precursors. As a rule of thumb, the metal center of the precursor dictates the chemical stoichiometry of the nanoparticles.

Due to the ample presence of oxygen in the reaction chamber of the plasma, precursor byproducts (ligands and fragments of ligands) are usually fully oxidized to inert gaseous species, e.g. mostly CO\textsubscript{2} and/or vapor H\textsubscript{2}O. Analyzed nanoparticles fabricated with this technique are usually found in their highest oxidation state, i.e. using ferrocene results in the formation of Fe\textsubscript{2}O\textsubscript{3} nanoparticles [28].
1.3.4: Selected DC Microplasma Applications

Plentiful studies have been reported so far using DC microplasma reactor setups for nanoscale structure fabrication. They include the formation of nanoparticles, nanocrystals, nanofilms and even nanotubes. Some highlights are presented focusing on the formation of iron containing nanoparticles in an effort to set up a foundation to help classifying the contributions presented in later chapters (compare p. 138) of this dissertation.

Figure 18: Hollow cathode microplasma reactor system used to produce nanoparticles as precursors for CNT growth in a tube furnace. To grow the CNT’s, the nanoparticles are co-injected with H₂ and C₂H₂. Reproduced with permission from [22]. Copyright 2007, AIP Publishing LLC.¹⁶

An interesting application for the use of metallic nanoparticles, especially iron nanoparticles, is their capability to trigger and catalyze the growth of carbon nanotubes (CNT’s)

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either directly in a microplasma reactor system or in cascaded systems, e.g. a microplasma reactor connected to a hot oven or tube furnace. W.-H. Chiang et al. reported the fabrication of mono-metallic Fe and Ni nanoparticles from ferrocene and nickelocene respectively using a standard DC microplasma reactor setup (compare Figure 18).

The nanoparticles were subsequently injected with hydrogen (H₂) and acetylene (C₂H₂) into a tube furnace, catalyzing the growth of CNT’s on top of the initial nanoparticles. CNT’s fabricated that way are potentially interesting for nanoelectronics and nanocomposites [22-24]. A similar approach was described by S. Kona et al. He reported the use of ferrocene to deposit iron nanoparticle films on heated substrates with a DC microplasma reactor in order to trigger CNT growth in a CVD like approach [87]. P. A. Lin enriched this topic by reporting about high purity Fe nanoparticle fabrication and the effect of carbon impurities that can arise from using precursors with different ligands [101].

The technique is not limited to mono-metallic nanoparticles. In fact, it has been reported that multi-metallic nanoparticles like NiₓFe₁₋ₓ [24-28, 113], NiₓCu₁₋ₓ and even more complex structures [100] can be generated as easy as mono-metallic equivalents by co-injecting appropriate precursor materials. By optimizing the process parameters, precise control of the atomic ratios can be achieved. W.-H. Chiang for instance reported how fine-tuning the size and composition of multi-metallic NiₓFe₁₋ₓ nanoparticles can be used to optimize the chiral-selective fabrication of single-walled CNT’s (SWCNT’s), which is of major importance for nanomedicine applications [25]. P.A. Lin et al. reported the incorporation of Fe into multi-metallic nanoparticle structures to form tri-metallic nanoparticles, i.e. Ni₁₋ₓ₋ₓFeₓCuₓ, for potential applications in novel nanoelectronics. She further presented how this technology can be adapted to control atomic
fractions of multi-metallic nanoparticles, thus pushing the boundaries further in terms of composition complexity (compare Figure 19) [100].

The continuous process underlying this technique and the scalability of individual DC microplasma reactor units into arrays make it versatile and interesting for industrial applications. Conceptually, D. Mariotti and R.M. Sankaran reported that cascaded arrays of nanoparticle generating units, shown in Figure 17, are technically capable of producing multilayered nanoparticle films [112].

Figure 19: DC microplasma setup operated under atmospheric conditions showing the production of multi-metallic nanoparticles. The plasma gas and the precursors are injected co-jointly into the plasma. From there, they are decomposed and the metal centers nucleate together to form multi-metallic nanoparticles. The organic ligands are oxidized to gaseous species (CO₂) because of the presence of oxygen in the reaction chamber. From [100]. © IOP Publishing. Reproduced with permission. All rights reserved. ¹⁷

¹⁷ See Appendix A: Permissions for permission. Link to full text: http://dx.doi.org/10.1002/anie.201101881
Each individual array or even each individual unit could be fed with different precursor materials. The films produced that way can therefore consist of either mono-metallic or multi-metallic particles allowing for very complex structures to be built in a continuous process. A concept drawing of this process is shown in Figure 20.

However, all fabrication methods presented so far have one problem in common – they operate under ambient conditions, which can cause problems originating from ambient process contaminations. These contaminations have the potential to influence the unique surface properties of nanoparticles, i.e. catalytic activity, optical properties, etc. Therefore many industrial applications require very clean process and analysis environments, i.e. clean rooms and integrated vacuum systems. A proof-of-concept approach showing that DC microplasma reactor systems can be adapted to work in clean vacuum environments can therefore be seen as advancement of this technology. It would not only allow contamination-free fabrication of nanoparticles directly in vacuum, in addition, it would enable the contamination-free analysis of those particles, which is especially important for surface sensitive analysis techniques, i.e. photoemission spectroscopy. In that light, chapter 6 of this dissertation takes on this challenge and presents the adaption of a DC microplasma reactor system into a multi-chamber photoemission spectroscopy system, enabling direct in vacuo fabrication and contamination-free electronic structure characterization of nanoparticles (compare p. 138).
Figure 20: Concept drawing of arrays of nanoparticle producing microplasma units stacked and cascaded to form nanoparticle multilayer films continuously while a substrate is moved in scanning direction. This method is expandable to incorporate desired number of multilayers. Each layer can conceptually consist of different materials. This technique is very versatile and its continuous processing scheme makes it interesting for industrial applications. From [112]. © IOP Publishing. Reproduced with permission. All rights reserved. 18

1.4: Significance of the Electronic Structure Characterization

The core concept used to characterize materials in this dissertation was the electronic structure of materials. This chapter is dedicated to talk about the general impact and importance of the electronic structure in the scope of materials science and what we can learn from its characterization.

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Understanding, analyzing and manipulating the electronic structure of novel materials is the key for their advancement, but also challenge in the world of materials science and materials characterization in the 21st century. The availability of fast supercomputer simulations and optimized algorithms based on quantum mechanical equations, allows for complex electronic structures to be calculated nowadays. This approach technically allows to tailor-design properties of materials to one’s liking, making it a very powerful and complimentary method to classical experimentation. However, understanding the core principles of a material’s electronic structure and its interaction in contact with other materials not only from a theoretical standpoint but also an experimental one is necessary to achieve further advancement in the development of new materials, material interfaces and to use them in real world applications. In general, the electronic structure is a reflection of how electrons are distributed in a material, in what fashion they interact with each other, or how they react to external stimuli. Therefore, analyzing the electronic structure, e.g. with a photoemission spectroscopy system (PES) which allows probing the electronic density in a material directly, enables the prediction of a material’s behavior in terms of its electronic properties with high precision. Some of these properties include (super)conductivity [34], resistivity [152], magnetic properties [15], band structure [121], thermoelectricity [8, 145], dielectric properties [157], plasmons [137, 146], etc. The ability to precisely manipulate the electronic structure, in extreme cases reaching manipulations of single atoms, is object of a wide field of research nowadays. Some selected “hot topics” include applications of novel materials for spintronics [153], quantum computation [38, 122], non-volatile memory arrays [91, 139], thin film transistors [80], and more. Manipulations of materials on the order of less than 100 nm are common today and are used to tailor design the electronic structure for application specific needs. These manipulations push the boundary of existing
fabrication and characterization technologies further every day. The ever ongoing down-sizing of electronic devices over the last decades created a necessity for new fabrication techniques capable of panning along with the increasing miniaturization. For that purpose, technologies had to be invented capable of achieving this high level of precision. For example, *atomic layer deposition* (ALD) was designed to coat materials with high conformity thin films, often less than 10 nm thick. These tools are often used in conjunction with PES which gives direct access to the elemental makeup of materials, quantitative composition, oxidation state, crystal structure and orientation, surface termination and more, making those techniques very powerful if used co-jointly. Large integrated UHV systems are used nowadays combining fabrication, analysis and manipulation systems, allowing for precise experimentation in situ without exposing the material to ambient conditions [71, 72, 76, 140].
CHAPTER 2: METHODOLOGY

2.1: Atomic Layer Deposition

Atomic layer deposition (ALD) is a modern gas phase based thin film deposition technique that can best be compared to deposition techniques like chemical vapor deposition (CVD) [14, 39, 77] or physical vapor deposition (PVD) [110, 115]. While all three methods aim at a similar target – namely the gas phase deposition of vaporized precursors on substrates to coat them with a thin film – ALD is superior over the other methods in at least three ways. First, the precursors used in the process are not only vacuum gas phase stable but also inert to reacting with each other. A simple detail that is a key advantage over other methods because the precursors can only react with the surface of the substrate, given optimized deposition conditions, and not with the reactor walls, injection lines or any other parts of the reactor, thus preventing unwanted or uncoordinated thin film growth. Second, the precursors are injected sequentially rather than simultaneously. In other words, they never encounter each other in the gas phase where they could potentially react with each other. This is made possible by intermediate purging with an inert gas like argon or nitrogen. The sequential sequence further enables a precise control over the thin film thickness and flatness. Third, due to the substrate surface-bound reaction scheme, excellent step coverage can be achieved. This leads to highly conformal thin films on flat substrates but more so on substrates including high aspect ratio features like trenches, vias, etc. Even 3D features like holes, loops and non-surface exposed
features can be coated with high conformity thin films [41, 85, 138]. The superiority in terms of step coverage compared to other methods like CDV and PVD is shown in Figure 21. Common precursors used in ALD usually consist of specifically designed organometallic molecules that greatly have improved in variety over the last two decades, allowing the deposition of nearly unlimited combinations of materials nowadays including metals, semiconductors and insulators [57, 97].

![Figure 21: Comparison of the step coverage for a) CVD, PVD and b) ALD. It is shown that ALD has highly conformal step coverage even on parts of the substrate not facing the source. This is a key advantage of ALD over other deposition methods.](image)
2.1.1: Methodical Foundation

*Atomic layer deposition* (ALD) is a modern thin film deposition technique. Its core principle however was initially proposed by the organometallic chemist V. Aleskowsk in the 1950’s. Initially, he called the method *molecular layering* (ML) due to the effect of using molecules to build thin films layer-by-layer. From there it took about 20 years until in the 1970’s a team of Finnish scientists around T. Suntola and coworkers [142] considered this technology for industrial applications in electroluminescent flat panel displays (TFEL). Back then, Suntola renamed the method to *atomic layer epitaxy* (ALE) which established itself as the common name for this technique at that time. The name was insofar an interesting choice as ALD, as we know it nowadays, is known to grow non-epitaxial, poly-crystalline thin films rather than epitaxial, single-crystalline thin films. It took until the late 1990’s to catapult ALD from what was considered a niche-technology with sparse applications and rare publications to the mainstream exceeding 1000 publications yearly. The ever continuous efforts of down-scaling microelectronics at the beginning of the 21\textsuperscript{th} century created the necessity for a thin film deposition technique that was capable of producing highly conformal thin films on levels of thicknesses not achieved before. At that time, the technology reached its highest level of publicity when Intel announced the adaptation of the deposition method into their HfO\textsubscript{2}-based high-dielectric CMOS transistor production line. Nowadays, many applications exist, utilizing ALD thin films for ample reasons. With a better understanding and utilization of the deposition method, it was given its name as we know it nowadays: *Atomic Layer Deposition*, mainly to eliminate the controversy with other deposition methods like *pulsed laser deposition* (PLD) that truly produces epitaxial thin films and to instantiate ALD as its own method [50, 138, 141, 142].
2.1.2: General Reactor Layout

A typical ALD reactor consists of the following modules:

1. Reaction chamber,
2. Precursor/reactant delivery system,
3. Exhaust pumping system,
4. Reactor control.

A simplified version of two of the most used reactor types – the thermal ALD reactor and the plasma-enhanced ALD reactor – are shown in Figure 22.

The reaction chamber is usually heatable and equipped with a heatable sample stage to allow the samples and the chamber to be heated individually during the ALD process. Heating the sample and chamber respectively serves two purposes: First it prevents condensation of precursor material in unwanted spots and in a thermal ALD reactor, the heated sample stage is used to supply the necessary activation energy for the reaction. The volume of the reactor body is usually kept as little as possible to allow injected precursors to fill the chamber homogeneously as fast as possible in order to keep the pulsing/purging times minimal. The precursor/reactant delivery system consists of two individual injection lines for precursor and reactant. However, most plasma-enhanced ALD reactors have only one injection port for precursors due to the fact that the plasma gas and reactive species created within serve as reactant, making a second injection line redundant. In most cases, the injection lines are connected via multiple valves to individually heatable precursor and reactant reservoirs, allowing for the separate injection and heating of those materials.
Figure 22: Simplified version of a) a thermal ALD reactor and b) a plasma-enhanced ALD reactor. Both reactor types are usually equipped with a heatable sample stage, exhaust pump lines with a shut-off valve, allowing disconnecting the reaction chamber from the pump lines, and injection lines for precursor and reactant each line equipped with a shut-off valve, allowing precise dosing of precursor material into the chamber. Note that a plasma-enhanced ALD reactor normally only has one inject port for precursor material due to the fact that the reactant is usually reactive species created from the plasma gas.

Further, a carrier gas is used in most reactor types helping with the transportation of the precursor material into the reaction chamber. The gas delivery system is normally enclosed inside a fume hood because of the toxicity of most ALD precursors. The exhaust system is used to purge leftover precursor and reactant from the reaction chamber. In most reactors a standard roughing vacuum pump filled with poly-fluorinated pump oil (Fomblin PFPE) is used to prevent the reaction of leftover precursor or reactant with pump oil. The reactor control is usually tied together in an integrated system including the control hardware with a backend interface to the
individual parts and a front-end user interface that allows convenient control and monitoring of all sub systems. The user interface usually allows programming the ALD reactor for various ALD sequences. Once programmed, the reactor runs automatically until the sequence is completed [50, 97, 138].

2.1.3: Reaction Principle

To illustrate the reaction principle of ALD in greater detail, one of the most well-studied ALD reactions since the technology was invented shall be considered – the reaction of trimethyl aluminum (Al(CH$_3$)$_3$) and H$_2$O, forming the vastly used high-k dielectric material Al$_2$O$_3$ [54, 138]. A simplified reaction is shown below (compare Figure 23).

$$\text{Substrate-OH}^* (s) + \text{Al(CH$_3$)$_3$} (g) \rightarrow \text{Substrate-O-Al-CH$_3$}^* (s) + \text{CH}_4 (g),$$

$$[\cdots]\text{-Al-CH$_3$}^* (s) + \text{H}_2\text{O} (g) \rightarrow [\cdots]\text{-Al-OH}^* (s) + \text{CH}_4 (g),$$

$$[\cdots]\text{-Al-OH}^* (s) + \text{Al(CH$_3$)$_3$} (g) \rightarrow [\cdots]\text{-Al-O-Al-CH$_3$}^* (s) + \text{CH}_4 (g).$$

Solid reactants or reaction products are denoted with (s) and gaseous reactants and reaction products are denoted with (g).

The ALD reaction is based on two self-limiting half-reactions also referred to as the key-lock-principle. This picture is used to symbolize that the precursor can only react with the reactant and vice versa, similar to how each key fits only into a specific lock.
Figure 23: Illustration showing the ALD growth of Al$_2$O$_3$ on an activated and hydroxyl group terminated substrate based on the alternating injection of trimethyl indium and water vapor. The simplified reactions are displayed. After injection of the precursor, it reacts with the surface hydroxyl groups to form an intermediate methyl group terminated product, binding Al to the existing oxygen atoms on the surface and releasing methane. The successive injection of water changes the surface groups into hydroxyl groups while more methane is released. The cycle is repeated until desired thickness is reached.

However, the reaction scheme is as follows. Initially, the activated surface of a substrate, e.g. by temperature, radiation, etc. is exposed to the gaseous precursor. The precursor reacts with the activated surface and forms an intermediate species under the release of small gaseous molecules of methane. The release of those gaseous molecules is not limited to methane. In fact in similar reactions, molecules like carbon dioxide, carbon monoxide, water, etc. are common.
The precursor reacts with the surface until all activated surface groups have reacted and the surface is covered. Once this point is reached, the reaction stops due to the inertness of the precursor towards a reaction with itself. Leftover precursor gas is purged from the system using an inert gas like argon or nitrogen prior to the injection of the reactant water. Once it is injected, it reacts with the remainder of the methyl groups in a similar fashion, releasing more gaseous molecules of the same kind. At this point, the individual intermediate metallic species on the surface start interconnecting with each other, either directly or through linking oxygen. Once the surface is covered, the reaction stops again and leftover reactant is purged from the reaction chamber using the precursor gas. The alternating injection sequence is repeated until desired thickness is achieved. A cartoon of a general ALD sequence is shown in Figure 24 emphasizing the advantage of the alternating injection of self-limiting precursor gasses utilizing the key-lock-principle [50, 97, 138].

2.1.4: ALD Types

Atomic layer deposition can be operated in different ways, each of them having distinct advantages and disadvantages, making them viable and necessary depending on the type of application. Among those methods there are two major varieties: Thermal ALD and plasma-enhanced ALD (PEALD) sometimes also called plasma-assisted ALD or radical-assisted ALD. Thermal ALD is based on cascading binary ligand exchange reaction:

\[ A + B \rightarrow C + D_{\text{inert}}, \]
Where A and B stand for precursor and reactant respectively. The intermediate product C reacts sequentially with either precursor (A) or reactant (B) to continue the reaction. Each step of the reaction releases a reaction-inert by product $D_{\text{inert}}$.

**Figure 24**: General ALD sequence showing the self-limiting character of the ALD half-reactions in a simplified form. The sequence starts with the injection of the precursor gas. The precursor reacts with the substrate surface until it is covered. Excess molecules do not react with each other. After purging out leftover precursor gas, the reactant is injected. It reacts in a similar fashion with surface as the precursor. Leftover molecules are purged from the system and the cycle is repeated until the desired thickness is reached.
In this type of ALD, the substrate is heated to a temperature significantly higher than the rest of the reactor. This is creating a temperature gradient between the sample stage and the surrounding reactor, shifting the balance of the underlying chemical reaction ensuring that the reaction occurs predominantly on the substrate surface. The precursor gasses in thermal ALD are designed in such a way that the sum of the two half-reactions is exothermic. However, to initiate the reaction, the precursor gasses have to overcome a certain amount of activation energy. Under optimized reaction conditions, this energy is supplied as thermal energy by the heated substrate. For example, the thermochemistry and kinetics for the reaction of trimethyl indium and water predicted by DFT calculations is exothermic by 25.1 kcal/mol with an initial energy barrier of 14.1 kcal/mol for the adsorption reaction of trimethyl indium molecules on activated surface hydroxyl groups. The initial adsorption barrier for the second half-reaction, namely the reaction of water molecules with intermediate Al-clusters is calculated to 16.1 kcal/mol \[138\]. The biggest advantage of thermal ALD over PEALD is its superior step-coverage. Due to the coupling of the reaction and its initiation to the substrate surface rather than in the gas phase, everything that supplies enough activation energy is covered with high conformity. Even complex structures like vias, trenches, holes, loops, etc. are covered conformally. PEALD on the other hand only covers parts of the substrate that were exposed to the plasma during the ALD process. Other advantages of thermal ALD concern the thin film quality. Thermal ALD films are usually considered flatter and free from plasma induced damage. This damage can influence the growth rate negatively or diminish the performance of the thin film once embedded in larger structures.
Plasma-enhanced ALD is another variation of ALD based on radical reactions:

\[ \text{A} \rightarrow \text{A}^*, \]
\[ \text{A}^* + \text{B} \rightarrow \text{C}. \]

Here a plasma activates the reactant (A → A*). By sequential injection of the substrate with the precursor B and exposure to the plasma, the activated reactant A* co-reacts with the precursor B, forming the reaction products C. The plasma in PEALD usually consists of O\textsubscript{2}, N\textsubscript{2}, H\textsubscript{2} or a mixture thereof. Its main purpose is to serve as energy source, supplying the initial activation energy for the reaction. Over the years many different reactor types were created mainly varying the way either the plasma is produced or how direct or indirect the sample is exposed to the plasma. Worth mentioning is the radical-enhanced ALD reactor, belonging to the family of indirect plasma ALD reactors, using microwave plasma separated from the reaction chamber. The reactive species created in the plasma has to travel through tubing to reach the substrate. Another configuration is called RF diode reactor belonging to the class of direct plasma ALD reactors. Here the sample that is usually grounded serves directly as one of the electrodes to create RF type direct plasma. PEALD precursors are designed to react with molecules that are standardly used to create plasmas which make a separate reactant injection unnecessary. Typically, the molecules from whom the plasma is created take over the functionality of the reactant. In rarer cases of thin film processing, additional reactants are used. In these cases, the reactants are usually injected separately into the reaction chamber either through a showerhead embedded into one of the plasma electrodes or separately through an injection port at the side of the plasma. Plasma-enhanced ALD has become more and more
popular over the last decade. The method has several advantages over thermal ALD from which the three main advantages shall be mentioned here. First, the larger availability of precursors allows for a larger combination of materials to be fabricated. Due to the higher energy in the plasma it is unproblematic to create materials that need higher activation energies like nitrides, carbides, etc. Due to energy limitations in thermal ALD, these materials are harder or impossible to fabricate. In special cases involving metals like Ti and Ta and their nitrides, no precursors are known to exist for thermal ALD, which makes PEALD the only ALD variation for fabrication. Another advantage is based on the source of the activation energy. In thermal ALD the substrate needs to be heated to high temperatures in order to supply enough energy for the reaction to start. In PEALD on the contrary, the activation energy is supplied by the plasma instead of the substrate. This allows for the substrate to be maintained at lower temperatures or not being heated at all. This in turn allows for a wider variety of more temperature sensitive substrates to be used in the process. The higher energy in the plasma further causes the creation of a higher number of active surface sites with each subsequent plasma exposure, leading to a higher thin film density and elevated growth rates. In PEALD it is common nowadays to use the plasma for further substrate and thin film processing, giving this method a wide selection of treatment possibilities including cleaning, passivation, nitridation, oxidation, etc. Some of the major disadvantages of PEALD over thermal ALD include limited control over thin film thickness and inferior step coverage due to the decoupled initiation of the reaction from the substrate surface as well as thin film damage that can occur when the sample is exposed to the plasma for prolonged amounts of time [50, 97, 138].
2.1.5: ALD Modes

The ALD sequence, meaning for how long and how fast the precursors and reactants are injected respectively for how long a sample is exposed to the plasma, is important for the quality of the final thin film (density, flatness, conformity, step-coverage, etc.). An ALD reactor can generally be operated in two modes: continuous flow mode and stop flow mode. Both are fundamentally different from each other in terms of pulsing, sometimes called injecting, and purging of the precursors and reactants respectively (Figure 25). The most common mode used nowadays (especially in the industry) is the continuous flow mode in which the precursors and reactants are injected very rapidly while the reaction chamber is connected to the exhaust pumping lines. This creates a continuous viscous flow of carrier gas and injected precursors and reactants to the exhaust pumps. This mode allows for very fast pulsing/purging cycles, making it possible to build thick thin films in a reasonable amount of time. However, due to minimal time for the precursor and reactant to react with the surface, the step coverage is usually inferior to operating a reactor in stop flow mode [50].

In stop flow mode on the other hand, the pulsing or injection cycle is subdivided into two parts – fill and hold. In the fill part of the injection cycle, the chamber is filled with precursor or reactant which is followed by a variable hold time. One this time has passed the gasses are purged from the system. To be able to operate an ALD reactor in that mode it is necessary to have a shut-off mechanism in place that can quickly and periodically isolate the reaction chamber from the exhaust pumping lines allowing for the precursor and reactant to remain in the reaction chamber. Usually pneumatic valves tied into the ALD control program are used for that purpose. The prolonged time in which the samples are exposed to the precursor and reactant
allows for the underlying reaction to happen completely which results usually in perfect step coverage and very flat films. It takes much longer to achieve a certain thick thin film which is the major disadvantage of this mode [81, 97, 138].

**Figure 25:** Display of the different ALD modes distinguishing between continuous flow and stop flow. In continuous flow mode, the precursors and reactants are injected very rapidly and without cutting off the chamber from the exhaust pumping lines. In stop flow mode, the reactor chamber is cut off from the exhaust lines during injection, allowing the precursors to fill up in the chamber.

### 2.2: Photoemission Spectroscopy

Photoemission spectroscopy (PES) is an UHV analysis technique that was mainly used throughout this dissertation to analyze the electronic structure of materials based on generated photoelectrons, often referred to as density of states (DOS), as a function of their binding energy or kinetic energy respectively. Generally, the technique can be sub-categorized into four
variations. Each of them is used to scan a different energy range, giving access to the complete spectrum of the electronic structure if used in conjunction. The four main variations are: *Low Intensity X-Ray Photoelectron Spectroscopy* (LIXPS), *X-Ray Photoelectron Spectroscopy* (XPS), *UV Photoemission Spectroscopy* (UPS) and *Inverse Photoemission Spectroscopy* (IPES). Besides those four variations, others more specialized ones exist including *Angle-Resolved X-Ray Photoelectron Spectroscopy* (ARXPS), *Auger Electron Spectroscopy* (AES), *Electron-Impact Energy-Loss Spectroscopy* (EIS), and others. Those variations will not be further discussed in the scope of this particular dissertation because they hold no relevance but were mentioned for reasons of completeness and were further supposed to emphasize that PES possesses applications beyond the scope of what is presented here in this dissertation. Photoemission spectroscopy is based on the *photoelectric effect* first observed by Heinrich Hertz in 1887 [64] and later described by Albert Einstein in his revolutionary paper in 1905 [40]. His theory was later awarded with the Nobel Prize in 1921 and is assumed to have initiated modern quantum theory. It took however until the 1950’s before a team around Siegbahn et al. build the first spectrometer using this effect [124]. Based on the excitation energies used in the process, the maximum penetration depth of the incident photonic radiation is not higher than a couple microns, giving the method its characteristic surface sensitivity which is its greatest advantage [2, 6, 20, 70].

In this dissertation specifically, LIXPS was used to determine the material work function, interface dipoles and the presence of charging effects and UV light induced surface alterations. XPS was used to determine the energetic structure of the core level, UPS was used to determine the energetic structure of the valence band and IPES was used to determine the energetic structure of the conduction band.
2.2.1: The Photoelectric Effect

In the classic interpretation of the photoelectric effect, a three step model can be used to describe the formation of free photoelectrons. These photoelectrons can be used in a photoemission experiment to determine the electronic density as a function of the binding energy or kinetic energy respectively. A simplified version of the three step model is shown in Figure 26. LIXPS, UPS and XPS operate based on this principle. IPES on the other hand is based on the inverse process also referred to as inverse photoelectric effect.

**Figure 26:** Simplified schematic of the three step model used to describe the photoelectric effect classically. Shown is a) the photo excitation of initial state electrons by photonic radiation into unoccupied final state orbitals, b) the ballistic transport of final state electrons to the material surface undergoing elastic and inelastic scattering and c) the escape into vacuum by overcoming the surface potential or work function of the material.

In the first step of this model – also called *photoexcitation step* – the incident photonic radiation is absorbed by electrons in the material lifting those electrons, called initial state
electrons, from their initial state orbitals at a specific binding energy into energetically higher unoccupied orbitals. These states of higher energy are also referred to as final state. In a second step, the excited electrons are transported to the surface of the material by ballistic transport. In that process many of them collide with other electrons on the way. Those collisions can be elastic and inelastic. If the collision was inelastic, the electron loses parts or all of its kinetic energy which means it loses the energetic information of the binding state it originated from. Those electrons have no value in a photoemission experiment and are referred to as secondary electrons. These electrons are detected as background noise in a photoemission spectrum. The electrons that arrived at the material surface without undergoing inelastic scattering are called prime electrons and are those that still contain the energetic information of their origin. If the electron possesses enough energy to overcome the surface potential of the material, or in other words, has a higher energy than the work function of the material, it can escape into vacuum which is the final step of the photoemission process. Once escaped into vacuum, the electrons are detected in an energy dispersive electron detector at which their kinetic energy can be evaluated. A simple relation can be used to correlate the kinetic energy of the photoelectron $E_{\text{kin}}$ with the energy of the incident radiation $h\nu$, the material work function $\Phi$ and the binding energy of the initial electron $E_B$. It shall be noted that final state screening effects $E_{\text{screen}}$, caused by relaxation processes of the electrons after photo excitation, need to be considered when evaluating the initial binding energy of the electron. Hence, the binding energy of an electron can be calculated by:

$$E_B = h\nu - E_{\text{kin}} - \Phi - E_{\text{screen}}.$$  (9)
A typical XPS spectrum displays the intensity $I$ or the count rate of photoelectrons in arbitrary units (a.u.) as a function of binding energy or kinetic energy in electron volts (eV) (Figure 27).

**Figure 27:** Typical non-background corrected PES survey spectrum showing the count rate of photoelectrons as a function of binding energy or kinetic energy respectively. At high binding energy, the amount of secondary electrons is high, resulting in a high background. This background reduces progressively in a step-wise fashion as the spectrum approaches lower binding energies. The steps originate as a consequence of the energy dispersive analyzer system. Typically, the analyzer scans from high binding energies (left of spectrum) to low binding energies (right of spectrum). Every time an emission feature is surpassed, less secondary electrons are created which results in a smaller total count rate.

The PES spectrum shows a high background for high binding energies. This background is a consequence of the formation of secondary electrons that are created in the second step of the photoemission process. Analyzers in a photoemission experiment usually scan from high to low binding energy. The background caused by secondary electrons reduces progressively as the analyzer approaches lower binding energies. In fact, after each emission feature is passed, the
overall intensity drops significantly, giving the PES spectrum its characteristic step structure. The amount of photoelectrons generated at a specific binding energy is mainly dependent on the so called *ionization cross section* $\sigma$ that describes the interaction or cross section of the incident photonic radiation with the wave function representation of the electron, giving a probability for successful photo excitation. Further factors influencing the amount of generated photoelectrons are related to the atomic concentration of a particular element $n$, the analyzer transmission function $T(KE)$, the angular asymmetry factor $L$, the inelastic mean free path $\lambda(KE)$ and the emission angle $\theta$. The ionization cross section $\sigma$ and the inelastic mean free path $\lambda(KE)$ are usually combined into a so called *sensitivity factors* $s$. The values are tabularized for all important elements in the manual of the particular PES system or integrated into the analysis software directly. Due to the fact that the sensitivity factor is different for different elements means that the intensities of peaks for different elements are not directly correlated to their quantity in the analysis volume of the sample. They can therefore not be used to infer the stoichiometric composition of the material directly. However, correcting the peak intensities with their respective sensitivity factors $s$, enables a precise quantification [2, 6, 20, 70].

2.2.2: The Inverse Photoelectric Effect

The inverse photoelectric effect is similar to the photoelectric effect. The premise however in this concept is that electrons are used to create photons. The energy of these photons $E = h\nu$ is related to the unoccupied electronic states in a material and can be described as:
with the energy of the initial unoccupied state $E_i$ and the energy of the final state radiative decay $E_f$. The inverse photoelectric effect can be described classically with an inverse three step model in a similar fashion to the three step model used to describe the photoelectric effect. A simplified sketch is shown in Figure 28. The initial electron with defined kinetic energy impinges on the material surface. From there it binds to an unoccupied state. In a final step it can decay either radiative, by emitting a photon with energy $h\nu$, or non-radiative through inelastic scattering with other electrons. In the second process the electron can lose parts or all of its kinetic energy rendering it useless.

Figure 28: Simplified sketch of the inverse three step model used to describe the inverse photoelectric effect. In a first step, an electron of defined kinetic energy impinges on a material surface. From there it binds to an unoccupied electronic state in the material. In the last step the electron can decay radiative in order to create a photon with the energy $h\nu$, or non-radiative through inelastic scattering in which the electron can lose parts or all of its kinetic energy.
The emission cross-section in IPES is much smaller compared to the ionization cross section in PES leading to reduced intensities in IPE-spectra. This ratio can be calculated exactly but will not be elaborated upon in the scope of this dissertation [65, 66, 135, 162].

2.2.3: X-Ray Photoelectron Spectroscopy (XPS)

X-Ray Photoelectron Spectroscopy (XPS) is a variation of Photoemission Spectroscopy (PES) used to probe the density of states (DOS) of core level electrons. This technique allows the analysis of the elemental composition, chemical environment of individual elements and determination of the thickness of thin films grown on top of substrates. In typical setups, X-rays generated by an X-ray gun are used to create the incident photonic radiation. Standard X-Ray guns used in that technique are equipped with Mg and Al anodes that produce characteristic Kα radiation by accelerated electron impact with the anode at 1253.6 eV and 1486.6 eV respectively. This energy allows the radiation to penetrate a material’s surface deeply. However, the elastic escape length of photoelectrons is only on the order of a couple nanometer. This fact gives the technique its characteristic surface sensitivity. In the scope of this dissertation, XPS was performed using Mg Kα radiation. Figure 29 shows a simplified sketch of XPS setup used in this dissertation. The incident radiation creates photoelectrons via the three step model (compare p. 61). The vacuum-ejected photoelectrons then travel into an analyzer system where their intensity is recorded as a function of binding energy. The analyzer system allows energy dispersive scanning of the photoelectron intensity by applying a varying electrostatic potential to the analyzer dome. X-ray gun and sample are positioned in such a way that angle between incident radiation and propagation direction of photoelectrons is 54.7°, also referred to as magic angle. In

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this configuration, angular dependent effects that alter peak positions and intensities are excluded. It shall be noted that a variation of XPS exists, i.e. Angle Resolved XPS that specifically varies the angle between analyzer and surface normal of a sample in order to derive if an emission feature is related to a surface state or the thickness of certain thin films. In the scope of this dissertation, this technique bears no relevance and is therefore not further discussed.

Within the limits of XPS, two types of spectra are generally differentiated – survey spectra and high magnification spectra. The survey spectrum is usually recorded first and gives an overview over the elemental composition of the analysis volume. This spectrum’s advantage lies in the usage of higher pass energy in the analyzer system which allows more electrons to reach the detector. This results in a higher signal to noise ratio for individual core level emission features but sacrifices energetic resolution. This fact is acceptable as the survey spectrum is only supposed to give a qualitative overview of the elemental composition in the analysis volume. A typical survey spectrum is shown in Figure 27. Once a survey spectrum is recorded and the qualitative elemental composition is revealed, high magnification spectra of specific points of interest, i.e. the core level emission features of elements of interest, can be recorded. Usually, the core level emission feature with the highest intensity is measured. High magnification spectra have a much lower intensity in comparison to survey spectra due to lower analyzer pass energy. However, the resolution is drastically increased, allowing detecting details like multiplet peaks containing emission features from elements embedded in different chemical environments or small peak shifts due to structural or chemical changes.

The binding energy of a core level emission feature is directly related to its chemical environment. Treating a sample surface, i.e. deposition, annealing, sputtering, UV exposure, etc., can induce a shift of the emission feature. Analyzing this shift, referred to as chemical shift,
be used to extrapolate important information about the elements in a material including general structural bonding, oxidation state, coordination state, hybridization, etc. XPS can also be used to evaluate the thickness of a thin film grown on top of a material. For that purpose the core level emission features of the substrate has to be measured before and after deposition. The intensity attenuation of the substrate emission feature is a function of the thin film thickness, i.e. electrons have to travel through the thin film on top of the substrate.

**Figure 29:** Typical XPS setup showing the formation of photoelectrons by bombarding a material with incident X-ray radiation. Vacuum-ejected photoelectrons travel through an analyzer system where their intensity as a function of binding energy is recorded. The hemispherical analyzer system shown in this picture allows energy dispersive scanning of the photoelectron intensity based on the electrostatic potential applied to the dome.
With increasing thin film thickness the substrate signal is attenuated. This method assumes a perfectly conformal thin film in which defects are not reflected, i.e. holes that expose the substrate to the incident radiation would increase the overall measured emission intensity of the substrate signal, ultimately leading to an underestimation of the thin film thickness. Once the attenuated signal strength is determined, the intensity of the pre-deposition emission feature \( I_0 \), the attenuated signal \( I \) and the electronic mean free path \( \lambda \) can be used in a Lambert-Beer relation to calculate the thickness \( d \). The relation is given as:

\[
d = \lambda \cdot \ln \left( \frac{I_0}{I} \right) \tag{11}
\]

In the scope of this dissertation, XPS was used to determine the general elemental composition of the fabricated thin films, the influence of the thin film to the core level emission features of the underlying substrates, the surface termination of the thin films and the thickness of the thin films [2, 6, 20, 70].

2.2.4: Low Intensity Photoemission Spectroscopy (LIXPS)

Low intensity X-ray photoelectron spectroscopy (LIXPS) is a variation of XPS that can be used to determine the magnitude of a material’s work function. The work function describes the energy needed to eject an electron from the Fermi-level into vacuum. It is a characteristic material property that is associated to its surface rather than its underlying bulk structure. Therefore the technique allows the determination of small material alterations occurring on the surface [2, 6, 20, 70]. In LIXPS, the excitation source (X-ray gun) used to create photoelectrons
is operated in standby mode, thus only emitting a low photon energy. In that setup, only electrons close to the Fermi level can escape, giving the technique its characteristic surface sensitivity. Its reliability has been confirmed by comparison with Kelvin probe measurements [11]. In many photoemission experiments, the work function is determined by using the secondary edge in UPS spectra (compare Figure 31). However, this method can have one distinct disadvantage when oxide materials (InSnO$_3$, TiO$_2$, etc.) are investigated. When radiating those materials with UV light, it has been demonstrated previously that photochemically induced surface reactions, i.e. surface hydroxylation, can occur that alter the material surface by introducing a surface dipole [56]. This dipole further alters the work function and therefore needs to be taken into account in these situations. LIXPS does not cause those surface reactions due to the low photon flux used in the method. In a typical photoemission experiment that includes exposing the sample to UV radiation, i.e. UPS characterization, LIXPS can be performed before and right after UPS to capture eventual surface altering effects caused by the UV exposure. An example of the effect is shown in Figure 30.

Here, an indium tin oxide sample has been characterized by LIXPS and UPS in the following sequence: LIXPS – UPS – LIXPS. LIXPSa and LIXPSb show the measurement of the work function in comparison with the secondary edge derived from intermittent UPS. It can be clearly seen that both LIXP-spectra are shifted, suggesting the formation of a permanent dipole that is inherent with a permanent shift of the work function.
Figure 30: Intensity as a function of binding energy in a typical LIXPS – UPS – LIXPS work function measurement. It can be clearly seen that the two LIXP-spectra are shifted, suggesting the formation of an interface dipole and therefore a permanent alteration of the work function due to the intermittent UV light exposure.

In the scope of this dissertation, LIXPS was used to determine the work functions at the Au | Ru(O₃) and TiO₂ | In₂O₃ interface respectively. From those measurements, the interface dipole, the presence of surface related charging effects and UV radiation induced surface modifications were inferred.

2.2.5: UV Photoemission Spectroscopy (UPS)

UV Photoemission spectroscopy (UPS) is a variation of Photoemission Spectroscopy (PES) used to probe the valence band electronic density of states of a material. In comparison to
XPS, this technique uses a capillary discharge UV lamp to create the incident photonic radiation. However, the same analyzer system is used for XPS and UPS. The discharge lamp is usually operated with He. By applying a certain voltage across the electrodes within the lamp, He is ionized and emits photons mainly from the He(I) and He(II) line. For UPS the lamp is operated in a configuration that it emits mainly photons from the He(I) line at 21.2182 eV. The energy of incident photons in UPS is much lower than the incident radiation used in XPS (compare Mg K$_\alpha$ at 1253.6 eV).

**Figure 31**: UP-spectrum of sputter clean gold. The secondary edge at high binding energy is followed by a hump due to inelastically scattered electrons. The valence band structure of gold is followed. The resolution of UPS is high enough to resolve the hyper-fine structure in the valence band emissions of gold. The characteristic Fermi-edge for a metal can be seen at the low binding energy end of the spectrum. UPS systems are usually calibrated that the Fermi-edge is at 0 eV.
The energy from the He(I) line is just enough to create photoelectrons from low binding energy electrons, i.e. the valence band at energies from 20 – 0 eV. It shall be noted that XPS is capable to probe those energy levels too. However, the major advantage of UPS lies in its high resolution of about 10 meV due to the narrow linewidth of the electronic transition in the discharge process, which allows a more precise analysis of the hyper-fine structure of emission features in the valence band. Figure 31 shows the general structure of UP-spectrum taken on sputter clean gold.

The spectrum can be subdivided into 4 parts. First, the secondary edge, where secondary electrons are created that have just enough energy to escape the material surface. This edge can therefore be used to extrapolate the work function of a material. This is followed by a high intensity hump in which a large amount of secondary electrons, or in other words inelastically scattered electrons, escape the material surface. Due to their inelastic nature, they bare no relevant information about the electronic structure. Going to lower binding energies, the spectrum shows the valence band structure. On very clean samples, even hyper-fine structures are visible which emphasizes how important the UHV domain is for this type of measurement. UPS is so surface sensitive that miniscule contaminations have drastic influence into the UP-spectrum structure.

Past the valence band structure towards even lower binding energy, a drop in intensity is usually observed which marks the cutoff of the highest occupied molecular orbital (HOMO), also referred to as valence band onset or HOMO onset. This onset coincides with the Fermi level for metals (at 0 eV) and is shifted to higher binding energies for semiconductors and insulators. The HOMO onset is an important material characteristic because it allows to determine the band gap of a material (if the conduction band onset is known or was measured for instance with IPES) or
the energetic strength of hole injection barriers that form in heterojunctions, i.e. after deposition of a thin film [2, 6, 20, 70].

In the scope of this dissertation, UPS was mainly used to determine the position of the secondary edge when investigating the $\text{In}_2\text{O}_3|\text{TiO}_2$ heterojunction in order to determine its position relative to those observed in LIXPS characterization. This was done in an effort to evaluate the presence of charging artifacts and surface altering effects.

2.3: Experimental Setup

Analyzing the electronic structure of thin films and thin film interfaces is a challenging task. Due to the high surface sensitivity of characterization methods like PES, large integrated vacuum systems are necessary that enable in-situ experimentation and provide in-situ sample cleaning and preparation techniques. In this dissertation in particular, a commercially available UHV multi-chamber system (SPECS) operating at a pressure of $5 \times 10^{-10}$ Torr was used to perform the experiments. Besides other not for this dissertation relevant systems, the main chamber is attached to an ALD reactor, a nanoparticle injector, a PES characterization system and a sputtering system. A detailed explanation of the system’s layout is discussed in the following chapter. The individual sample preparation and cleaning procedures are described in their respective chapters.
2.3.1: UHV Multi-Chamber System

The SPECS UHV multi-chamber system used in this dissertation integrates an UHV photoemission spectroscopy system with an atomic layer deposition reactor, a nanoparticle injector and several other components necessary to clean and process samples in-situ. A simplified schematic is shown in Figure 32.

**Figure 32:** Simplified schematic of the UHV multi-chamber system used for experimentation. The chamber integrates a PES analysis system with an ALD reactor, a nanoparticle injection system and an electro-spray system. The multi-chamber is further equipped with a glove box and sputter/anneal chamber allowing versatile sample cleaning and processing.
The advantage of this system is the ability to transfer samples within the vacuum atmosphere without the need of exposing them to the ambient. This was necessary to enable precise characterizations of the electronic structure of the investigated materials. ALD reactors are usually operated under roughing vacuum conditions (approx. $10^{-3}$ Torr). In order to enable sample transfer into an UHV domain, a second pump line was installed so that the reactor could be pumped down to a base pressure of $1 \times 10^{-8}$ Torr, thus enabling the transfer into the UHV domain.

The intermediate vacuum chamber in between ALD reactor and PES system, operated at a base pressure of $5 \times 10^{-10}$ Torr, was mainly used to sputter clean samples. For that purpose, an Ar$^+$ ion sputtering system was used equipped with a SPECS IQE 11/35 ion source. The procedure was performed in an Ar atmosphere of $5 \times 10^{-6}$ Torr. The PES characterization (LIXPS, XPS and UPS) was performed with a dual filament X-ray gun (SPECS XR50) using Mg K$_\alpha$ radiation and a differentially pumped capillary discharge UV lamp (SPECS UVS 10/35) in conjunction with a semi-hemispherical electrostatic energy analyzer system (SPECS PHOIBOS 225).

To support the PES characterization, *atomic force microscopy* (AFM) and *transmission electron microscopy* (TEM) were performed to investigate the surface morphology in selected cases (compare p. 116 and p. 138). Ambient AFM was performed on a Park Scientific XE 70 with the XEI software used for image processing. High resolution transmission electron microscopy was performed on a TECNAI F-20 TEM system using Cu coated carbon grid substrates (TEM grids) in substitution for the normal substrate.
CHAPTER 3: DESIGN AND TECHNICAL IMPLEMENTATION

3.1: Building a Stop-Flow Type Thermal ALD Reactor

An integral part of this Ph.D. project was focused on conceptualization, building and integration of an ALD reactor into a pre-existing UHV multi-chamber system to allow fabrication of ALD thin films and thin film interfaces in conjunction with their electronic structure characterization via photoemission spectroscopy completely in vacuum. This allows contamination free electronic structure characterization due to the direct in-situ connection to the UHV PES characterization system, which is the major advantage of this unique setup. In the conceptualization phase, ALD type and mode were determined in order to plan the reactor layout. It was decided to build a stop-flow type thermal ALD reactor (compare 2.1.4: and 2.1.5: respectively). The stop-flow mode was chosen because of the possibility for prolonged exposure times of samples with precursors and reactants, which can lead to higher growth rates and a better thin film quality in terms of conformity, defectiveness, etc. The disadvantage of having lower pulse frequencies and therefore longer ALD sequences was not a concern in the scope of this dissertation, especially because this reactor is experimental rather than a commercial product where pulsing times may need to be optimized to achieve fast sequencing. Further it was decided to choose the thermal reactor concept over the plasma-enhanced one, mainly because these reactor types are easy to build, use and control. It shall be noted that the top flange in the reactor
body is large enough to equip a plasma source, which would add PEALD capabilities to the reactor and may be an attachment for a future project.

3.2: Reactor Layout

The reactor consists of four parts: reactor body, gas delivery system, exhaust/transfer pumping system and control. It is equipped with 5 independently regulated heater systems in exhaust, reactor body, sample stage, injection lines and precursor reservoir. Figure 33 shows the initial CAD concept drawing of the reactor and how those parts are reflected in the later implementation.

**Figure 33:** a) Conceptual drawing of the individual parts that were planned for the ALD reactor and b) ALD reactor after implementation. The control system seen in part b) is not shown in the conceptual drawing as it was implemented at a later stage.
The reactor control was added at a later stage of the implementation process which is why it is not reflected in the concept drawing. The specifics of the individual parts of the reactor will be discussed in the following chapters.

3.2.1: Reactor Body

The reactor body is equipped with a conduction-type sample heating stage mounted on a bi-directional manipulator. The heating element (custom shaped Cu block with feedthrough for ceramic rod enclosed Ta wire) is equipped with a thermocouple to allow temperature monitoring. The stage can be heated progressively from 25-700 °C enabling the use of a wide variety of thermal ALD precursors. The reactor body is further equipped with a quartz crystal micro balance (QCM) for online monitoring of the thin film thickness. The reactor body can be individually heated from 25 – 150 °C with an external conduction-type heating tape. It can therefore easily be baked out for cleaning and heated during ALD to prevent the adsorption of precursor material, especially H$_2$O, on the reactor walls. A sample transfer arm completes the reactor body. This arm is used to position the sample on the sample stage and allows the transfer in and out of the UHV domain.

3.2.2: Gas Delivery System

The gas delivery system consists of two individual injection lines, one for precursors and one for reactants. The injection lines consist of stainless steel tubing attached to the reactor body,
allowing precursor and carrier gas to enter the main reactor chamber. A simplified concept
drawing of the gas delivery system and its final layout is shown in Figure 34.

In each injection line, two high vacuum capable, pneumatically actuated ALD valves are
attached to the tubing. The valves are again attached to 50 ml stainless steel reservoirs. These
reservoirs hold the volatile precursor material and are easily interchangeable.

Figure 34: a) Simplified version of the concept drawing for the gas delivery system. Two
separate injection lines for precursors and reactants are connected to multiple individually
heatable reservoirs allowing for the sequential injection of multiple different materials. A
reaction-inert carrier gas whose flow is regulated by mass-flow controllers (MFC’s) is used to
help the transportation of precursors and reactants into the reaction chamber; and b) gas delivery
system after implementation. The carrier gas flow is marked with red arrows. The whole system
is encapsulated in a fume hood to prevent the exposure of users with precursor material in case
of leaking material reservoirs. This is important in order to protect users especially given the
high toxicity of many ALD precursors.
This enables the quick and easy change of precursor material without breaking the vacuum inside the reactor. Some ALD precursors need to be heated during the ALD process in order to achieve the desired volatility which is why one reservoir in the reactant injection line is equipped with a heater. This heater is progressively heatable from 25 – 150 °C allowing a wide variety of low volatility precursor materials to be used. Ar carrier gas is used in each injection line to help transporting the precursor material into the reactor body. The flow of the carrier gas can be regulated by mass-flow controllers (MFC’s) in progressive steps from 0 – 200 ml/min. The controllers were calibrated externally, using Ar gas. The calibration factors are directly embedded into the control software. The whole gas delivery system is enclosed in a fume hood connected to the main air ventilation system to prevent exposure of users with toxic precursor material in case of leaking or improperly sealed precursor reservoirs.

### 3.2.3: Exhaust System

The exhaust system consists of two individual pumping lines – a roughing vacuum line and a high/ultra-high vacuum line. A simplified schematic is shown in Figure 35.

The roughing vacuum line consists of a pneumatically actuated UHV valve connected to an exhaust pipe and a roughing vacuum pump. The pneumatic valve allows quick isolating of the reactor body from the exhaust pipe. This configuration is essentially necessary to operate the reactor in stop-flow mode (see p.58). The exhaust pipe is terminated by an Edwards E2M30 two stage rotary pump, equipped with oil mist filter and POSI-trap to prevent oil spilling into the exhaust ventilation pipes and vacuum system respectively. Continuously pumping precursor material through the pump requires special pump oil.
Figure 35: Simplified version of an exhaust system with dual pumping lines. The roughing vacuum line is usually used to operate the ALD reactor. A separate pump line is attached to a turbo vacuum pump allowing the connection of the system to the ultra-high vacuum system. Both pump lines are separated by shut-off valves allowing to individually connecting them to the reaction chamber. The roughing line valve is pneumatically actuated for quick intermittent isolating of the reaction chamber.

Therefore, the pump is filled with Fomblin pump oil that is poly-fluorinated, thus making it especially reaction inert. The roughing vacuum pump line is further equipped with a pirani gauge to monitor pressure and a conduction-type heater system, so the exhaust pipes can be heated during the ALD process, preventing unwanted condensation of precursor material to condensate on the inside walls. The high/ultra-high vacuum line consists of a manual UHV valve, a Pfeiffer TC600 turbo pump, an exhaust pipe and a roughing vacuum pump. Both pumping lines are necessary to enable the ALD process on one hand, usually performed under roughing vacuum conditions, and to enable sample transfer on the other, which requires at least
high vacuum or better ultra-high vacuum conditions. The reactor body can be pumped down to a roughing vacuum base pressure of $1 \times 10^{-3}$ Torr for ALD processes and to $5 \times 10^{-9}$ Torr for sample transfer into UHV.

### 3.3: Reactor Control

This chapter is dedicated to talk about the ALD reactor’s hardware and software control.

#### 3.3.1: Hardware

The control hardware is composed of 4 individual modules – turbo pump controller, IGC100 pressure monitor, reactor control box and sample stage heater power supply. All modules are shown in Figure 36. The turbo pump controller regulates the turbo pump and shows its actual status. The turbo pump is operated in manual mode and is only running if a sample needs to be transferred into vacuum or if the reactor body is baked out for cleaning. The pressure inside the ALD reactor is measured by two pirani gauges in exhaust pipe and reactor body while operating under roughing vacuum conditions and by a nude ion gauge when operated in high and ultra-high vacuum. The IGC 100 is tied into the LabView program allowing easy pressure monitoring from the user interface.

The sample stage heater power supply is connected to feedthroughs within the sample stage manipulator allowing heating of the Ta wire by DC current directly. The power supply is tied into the reactor control and in conjunction with the embedded thermocouple in the sample stage allows a precise temperature control.
Figure 36: a) Interior of controller box with custom PCB based on Arduino microcontroller system, power supply and solid state relays for heater control; and b) overview over hardware control system showing sample stage heater power supply, controller box, pressure monitor and turbo pump control.

The reactor control box integrates all hardware modules and allows connecting them with the LabView based user interface. The main control unit (shown in Figure 36 a)) is based on the popular microcontroller platform – Arduino, that was modified for this particular application. A 4 layer PCB was custom designed using KiCAD, a popular open-source application used to design PCB’s. The PCB integrates all necessary control functions on one 5 x 6 inch board and controls all vital sub-modules of the ALD reactor including heaters, valves, temperature monitoring and MFC control. The USB based PC interfaces allows bidirectional communication between user interface and microcontroller unit (MCU). A KiCAD schematic and the manufactured PCB with soldered-on microchips is shown in Figure 37.
3.3.2: Software

The control software for the ALD reactor is based on C++ and was conceptualized with the idea of having an easy to use, self-explanatory unified PC user interface that allows control and programming of the ALD reactor on one side and monitoring of all necessary parameters on the other. A simplified flow-chart of the control software structure is shown in Figure 38. Details about the user interface will be discussed separately (see p. 85).

3.3.3: User Interface

The user interface was built with LabView. It uses the LabView Interface for Arduino library (LVIFA) which handles the correct communication between the Arduino MCU and
LabView (checksum, etc.). It is built modular and includes temperature control, ALD sequence, mass-flow control, pressure monitoring and debugging.

**Figure 38**: Simplified flow chart of an ALD reactor control. A central micro controller unit (MCU) controls the valve, the carrier gas flow and the individual temperature zones. The MCU is communicating with a PC giving back feedback to a user interface which allows the user to control the reactor.

The temperature control module is shown in Figure 39. It allows control of all 5 heating zones individually. Each unit is encapsulated with software PID control, allowing setting the temperature with a precision of ± 0.5 °C. Cold-junction compensation allows measuring the temperature of the ambient in relation to the temperature of the heated element. Each unit is further equipped with its own fault detection, making it possible to detect open circuit, short
circuit and faulty ground conditions which allows easy and fast detection of eventually wrong or broken connections.

**Figure 39:** Temperature control module of the user interface for all 5 heating zones. The temperature control unit on the PCB back-end is equipped with cold-junction compensation effectively allowing measuring the temperature of the heated elements in relation to the ambient temperature. Each temperature unit is fully software PID controlled, allowing setting temperatures in a range of ± 0.5 °C precisely.

ALD “recipes” can be programmed by using the ALD sequence module. This module was designed with ease of use in mind, enabling programming of the ALD reactor without prior knowledge of the system. The user can choose a material, injection times, soak and purge times and the total cycle count. Even the deposition of multiple materials can be programmed up to a combined total cycle count of 200. The sequence is then submitted and stored on the PCB. This makes sure that in case something happens to the control software, i.e. power outage, etc., the
ALD reactor can continue its sequence. Once the reactor is initialized, the total deposition time is calculated and presented to the user. The interface further informs the user of the current step in the ALD sequence. The reactor runs fully automated until the sequence is completed.

![ALD Control Program v6.0](image)

**Figure 40:** ALD sequence module of the user interface. This module enables programming of one or multiple ALD sequences. The module is structured with ease of use in mind. Once a material is selected, the user chooses soak, purge and injection times as well as the total ALD cycle count. The sequence is submitted and then stored on built-in memory on the PCB. Once the sequence is initiated, the total time is calculated and the reactor operates fully automatic until the sequence is completed.

The flow of carrier gas can be regulated using the mass-flow control module shown in Figure 41. A progressive mass-flow from 0 – 200 ml/min. can be set. The controller itself has a built-in flow-sensor that feeds back the actual flow back to the user interface, allowing a comparison of actual and set values as a function of time. This enables easy detection of mass-flow variations and the detection of system errors.
Figure 41: Mass-flow module of the user interface. With this module the mass-flow of carrier gas can be regulated. Precursor and reactant injection lines are individually controllable from 0 – 200 ml/min. The mass-flow controllers have a built-in flow sensor that allows monitoring of the actual mass-flow with the set point.

The user interface further allows monitoring of two different pressures domains during ALD deposition – directly within the chamber and in the exhaust pipe. The pressure monitoring module shown in Figure 42 can be used to visualize and record those pressures measured in the system. The pressure log can be used to verify the correct injection behavior for an ALD sequence. It can be further used to estimate the formation of gaseous species within the reaction chamber that usually occur as by-products in the ALD reaction.

The last module of the user interface is the debug module shown in Figure 43. It is used to monitor the performance and eventual errors of the system. It is programmed with error handling capabilities, letting the user know if something is wrong within the communication protocol between MCU and LabView or the program itself.
**Figure 42:** Pressure monitoring module of the user interface. This module allows monitoring two pressure domains during ALD deposition – within the chamber and in the exhaust pipe. Monitoring the pressure allows a qualitative verification of the ALD process and gives an estimation of the formation of gaseous by-products within the reaction chamber that occur usually due to the nature of the ALD reaction.

This module is not needed to operate the ALD reactor itself. However, it enables advanced users to quickly resolve issues related to the program. **Figure 44** shows the programming mask of the user interface. The interface uses object oriented programming in conjunction with asynchronous message control (AMC), a standard used in industrial applications.

It is composed of 4 sub-modules including object instantiation, constants initialization, message queue builder and message execution. For example, the user gives a command, i.e. setting injection times, turning on heaters, etc. and the program responds by transforming this
command into a string format message that is added to the message queue. The priority of the message determines its place in the queue.

**Figure 43:** Debug window of the ALD control software giving advanced users the ability to troubleshoot eventual errors in the system quickly.

The message executer repeatedly performs actions based on the first message in the queue. The asynchrony allows building and executing commands independently from each other, making this protocol very fast and powerful.
Figure 44: Display of the LabView programming mask on which the user interface is built. The program uses the object oriented programming technique in conjunction with asynchronous message control (AMC), a standard also used in industry applications. The program consists of 4 main parts including the object instantiation, constants initialization, building a message queue based on given commands and priority and executing those commands in the message handler.

3.4: Integration of a Nanoparticle Injector System

A nanoparticle injector system (NPI) based on an atmospheric pressure DC microplasma reactor system [100, 112, 113] was conceptualized, built and integrated into the ALD reactor. This was initially done in an effort to enable co-deposition of nanoparticles and ALD thin films in vacuum. A schematic of the process is shown in Figure 45.
Figure 45: Concept of alternating ALD and nanoparticle injection to fabricate complex multi-component structures.

However, it shall be noted that in the scope of this dissertation, the implementation of the injector system in conjunction with a proof-of-concept fabrication of Fe$_2$O$_3$ nanoparticles was the focus. It was shown that the technology can be successfully integrated into a multi-chamber vacuum analysis system and nanoparticles can be fabricated reliably in a vacuum environment. Prior to this dissertation, this particular technology was only operable under atmospheric pressure conditions, which means that nanoparticles fabricated that way were prone to many sources of contamination. These contaminations can influence the electronic structure, thus rendering a characterization difficult. The integration of the technology into the ALD reactor allows fabrication of nanoparticles in a contamination-free environment, enabling precise electronic structure characterization without ambient influences. In that light, the proof-of-
concept approach presented here is already a major advancement. The following chapter 
illuminates the reactor layout and its functionality. More information about the study performed 
as part of this dissertation can be found on p. 138.

3.4.1: NPI Layout and Functionality

The NPI system, shown as simplified schematic in Figure 46, consists of two individual 
injection tubes that are joined externally and then fed into the ALD reactor body. Each injection 
tube is terminated by a mass-flow controller on one end, allowing individual regulation of a 
carrier gas progressively from 0 – 200 ml/min. In the scope of this dissertation, Ar was chosen as 
carrier and plasma gas. A material reservoir is installed in one of the injection lines, holding a 
volatile precursor, i.e. ferrocene, cobaltocene, nickelocene, etc. The metallic center of the 
organo-metallic precursor determines the species of nanoparticles produced. The second 
injection line serves two purposes: first, it can be sued to dilute the precursor gas loaded carrier 
gas stream and second, it can be used to install a second precursor reservoir to enable co-
deposition of multi-metallic nanoparticles. The inside part of the injector system is composed of 
two electrically separated tubes that are joined by a quartz tube. The quartz tube serves as 
housing for the plasma. The upper tube is terminated by a capillary that is also used as cathode. 
The capillary is installed in such a way that the tip is inside the quartz housing. The cathode is 
connected by a HV feedthrough to an external power supply. The lower tube is electrically 
floating. A stainless steel mesh inside the tube is used as anode.

The mesh is installed in the tube in such a way that the distance between capillary tip and 
mesw is well defined. This is necessary to control the size of the nanoparticles which is primarily
dependent on the nucleation time in the plasma, or in other words on the length of the plasma. Typical distances are 3 – 10 mm.

**Figure 46:** Schematic of the NPI system. Two injection line controlled by mass-flow controllers are joined externally. In one line, a precursor reservoir is installed holding a volatile precursor. The plasma is created in vacuum. The volatile precursor is decomposed inside the plasma forming nanoparticles based on the distance between cathode and anode.
To deposit nanoparticles, the injector is lowered onto the ALD sample manipulator. The manipulator is connected to ground and therefore connects the anode to ground. Applying a HV to the cathode allows the formation of a DC microplasma in between capillary and mesh. Once stable plasma conditions are achieved, nanoparticles can be fabricated by mixing precursor materials into the carrier gas stream.
CHAPTER 4: ELECTRONIC STRUCTURE INVESTIGATION OF ATOMIC LAYER DEPOSITION RUTHENIUM(OXIDE) THIN FILMS USING PHOTOEMISSION SPECTROSCOPY

4.1: Abstract

Analyzing and manipulating the electronic band line-up of interfaces in novel micro- and nanoelectronic devices is important to achieve further advancement in this field. Such band alignment modifications can be achieved by introducing thin conformal interfacial dipole layers. Atomic layer deposition (ALD), enabling Ångstrom-precise control over thin film thickness, is an ideal technique for this challenge. Ruthenium (Ru$^0$) and its oxide (RuO$_2$) have gained interest in the past decade as interfacial dipole layers because of their favorable properties like metal-equivalent work functions, conductivity, etc. In this study, initial results of the electronic structure investigation of ALD Ru$^0$ and RuO$_2$ films via photoemission spectroscopy are presented. These experiments give insight into the band alignment, growth behavior, surface structure termination, and dipole formation. The experiments were performed in an integrated vacuum system attached to a home-built, stop-flow type ALD reactor without exposing the samples to the ambient in between deposition and analysis. Bis(ethylcyclopentadienyl)ruthenium(II) was used as precursor and oxygen as reactant.

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analysis chamber was outfitted with X-ray photoemission spectroscopy (LIXPS, XPS). The determined growth modes are consistent with a strong growth inhibition situation with a maximum average growth rate of 0.21 Å/cycle for RuO$_2$ and 0.04 Å/cycle for Ru$^0$. An interface dipole of up to $-0.93$ eV was observed, supporting the assumption of a strongly physisorbed interface. A separate experiment where the surface of a RuO$_2$ film was sputtered suggests that the surface is terminated by an intermediate, stable, non-stoichiometric RuO$_2$/OH compound whose surface is saturated with hydroxyl groups.

4.2: Introduction

Advancements in micro- and nanoelectronic devices like MOSFET’s, RAM’s, capacitors, etc. benefit from the ability to precisely analyze and manipulate the electronic band line-up of interfacial structures. Due to the different electronegativity of atoms at an interface, dipoles can form that influence the electronic band line-up. The tailor-design of such interfaces can lead to an improved device performance. This can be done for instance by introducing ultra-thin, high conformity dipole layers of sub 10 nm to modify the band alignment, and with that control charge transfer (or blockade) [94, 129, 150, 154]. Dipole layers ideally are defect-free and uniform. Atomic layer deposition (ALD) with its self-limiting precursor gas based reaction enables Ångstrom-precise control over thickness and results in very homogeneous coatings. Hence it is ideal for this application [50, 86]. The large variety of different precursor materials that has been developed in recent years enables the formation of dipole layers for a variety of interfaces [57, 97]. In that light, transition metal thin films like metallic ruthenium (Ru$^0$) and its naturally occurring, stable, conductive oxide (RuO$_2$) have recently attracted interest due to their
suitable properties like high work function (4.7 eV for Ru \[1\] and 5.1 eV for RuO\(_2\) \[165\]), low resistivity (7.1 \(\mu\Omega\)-cm for Ru and 20 \(\mu\Omega\)-cm for RuO\(_2\) in bulk \[67\]) and thermal/chemical stability \[58\]. This makes them suitable for dry and wet etching processes usually used in micro- and nanoelectronic device fabrication \[96\]. Therefore, these types of interfaces were studied extensively involving a number of substrates (Cu \[93, 94\], HF etched Si \[90\], p-type Si (100) with SiO\(_2\) overlayer \[43, 90, 128-130\], Ta\(_2\)O\(_5\) \[129, 161\], TaN \[129\], TiN \[43, 93\], Al\(_2\)O\(_3\) \[90\], TiO\(_2\) \[90\], HfO\(_2\) \[90\], ZrO\(_2\) \[90\]) and a variety of precursor and reactant combinations. The interface between Ru /RuO\(_2\) and Au has not been investigated to date.

In this study initial results of an in-situ electronic structure investigation of ALD deposited Ru\(^0\) and RuO\(_2\) films on gold via photoemission spectroscopy (LIXPS and XPS) are presented. The data illuminate the dipole formation at the interface and yield the electronic structure of the interface. Additionally, the growth behavior in relation to injection parameters and the chemical surface termination were determined. Due to the surface sensitivity of PES, it is essential to perform such experiments without exposing the ALD films to the ambient. This was achieved through in-situ sample transfer from the ALD reactor to the photoemission spectroscopy chamber. Oxidation and ambient contaminants have the potential to alter the ALD film surface, which would complicate electronic structure investigations if the samples were exposed to the environment between growth and analysis.

Our experiments verified in alignment with previous reports \[67, 83, 161\] that the thin film stoichiometry, e.g. its degree of oxidation, is strongly dependent on the amount of Ru precursor and O\(_2\) as well as the injection times and substrate material. We observed the formation of an interface dipole leading to the assumption of a strongly physisorbed interface. Sequential
removal of thin film material via sputtering followed by photoemission analysis revealed 
RuO$_2$/OH as a non-stoichiometric, stable compound on the surface saturated by hydroxyl groups.

4.3: Experimental Setup

11 ALD films were fabricated, each on an individual gold substrate. The experiments were split into two series using different Ru precursor and O$_2$ injection time ratios. This was done to investigate if and how those changes influence the thin film stoichiometry, the growth rate and growth behavior, as well as the magnitude of the interface dipole.

Throughout the first series, the Ru precursor gas injection time was fixed to 700 ms, while the O$_2$ injection time was set to 313 ms, 625 ms, 1250 ms, 5000 ms and 10000 ms, yielding a total of 5 ALD films. In the second series, the Ru precursor gas injection time was lowered to 175 ms, while a O$_2$ injection time of 50 ms, 100 ms, 313 ms, 625 ms, 1250 ms and 10000 ms was used, yielding a total of 6 ALD films. Each experiment was performed according to the sequence described below.

4.3.1: Sample Preparation

Glass slides coated with 100 nm Au on top of a 5 nm Ti adhesion layer (Deposition Research Lab, Inc.) were prepared by diamond scribing into 1x1 cm squares. After scribing, the samples were mounted onto sample holders to enable transfer within the vacuum system. The resistivity of each sample contact to the underlying sample holder was measured at three different spots to ensure good ohmic contact to prevent charging effects during photoemission.
spectroscopic analysis. In an effort of minimizing contamination prior to insertion into the vacuum chamber, the samples were cleaned with a sequence of methanol, isopropanol, acetone, and DI water to remove organic/inorganic remnants and dust particles before being blown dry with nitrogen. After loading the samples through a fast entry load lock into the vacuum system, they were sputtered for 30 minutes with Ar plasma (5 kV, ≥15 mA, 9 x 10⁻⁶ Torr Ar atmosphere). The samples were then transferred into the analysis chamber for photoemission analysis in order to establish reference spectra of the clean substrate.

4.3.2: ALD Sequence

After initial cleaning and photoemission spectroscopy characterization, the samples were transferred in vacuo into a home-built, stop-flow type ALD reactor [81], equipped with a pneumatic valve in between reaction chamber and pumping line, allowing to isolate the reaction chamber before each individual O₂ injection. This enabled the exposure of the samples to high doses of O₂ thus ensuring complete surface reaction prior to pump down and successive injection of Ru precursor material. Based on previous studies [93], the samples were heated to 270 °C. The Ru precursor bis(ethylcyclopentadienyl)ruthenium(II) (Ru(EtCp)₂, 98%, Strem Chemicals, Inc.) was heated to 80 °C, while the feeding and exhaust lines, as well as the reactor body were heated to 120 °C to prevent unwanted condensation. Oxygen (O₂, 99,993%, Airgas USA, LLC) was fed into the reaction chamber through a gas manifold at room temperature (25 °C) set to 3 PSI. Two individually controllable mass-flow controllers in Ru precursor respectively O₂ injection line were set to 80 ml/min. during deposition, helping the transportation of Ru precursor and O₂ to the reactor chamber. The reaction base pressure prior to all experiments was
measured in the reactor body and varied between 250 and 300 mTorr (mainly Ar atmosphere) throughout the experiments.

All 11 ALD films were deposited during 100 individual ALD cycles. The entire deposition process occurred under computer control via a custom designed control system. The ALD sequence was as follows: First, the Ru precursor gas was injected and immediately followed by a 10 s soak and 60 s purge period, allowing for leftover Ru precursor to be removed completely. In a second step, O\textsubscript{2} was injected, again followed by the same soak and purge periods. After repeating the sequence 100 times, the reaction was terminated and all leftover O\textsubscript{2} and carrier gas was purged out of the chamber. Then the sample was cooled to room temperature (approx. 25 °C) under high vacuum conditions (≤ 1 x 10\textsuperscript{-6} Torr).

4.3.3: Photoemission Analysis

For photoemission analysis of the ALD films, the samples were transferred to the ultra-high vacuum (≤ 9 x 10\textsuperscript{-10} Torr) analysis chamber. XPS and LIXPS analysis were performed using a SPECS PHOIBOS 225 hemispherical electrostatic energy analyzer and Mg K\textsubscript{α} excitation. The thickness d of the grown films was estimated using Lambert–Beer’s law:

\[
d = \lambda \cdot \ln \left( \frac{I_0}{I} \right).
\]
Where $I_0$ is the emission strength of the Au 4f core level emission measured on the uncovered substrate, $I$ is the attenuated emission intensity after coverage with a thin film, and $\lambda$ is the mean free path (5.73 Å, NIST database).

4.4: Experimental Results

4.4.1: Dipole Formation – LIXPS Work Function Analysis

The dipole potential at a particular interface can be determined by comparing the work functions derived from LIXP-spectra before (sputter clean Au) and after ALD layer deposition. A secondary purpose of the LIXPS measurements that were performed was the detection of potential charging artifacts during the UPS measurements needed to measure the valence bands electronic structure. This is done by measuring a LIXP-spectrum before and after the UPS measurement. If they yield the same secondary edge position, charging can be ruled out. If there are differences, charging artifacts need to be considered.

The LIXPS secondary edge spectra for both experimental series at 700 ms (a) and 175 ms (b) Ru precursor injection times are shown in Figure 47.

The solid lines represent the spectra measured before the UPS measurement and the dashed lines those measured after. In all measurements the determined cutoff energies appear to be at similar positions before and after the UPS measurements. This suggests that all investigated thin films were sufficiently conductive to prevent charging from occurring.
**Figure 47:** LIXPS spectra before (solid black line) and after (dashed red line) UV light radiation for Ru precursor injection times of a) 700 ms, and b) 175 ms as well as the modulated reaction injection times. The spectra indicate that there are no significant charging artifacts. All spectra are normalized and vertically offset for better visibility. Vertical lines are added as guidance for the eye. Each graph contains a LIXPS spectrum of sputter clean gold at the bottom for comparison. Reproduced with permission from [149]. Copyright 2015, AIP Publishing LLC.

**Figure 48** shows the work function as a function of $O_2$ injection time for both experimental series. Each data point corresponds to the work function derived from each of the eleven spectra shown in **Figure 47**. The extrapolated values are summarized in Table 1.
Generally, all deposited ALD films resulted in a reduction of the work function of the sputter cleaned Au substrates, which showed about 5.2 - 5.3 eV. The work function reduction increases with the O₂ injection time, resulting in maximum reduction values of -0.78 eV in experimental series a), and -0.93 eV in experimental series b). The magnitude of the observed dipole potentials suggests the formation of a strongly physisorbed interface rather than a chemical bond of covalent or ionic nature, with a negative charge on the Au substrate and a positive charge on the ALD film.
Table 1: Work function $\Psi_{WF}$ and dipole potentials $\Delta_d$ vs. $O_2$ injection time for both experimental series determined from Figure 47. All work function values were derived by fitting a line into the secondary edge features of the spectra. The work function values of sputter cleaned Au, metallic Ru and RuO$_2$ were added for comparison. The error margin of the shown values is ± 0.1 eV. Reproduced with permission from [149]. Copyright 2015, AIP Publishing LLC.

<table>
<thead>
<tr>
<th>$O_2$ Injection Time [ms]</th>
<th>Work Function $\Psi_{WF}$ [eV]</th>
<th>Dipole $\Delta_d$ [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>700 ms Ru(EtCp)$_2$</td>
<td>175 ms Ru(EtCp)$_2$</td>
</tr>
<tr>
<td>Au ref.:</td>
<td>5.1$^1$</td>
<td>5.2$^1$</td>
</tr>
<tr>
<td>Ru$^0$:</td>
<td>4.7$^2$</td>
<td></td>
</tr>
<tr>
<td>RuO$_2$:</td>
<td>5.1$^3$</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>-</td>
<td>4.64</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>4.60</td>
</tr>
<tr>
<td>313</td>
<td>4.62</td>
<td>4.41</td>
</tr>
<tr>
<td>625</td>
<td>4.58</td>
<td>4.36</td>
</tr>
<tr>
<td>1250</td>
<td>4.55</td>
<td>4.32</td>
</tr>
<tr>
<td>5000</td>
<td>4.41</td>
<td>-</td>
</tr>
<tr>
<td>10000</td>
<td>4.32</td>
<td>4.27</td>
</tr>
</tbody>
</table>

$^1$Literature: 5.3 eV [4, 12, 61, 63]
$^2$T. Altonen et al. [1]
$^3$H. Zhong et al. [165]
*No experimental data available

It is obvious from Figure 48 that the longer Ru precursor injection time (700 ms) resulted in a faster work function reduction. This suggests that the observed progression of increasing dipole potentials with increasing $O_2$ injection times is a result of an increasing surface coverage. During the early stages of the film growth the surface is only partially covered by the ALD film, resulting in a larger average work function across the surface than in later stages where the Au surface is completely covered, and the work function is dominated by the ALD film (Table 1).
4.4.2: Core Level Emission Features – XPS Analysis

There are three relevant core level emission features: 1) the O 1s emission at 525 eV – 537 eV, 2) the Ru 3d emission superimposed with the C 1s emission at 278 eV – 290 eV and 3) the Au 4f emission at 82 eV – 90 eV. The emission features of all 11 ALD films are shown in Figure 49 and the binding energies determined from those spectra are given in Table 2. Superimposed emission features were fitted and the resulting curves are added to the graphs.

**Au 4f:** The Au 4f doublet has a constant binding energy throughout the experiments owing to the chemical inertness of the Au surface confirming physisorption as the binding mechanism at this interface. The intensity of the lines is a measure of the film thickness due to the thickness dependent attenuation of the photoelectrons emitted from the Au surface. The much faster attenuation of the 700ms Ru precursor series confirms the lower growth rate of the 175 ms experiment. The average growth rates were determined to be 0.21 Å/cycle for the 700 ms series, while the 175 ms series only showed an average growth rate of 0.04 Å/cycle. The determined 700 ms rate is 50% lower than the 0.4 Å/cycle reported earlier [67]. This may be related to differences between the substrates resulting in different nucleation rates, or it is indicative of the formation of a different RuO₅ species.

**Ru 3d:** The graphs shown in figure 3 b) and e) can be subdivided into two groups: The initial low coverages yielded spectra that can be fitted with just one doublet at binding energies of 280.2 eV (3d₅/₂) and 284.4 eV (3d₃/₂). This corresponds to a spin-orbit split of 4.2 eV, which is in good agreement previous reports, suggesting the growth of metallic ruthenium (Ru⁰) [82]. At higher coverages, a fit with two doublets was necessary, accounting for two individual oxide species present in the interface.
Figure 49: XPS results for both experimental series with Ru precursor gas injection times of 700 ms (a-c) and 175 ms (d-f) showing three core level emission features (O 1s, Ru 3d superimposed with C 1s and Au 4f). Each spectrum corresponds to an individual experiment and each was done on a separate sputter cleaned substrate. Each spectrum is labeled with the used O\textsubscript{2} injection time. All spectra are normalized, background corrected and vertically offset for better visibility. The bottom spectrum in each graph represents the emission feature originating from a sputter cleaned Au substrate. Superimposed features were fitted and the resulting individual spectra are shown in blue/green. Graph c) and f) represent the Au 4f emission features pre and post deposition showing the attenuation of the signal as a thin film is deposited. The attenuation of the substrate signal was used to determine the thickness of the thin film. Reproduced with permission from [149]. Copyright 2015, AIP Publishing LLC.
The binding energies of the first doublet were determined to be 280.8 eV (3d\(_{5/2}\)) and 285.0 eV (3d\(_{3/2}\)), while the second doublet is located at 282.3 eV (3d\(_{5/2}\)) and 286.5 eV (3d\(_{3/2}\)). According to Kim et al. these binding energies suggest the formation of RuO\(_2\) and an intermediate but stable compound most closely related to RuO\(_2\) with an additional hydroxyl group\(^{82}\). Figure 4 shows the binding energy of the Ru 3d\(_{5/2}\) components depending on the O\(_2\)/Ru precursor injection ratio. The step in the graph indicates that metallic ruthenium (Ru\(^0\)) is formed any time the O\(_2\)/Ru precursor ratio is below 1, whereas a mixture of RuO\(_2\) and RuO\(_2\)/OH is formed when this threshold is exceeded.

**Figure 50:** 3d\(_{5/2}\) binding energy of Ru\(^0\) and RuO\(_2\) as a function of O\(_2\) to Ru precursor injection ratio. The graph contains the literature values of the emission features for both species (blue area) as mentioned in Table 2. The horizontal axis is split to better accommodate the differing injection ratios. Data derived from using a Ru precursor injection time of 175 ms is shown in red whereas data derived from using a Ru precursor injection time of 700 ms is shown in black. Reproduced with permission from [149]. Copyright 2015, AIP Publishing LLC.
**O 1s:** Similar to the series of Ru 3d spectra the O 1s spectra show more complexity for thicker films. The initial lower coverages show lines at 529.6 eV ± 0.1 eV and 531.2 eV. The emission feature at higher binding energy can be assigned to oxygen (O²⁻) arising from a Ru-O bond present in RuO₂ [46]. However, it is more difficult to assign the lower BE component. Due to the overlap of the emission feature arising from hydroxyl groups (OH) with the binding energy that would be expected from the oxygen coordinated in the intermediate compound on the surface, it is difficult to determine exact the emission intensity. The O 1s emission features occurring below the Ru precursor threshold at which the oxide forms have binding energies of 531.2 eV and 530.3 eV. These are the expected emission features resulting from the hydroxyl groups that are related to the growth mechanism. This mechanism relies on covalent Ru-O bonds at the surface layer as anchor points.

**C 1s:** It is difficult to evaluate the C 1s emission component due to the direct overlap with the Ru 3d emissions. However, for Ru precursor injection times of 700 ms and O₂ injection times low enough to cause the formation of metallic ruthenium, the relative carbon concentration is significantly higher compared to when the Ru precursor injection time is lowered to 175 ms (compare Figure 47) or oxide is formed at 700 ms. This suggests that the majority of the organic Ru precursor material (e.g. cyclopentadienyl rings) not reacting under these conditions renders the surface carbon rich. This result further supports the low average growth rate and the metallic nature of the films that were observed in these cases.
Table 2: Summary of the core level emission features of both experimental series determined from Figure 49 in comparison with literature data. Reproduced with permission from [149]. Copyright 2015, AIP Publishing LLC.

<table>
<thead>
<tr>
<th>O₂ Injection Time [ms]</th>
<th>O 1s</th>
<th>C 1s</th>
<th>Ru 3dₓ/ᵧ</th>
<th>Au 4fₓ/ᵧ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OH</td>
<td>O²</td>
<td>RuO₂/OH</td>
<td>RuO₂</td>
</tr>
<tr>
<td>Literature:</td>
<td>530.8³ 529.4²</td>
<td>284.5¹</td>
<td>286.6 – 286.8¹</td>
<td>284.9 – 285.2¹</td>
</tr>
<tr>
<td>Ru Precursor gas injection time: 700 ms</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
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<td>530.2</td>
<td>285.2</td>
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</tr>
<tr>
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<td>285.1</td>
<td>-</td>
</tr>
<tr>
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<td>285.1</td>
<td>286.4</td>
</tr>
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</tr>
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<td>529.7</td>
<td>285.3</td>
<td>286.6</td>
</tr>
</tbody>
</table>

¹H. Kim et al. [82] ²A. Foelske et al. [46] ³CRC Handbook of Chemistry and Physics 2011 [63]
4.4.3: Surface Termination of the Prepared ALD Films

The evaluation of the Ru 3d features is complicated by the overlap with the C 1s lines. This is especially problematic if the surface termination of the prepared films is to be evaluated. To shed some more light on this topic, the surface of an additional ALD film (Ru precursor to O₂ injection time: 175 ms to 1250 ms) was sputtered with Ar ions (5 Min., 5 kV, 9 mA, 9 x 10⁻⁶ Torr Ar atmosphere) and characterized by LIXPS and XPS. The sputtering/characterization sequence was repeated three times to create a depth profile. The results are shown in Figure 51. The determined values for work function, thickness and core level binding energies are summarized in Table 3.

Table 3: Summary of the thin film thickness, work function and core level binding energies determined from Figure 51. Error margins are the result of the analysis system’s resolution of ± 0.1 eV. Literature values are added for all determined binding energies. Reproduced with permission from [149], Copyright 2015, AIP Publishing LLC.

<table>
<thead>
<tr>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>O 1s</td>
</tr>
<tr>
<td>Literature RuO₂: [63, 82, 165]</td>
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<td>529.4</td>
<td>280.7 – 281.0</td>
</tr>
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<td>4.45</td>
<td>529.6</td>
</tr>
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<td>15</td>
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<td>5.14</td>
<td>530.0</td>
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</tbody>
</table>
Figure 51: Results of LIXPS analysis (a) and core level emission features (O 1s, Ru 3d, Au 4f) (b) – d)) of the sputtering/characterization experiments. All spectra are normalized, background corrected and vertically offset for better visibility were applicable. Vertical lines are inserted as guidance for the eye. Reproduced with permission from [149]. Copyright 2015, AIP Publishing LLC.
The Au 4f core level emissions show the expected increase in intensity as the ALD film is thinned by the sputtering process during the three steps. The O 1s emission shifts from 529.6 eV to 530.0 eV after the first sputtering step corresponding to a shift of $\Delta_{BE} = +0.4$ eV while the shoulder associated to the hydroxyl group vanishes. This supports the conclusion that the surface is indeed terminated with OH groups. This is in contrast with conclusions drawn by Foelske et al. [46] from measurements on non-sputtered RuO$_2$, who assigned the binding energy of 529.4 eV to the O 1s emission to RuO$_2$.

In parallel, the Ru 3d emission undergoes a small shift from 280.9 eV to 280.8 eV. This needs to be considered in light of the analysis system’s absolute energy resolution of ±0.1 eV. The relative energy resolution of the system is considerably better due to the fact that peak positions are determined by fitting line shapes to a multitude of data points, which allows the detection of relative line shifts smaller than 0.1 eV. The measured binding energy is in good agreement with observations by H. Kim et al. [82]. Additionally, the underlying RuO$_2$/OH emission feature at a binding energy of 282.4 eV vanishes, indicating the removal of the RuO$_2$/OH surface layer.

The following two sputtering steps did not result in additional spectral changes, indicating that the bulk of the film is homogeneous.

4.5: Conclusions

In this study a home-built ALD reactor attached to an ultra-high vacuum photoemission analysis chamber (XPS, UPS, and IPES) was used to produce 11 ALD films with various Ru precursor and O$_2$ injection times. This setup allowed PES of the ALD films without influence
from the ambient, which has the potential of altering the ALD film surface (oxidation, ambient contaminants), thus complicating the analysis. It was shown that the O₂ to Ru precursor injection ratio ultimately determines the oxidation state of the ALD film. For ratios below 1, metallic ruthenium (Ru⁰) was produced in comparison to a ruthenium oxide blend (RuO₂ and RuO₂/OH) if this ratio was exceeded. In all cases, the work function analysis revealed the RuOₓ/Au interface to be strongly physisorbed with dipole strength’s up to -0.93 eV. All ALD films had good ohmic contact with the substrate and a strongly reduced average growth rate based on an assumed longer than normal nucleation phase of 0.21 Å/cycle (RuO₂ and RuO₂/OH) respectively 0.04 Å/cycle (Ru⁰) due to lacking chemical bonding sites on the substrate.

Additional experiments where the surface of a prepared RuO₂ film was sputtered show that hydroxyl groups are only present in the top-most layer, most likely as a consequence of the growth mechanism. Further sputtering resulted in no spectral changes, revealing the homogeneity of the underlying RuO₂ ALD film.
CHAPTER 5: INVESTIGATION OF THE DIPOLE FORMATION AND GROWTH BEHAVIOR AT In$_2$O$_3$|TiO$_2$ HETEROJUNCTIONS USING PHOTOEMISSION SPECTROSCOPY AND ATOMIC FORCE MICROSCOPY$^{20}$

5.1: Abstract

According to the International Technology Roadmap for Semiconductors, it is important to investigate alternate routes for device improvement as we approach miniaturization limits. A major problem is related to unwanted band alignment at heterojunctions introducing parasitic resistance, hindering effective electron transport across the junction. One way to approach this problem is by tailor-designing the band structure at interfaces with ultra-thin dipole layers. Often these layers do not exceed 1 nm, making sophisticated deposition techniques necessary. Atomic layer deposition (ALD) is known for its Ångstrom-precise thickness control, making it ideal for this task.

Here we present the investigation of the dipole formation and preparation method dependent growth behavior of ALD In$_2$O$_3$ at In$_2$O$_3$|TiO$_2$ heterojunctions. Further, we report on influences related to UV light exposure. We subjected solvent and in-situ cleaned anatase and rutile films to sequences of ALD, resulting in various thick In$_2$O$_3$ films. The dipole strength and thin film thickness was evaluated by analyzing the sample’s electronic structure with

$^{20}$ The content of this chapter is subject for publication in the Journal of Applied Physics. Manuscript is under review at the publication date of this dissertation.
photoemission characterization. To keep ambient contaminations minimal, the experiments were performed in a stop-flow thermal ALD reactor integrated with an UHV photoemission characterization system.

Our results indicate the formation of a conformation dependent interface dipole, climaxing at monolayer thick ALD films with dipole strength of -0.16 eV and -0.36 eV for solvent cleaned anatase and rutile, and 0.71 eV on in-situ cleaned rutile. We further observed the UV induced surface hydroxylation, causing a surface dipole of -0.70 eV and -0.50 eV on anatase and rutile substrates respectively. Deposition with 1 ALD cycle on different cleaned rutile resulted in similar work function, suggesting the negligibility of the preparation method. The observed growth rates are aligned with previous results. Highest initial growth was observed on solvent cleaned rutile, followed by in-situ cleaned rutile and solvent cleaned anatase. Bulk In2O3 growth converged at 0.30 Å/c.

5.2: Introduction

When fabricating complex electronic devices made from a variety of different materials, i.e. MOSFET’s, FINFET’s, MOSCAP’s, DSSC’s, etc., it is often challenging to overcome problems arising from unwanted electronic band alignment at heterojunctions. These heterojunction interfaces can cause problems in terms of device performance, efficiency, reliability, durability, etc. [62]. The band misalignment is a consequence of the individual chemical nature of the materials at the heterojunction interface [84]. Factors like electronegativity, bonding type, crystal structure mismatch, defect states, contamination, etc. can cause unwanted effects like band bending and Fermi-level pinning [31]. This can result for
instance in unwanted electron and hole potential barriers (Schottky barriers), charge depletion layers, charge transfer (or blockade) or interface dipoles, affecting device performance negatively.

One way to address this problem is by introducing ultra-thin, pinhole-free and high-conformity interfacial dipole layers capable of altering the band structure on one side of a heterojunction, i.e. by altering the work function, relative to the other, supporting band alignment in desired direction. Precisely manipulating those layers, often below 1 nm, and analyzing their electronic structure impact is challenging and requires Ångstrom-precise deposition techniques integrated with ultra-high vacuum photoemission characterization systems. The ideal deposition technique for this task is atomic layer deposition (ALD) with its sequential injection of self-limiting precursors that allows layer-by-layer growth of materials with atomistic resolution, thus giving excellent thickness control [50, 86]. Over the past decades the development and availability of precursors has steadily increased which allows nowadays for a wide variety of dipole layers to be deposited [57, 97].

In that light, ample studies have been reported making use of ultra-thin and high-conformity dipole layers to improve device performance. Selected highlights include minimization of the parasitic resistance at source/drain heterojunctions in MOSFET’s [30-32, 69, 99, 109] and MOS-HEMT’s [164] through Schottky potential modulation, or using dipole layers as charge recombination barrier in dye-sensitized solar cells (DSSC’s) [16, 17, 37, 155]. Further efforts have been reported using ALD dipole layers to modify material surfaces for applications in gas sensors [42] and catalysts [42].

In this study we investigated the substrate conformation, i.e. anatase and rutile, dependent dipole formation at In$_2$O$_3$|TiO$_2$ heterojunctions and the influence of different cleaning methods.
for the ALD film growth behavior. We further studied the influence of UV light exposure in the experiments. For that purpose, a series of ultra-thin atomic layer deposition (ALD) In$_2$O$_3$ films of various thicknesses were grown on epitaxial rutile and anatase TiO$_2$ substrates. Additional rutile samples were fabricated to investigate the influence of UV light exposure for different substrate cleaning procedures used prior to In$_2$O$_3$ deposition. This was done in an effort to determine if and how the magnitude of the interface dipole and the growth behavior change as the thickness of the In$_2$O$_3$ thin film is increased from sub-monolayer to multilayer coverage, and if and how those factors differ based on the substrate conformation. To further support the growth behavior and surface characteristics of the In$_2$O$_3$ thin films, selected AFM results are presented giving insight into the surface morphology.

5.3: Experimental Procedure

Single-crystalline TiO$_2$ substrates of approx. 10 nm thicknesses were grown by pulsed laser deposition (PLD). Rutile (011) was grown on R-plane cut <11-20> Al$_2$O$_3$ substrates (MTI Corp.) and anatase (001) was grown on (100) LaAlO$_3$ substrates (MTI Corp.). The deposition procedure is described elsewhere [107]. The thin film epitaxy and flatness was verified by in-situ RHEED (compare Figure 55). For additional experiments, a commercially available single-crystalline (011) rutile crystal (10x10x1 mm) was bought from MTI Corp.

In the interest of keeping ambient contaminations to a minimum, the experiments were conducted in a home-built, stop-flow type [81] thermal ALD reactor that is part of a larger multi-chamber analysis system. The ALD reactor allows exposure of samples with ample amounts of precursor for prolonged times, thus ensuring high film quality and conformity. The analysis
system is outfitted for X-Ray photoelectron spectroscopy (XPS), UV photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES).

In a first series of experiments, ALD In$_2$O$_3$ was deposited on a solvent cleaned PLD anatase thin film substrate twice with 5 ALD cycle increments followed by four times with 10 cycle increments. Intermittent to each deposition, photoemission spectroscopy characterization was performed. The samples were transferred and stored in UHV for the duration of the experiment. The deposition sequence was repeated in a second set of experiments. However, this time a solvent cleaned PLD rutile thin film substrate was used instead of anatase. The rutile substrate was deposited with In$_2$O$_3$ twice with 1 ALD cycle increments, followed by one time with 3 ALD cycle increments, one time with 5 ALD cycle increments and four times with 10 ALD cycle increments. The altered sequence was used to accommodate for different ALD growth rates observed on both substrates, with the intention of enabling the investigation of the electronic structure of sub-monolayer and multilayer In$_2$O$_3$ coverages on both substrates.

In further experiments, ALD In$_2$O$_3$ was deposited on an in-situ sputter/annealed rutile crystal following the deposition sequence described before. However, in order to study the influence of UV radiation exposure for differently prepared substrates, i.e. ambient solvent based cleaning and UHV sputter/annealing based cleaning, the crystal was not exposed to UV light during intermittent electronic structure characterization (only once initially to see if a work function shift occurs after UV exposure; the crystal was cleaned again prior to performing deposition experiments).

UV light exposure can cause multiple effects on sample surfaces. For instance, if a sample is poorly conductive, the generated photoelectrons accumulate on the surface, thus causing the work function to shift to higher binding energy. Surface dipoles cause the same shift.
However, their origin and persistence is different. While charging effects are temporary in nature, surface dipoles permanently alter the surface of a sample, causing a permanent alteration of the work function. To study this effect, another solvent cleaned PLD rutile thin film was fabricated and exposed to UV radiation for 15 minutes (about the average time necessary to determine the valence band structure of a sample surface with UPS characterization). Its work function before and 5h after the treatment were taken in order to investigate the differences between the formation of permanent surface alterations, due to the formation of permanent surface dipoles, and charging effects as a consequence of poor sample conductance. A detailed experimental sequence is described below.

5.3.1: Substrate Preparation

LaAlO$_3$ substrates were prepared by diamond scribing into 1x1 cm squares and r-cut Al$_2$O$_3$ samples were ordered pre-cut in 10 x 10 mm dimensions. Once scribed, the samples were mounted with welded-on Ta wires onto samples holders allowing transfer and handling inside the vacuum system. In order to get the substrates as clean as possible prior to deposition and to study the influence of the preparation technique, two cleaning methods were employed. The first method was comprised of a series of solvent cleaning in an ultrasonic bath for 20 minutes using acetone, ethanol and DI water consecutively to remove organic and inorganic remnants. A final blow-dry with nitrogen was performed to remove residual solvent. For the second method, the sample was cleaned in-situ by a sequence of Ar plasma sputtering (1 kV, 10 μA, 9 x 10$^{-6}$ Torr Ar atmosphere) and UHV high temperature annealing (700 °C, 5 x 10$^{-9}$ Torr).
5.3.2: ALD Sequence

After cleaning the samples, they were loaded through a fast entry load lock into the ultra-high vacuum analysis chamber. Initial photoemission spectroscopy characterization was performed before the samples were transferred in in-situ to the ALD reactor. Optimal precursor gas injection parameters were extrapolated according to literature reports [95]. In addition, two individually controllable mass-flow controllers in precursor and reactant injection line respectively were set to 80 ml/min. during deposition, injecting Ar as carrier gas, supporting the transportation of the precursor gasses from the injection lines to the reaction chamber. The injection lines, chamber body and exhaust line were heated to 120 °C to prevent unwanted condensation of water vapor on the reactor walls. The substrates were heated to 230 °C. The average reaction base pressure of 350 mTorr (mainly consisting of Ar atmosphere) was monitored by pirani pressure gauges installed in the main chamber and exhaust line. Once stable temperature and gas-flow conditions were reached, the ALD deposition was initiated. The injection sequence was as follows: 1 s injection of trimethyl indium followed by 10 s soak and 60 s purge; 3 s injection of water vapor followed by identical soak and purge time. The deposition was run until the pre-set total cycle count was reached (5c, 10c, 20, 30c, 40c and 50c for anatase substrates and 1c, 2c, 5c, 10c, 20c, 30c, 40c and 50c for rutile substrates). Once deposition was completed, all leftover precursor and carrier gas was purged from the system and the sample was allowed to cool down to room temperature (approx. 25 °C) under high vacuum conditions (< 1 x 10^{-6} Torr).
5.3.3: Photoemission Analysis

Once the substrates reached room temperature they were transferred in-situ to the ultra-high vacuum (≤ 9 x 10^{-10} Torr) analysis system for photoemission spectroscopy characterization. Low-intensity X-Ray photoelectron spectroscopy (LIXPS) and X-Ray photoelectron spectroscopy (XPS) were performed using a SPECS PHOIBOS 225 semi-hemispherical electrostatic energy analyzer in conjunction with an Mg Kα X-ray gun excitation source. UV photoemission spectroscopy (UPS) was performed using a differentially pumped capillary discharge vacuum UV source (UVS 10/35) with He(I) (21.22 eV) excitation in conjunction with before specified analyzer system. LIXPS was performed with the X-ray gun on standby, in which the photon flux is minimal yet enough for work function determination.

The thickness d of the In₂O₃ thin films was evaluated considering the attenuation of the Ti 2p₃/2 core level emission feature before and after deposition according to Lambert-Beer’s law:

\[ d = \lambda \cdot \ln \left( \frac{I_0}{I} \right) \]  \hspace{1cm} (13)

where \( I_0 \) is the emission intensity of the feature before In₂O₃ deposition, \( I \) is the attenuated emission intensity after deposition and \( \lambda \) is the mean free path.
5.4: Experimental Results

5.4.1: Dipole Formation at In$_2$O$_3$|TiO$_2$ Interfaces

To investigate the dipole formation at In$_2$O$_3$|TiO$_2$ heterojunctions, the samples were subjected to the following photoemission spectroscopy sequence: LIXPSa – UPS – LIXPSb – XPS. This sequence was chosen because analyzing the work function before and after UPS characterization can reveal the presence of temporary surface charging artifacts and UV light induced reactions. Those reactions change the sample’s surface permanently and have to be taken into account when calculating interface dipoles [56]. In this study, the individual work function $\Psi_{WF}$ was determined by subtracting the excitation energy (21.22 eV) from the secondary cut-off in LIXP-spectra determined by linear regression. An uncertainty factor of 0.10 eV was added to account for the analysis system’s resolution. The dipole strength was evaluated by comparing the work functions of the substrate prior to UV light exposure with those received after deposition. Figure 52 shows the sequence of LIXP-spectra observed for In$_2$O$_3$ grown on solvent cleaned PLD anatase substrates before (black solid line) and after (red dashed line) UPS (a), and extrapolated values for the work functions and dipole strengths as a function of ALD cycles and In$_2$O$_3$ film thickness respectively (b). Figure 53 shows the same sequence for solvent cleaned PLD rutile. In addition, LIXP-spectra, work functions and dipole strengths for the in-situ cleaned rutile crystal are added to Figure 53 for comparison. All extrapolated values are summarized in Table 4.

Before UV light exposure, the work functions of the solvent cleaned substrates are determined to 4.60 ± 0.10 eV for anatase and 4.70 ± 0.10 eV for rutile (4.64 ± 0.10 eV for in-situ prepared rutile) respectively. These values are in good agreement with Gutmann et al. [56], and
others [147, 163]. However, taking LIXP-spectra after UV light exposure into account, a significant shift of 0.70 eV to higher binding energy is observed on anatase substrates. This lowers the effective work function to $3.90 \pm 0.10$ eV. For rutile, a shift of 0.50 eV to higher binding energies decreases the work function to $4.20 \pm 0.10$ eV. We suggest that this shift can be attributed to a surface dipole that forms by photochemically induced hydroxylation of oxygen vacancies on the surface under UV light exposure and the presence of residual water.

Figure 52: LIXP-spectra of a sequence of different thick In$_2$O$_3$ thin films on single-crystalline solvent cleaned PLD anatase (a) and extrapolated values for work function and dipole strength (b). Error bars represent the analysis system’s resolution of ± 0.1 eV. A 0.7 eV shift in work function can be observed as consequence of a UV induced surface hydroxylation. This shift has been taken into account for the calculation of the interface dipole.
This effect alters the substrate surface chemically; resulting in a hydroxyl (OH) dominated surface termination. TiO$_2$ surfaces are known for this behavior [56]. If no residual water is present while exposing the sample to UV light, this shift cannot be observed. This can be seen when comparing with work function measurements of in-situ prepared rutile.

Figure 53: LIXP-spectra of a sequence of different thick In$_2$O$_3$ thin films on single-crystalline solvent cleaned PLD rutile (a), in-situ sputter/annealed rutile (without exposure to UV light) (b), and extrapolated values for work function and dipole strength (c). Error bars represent the analysis system’s resolution of ± 0.1 eV. A 0.5 eV shift in work function can be observed as consequence of a UV induced surface hydroxylation on the solvent cleaned substrate. No shift is observed for in-situ cleaned rutile. The shift observed on solvent cleaned rutile has been taken into account for the calculation of the interface dipole.

The circumstance is further illustrated in Figure 54 a) in which work function measurements for differently prepared substrates are overlaid with the secondary edge received from UPS characterization. Only for the in-situ prepared substrate, the secondary edges of all
measurements (LIXPSa, UPS and LIXPSb) align, i.e. showing the same work function. We assume that the substrate is neither charged nor does it form a surface dipole as a consequence of UPS characterization. On solvent cleaned substrates however, LIXPSb and UPS secondary edge are coincident, but shifted from the initial work function measurement (LIXPSa), thus suggesting permanent alteration of the sample’s surface through UPS characterization. This shift was expected based on the preparation method in which DI water was used as final cleaning step, hence leading to large amounts of adsorbed water on the substrate surface.

Table 4: Summary of the work functions and dipoles for solvent cleaned anatase and rutile and in-situ cleaned rutile separated before and after UPS were applicable. Maximum dipole strengths observed in the ALD sequences before UV light exposures are marked in red.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>Solvent cleaned anatase</th>
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<tr>
<td></td>
<td>ψWF [eV]</td>
<td>ΔD [eV]</td>
<td>ψWF [eV]</td>
</tr>
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<td>After UPS</td>
<td>Before UPS</td>
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<td>-</td>
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<tr>
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</tr>
<tr>
<td>50</td>
<td>3.87</td>
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<td>-0.73</td>
</tr>
</tbody>
</table>

In order to quantify the extent of the suggested surface hydroxylation effect and compare it with the presence of artificial charging, another solvent cleaned PLD rutile substrate was

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21 No shift in work function has been observed after UPS characterization.
subjected to prolonged UV light exposure. UP- and LIXP-spectra taken before and at different times after UV light exposure are shown in Figure 54 b).

![Figure 54: LIXP- and UP-spectra for solvent cleaned PLD rutile and anatase and in-situ cleaned commercial rutile (a) and LIXPSa – UPS – LIXPSb (0 Min.) – LIXPSb (5 h) sequence of solvent cleaned PLD rutile (b). Part a) shows that LIXPSb and UPS spectra for solvent cleaned substrates are not coincident, suggesting alteration of the surface after UPS characterization. This shift is not observed if the substrate is cleaned in situ. Part b) illustrates the level of charging effects in comparison to a permanent alteration of the surface. It can be seen that UPS and LIXPSb spectra taken immediately and after 5h show coincident work function, indicating no charging effects present on the substrate surface.](image-url)
A shift of 0.5 eV is observed again, supporting previously made observations. When measuring the work function 5h later, the secondary edge remains at the same position, supporting the suggested surface hydroxylation effect rather than charging.

In LIXP-spectra of In$_2$O$_3$ thin films, a similar shift of smaller magnitude (up to 0.10 eV) is observed (compare Table 4). It is uncertain if UV induced hydroxylation in the presence of residually adsorbed water molecules can be made responsible in that case, because the samples were heated to temperatures above the condensation point of water (230 °C) for prolonged times, removing the majority of adsorbed water. We assume that UV light induced surface recombination effects of imperfectly hydroxylated In$_2$O$_3$ thin films or the presence of non-reacted, ligand-terminated surface groups cause the observed shift.

Figure 52 and Figure 53 indicate an initial work function drop (and the dipole strength increase) with incrementing ALD cycles, i.e. the thickness of the In$_2$O$_3$ overlayer increases. This trend is continued until the In$_2$O$_3$ thin film reaches a thickness of about 1 stoichiometric monolayer (2 – 4 Å [17]). After that, the trend is reversed. We suggest that the turnaround point is substrate and preparation method dependent, i.e. different growth rates for differently prepared substrates. The maximum dipole strength is observed after 20 ALD cycles for solvent cleaned anatase, after 2 ALD cycles for solvent cleaned rutile and after 10 ALD cycles for in-situ cleaned rutile. The corresponding maximum interface dipole strength based on LIXPS measurements is -0.86 eV for solvent cleaned anatase and rutile. The maximum dipole strength for in-situ prepared rutile is determined to -0.71 eV. Due to the fact that the investigated junction is a semiconductor-semiconductor heterojunction, band bending effects can occur as a consequence of charge transfer, thus altering the total dipole strength $\Delta_{tot}$ l. This effect needs to be taken into account when evaluating the total dipole strength (compare Figure 57 b)). To evaluate the amount of
band bending $\Delta_{BB}$ at the interface, the Ti 2p$_{3/2}$ core level emission features are compared before and after deposition. A shift of 0.1 eV to lower binding energy is observed (Figure 57 a)), thus increasing the total dipole strength to -0.96 eV for solvent cleaned anatase and rutile. The dipole strength for in-situ cleaned rutile increases to -0.81 eV. Anyway, the maximum dipole strength at the observed turnaround points is the same for different conformations (compare Table 4).

In order to correlate the interface dipole strength with the substrate preparation method, the work functions of solvent cleaned and in-situ cleaned rutile are considered (compare Figure 53). Both work functions are nearly identical initially (4.70 eV and 4.64 eV), indicating the similarity of the sample’s surface prior to In$_2$O$_3$ deposition. After UV light exposure however, previous discussed shift (0.5 eV) is only observed for solvent cleaned rutile, suggesting the absence of residual water on the in-situ prepared substrate. This renders the effective work functions 4.20 eV for solvent cleaned rutile and 4.64 eV for in-situ prepared rutile, a difference of 0.44 eV. After deposition of 1 ALD cycle equivalent of In$_2$O$_3$ however, the new work functions are nearly the same (compare Table 4). We assume that no matter if the substrate is cleaned with solvents under ambient conditions or if the substrate is in-situ sputtered and UHV annealed, the work function after deposition of 1 ALD cycle In$_2$O$_3$ result in almost identical values, hence the same interface dipole strength. We assume that a predominantly hydroxide terminated surface merely acts as anchor point boost for ALD precursors, influencing the growth rate but not the effective work function. In that light UV exposure may be investigated as growth rate booster, minimizing ALD nucleation times for material interfaces involving TiO$_2$, etc.
5.4.2: Growth Rate Analysis

The growth rate of In$_2$O$_3$ on solvent cleaned PLD anatase, rutile and in-situ prepared rutile was evaluated. This was done to investigate if and how the substrate preparation method and conformation influences the growth behavior. AFM measurements were performed on both substrates and In$_2$O$_3$ thin films to support the investigation. The ALD thin film thickness was derived according to equation 13. For that purpose high magnification XPS characterizations were performed at the Ti2p$_{3/2}$ core level emission feature ranging from 456 – 462 eV (compare supplemental Figure 57). The PLD film thickness was evaluated by comparing substrate core level emission features before and after PLD (La 3d for anatase and Al 2p for rutile). The observed signal attenuation suggests complete coverage according to supplemental Figure 57.

Table 5: Calculated thickness of ALD In$_2$O$_3$ thin films on solvent cleaned anatase and rutile and in-situ cleaned rutile.

<table>
<thead>
<tr>
<th>ALD cycles</th>
<th>solvent cleaned anatase</th>
<th>solvent cleaned rutile</th>
<th>in-situ cleaned rutile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>2.23</td>
<td>1.10</td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>2.90</td>
<td>1.69</td>
</tr>
<tr>
<td>5</td>
<td>0.62</td>
<td>7.61</td>
<td>2.30</td>
</tr>
<tr>
<td>10</td>
<td>1.32</td>
<td>8.91</td>
<td>3.09</td>
</tr>
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<td>20</td>
<td>2.11</td>
<td>12.72</td>
<td>6.40</td>
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<td>13.79</td>
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<td>17.83</td>
<td>10.29</td>
</tr>
<tr>
<td>50</td>
<td>12.16</td>
<td>18.99</td>
<td>13.00</td>
</tr>
</tbody>
</table>
Figure 55: AFM and average roughness profile along red line of PLD TiO$_2$-anatase on LAO (a) and PLD TiO$_2$-rutile on Al$_2$O$_3$ (c). AFM of In$_2$O$_3$ thin films and respective roughness profiles on top of the PLD anatase (b) and PLD rutile (d) are added. The included RHEED analysis verifies the single-crystal nature of the PLD substrates. The roughness $R_a$ corresponds to the whole area of investigation.
The In$_2$O$_3$ thin film thicknesses were extrapolated from Figure 58 and summarized in Table 5. The ALD film conformity was evaluated based on AFM measurements of In$_2$O$_3$ thin films after 50 ALD cycles (Figure 55). The measurements suggest that the ALD films are flat and highly conformal. Their average roughness $R_a$, measured across the complete area of investigation, is determined to 0.92 Å and 1.49 Å on anatase and rutile respectively, thus rendering the In$_2$O$_3$ thin film rougher when grown on rutile. This observation is in line with the observed initial roughness of the substrates, i.e. rutile is rougher than anatase (compare Figure 55 c)).

Figure 56 a) illustrates the growth rate as a function of ALD cycles. The difference indicates an enhanced growth rate on solvent cleaned rutile in comparison to its in-situ prepared counterpart or solvent cleaned anatase. It is assumed that a smaller step terrace width in conjunction with a rougher surface on rutile substrates ($R_a = 0.86$ Å) in contrast to anatase ($R_a = 0.35$ Å) provides a larger number of under-coordinated step-edge sites and therefore a larger amount of nucleation sites for the precursor material in the ALD process, thus boosting the initial growth rate. This assumption is supported by T. Lutrell et al. who reported step terrace widths for anatase up to 100 nm while step terraces observed on rutile had smaller sizes of 5 – 50 nm [107]. It is further assumed that the observed surface hydroxylation, i.e. the surface termination with hydroxyl groups, boosts the initial nucleation, which may explain the observed growth rate differences for differently prepared rutile substrates. The per cycle growth rate shown in Figure 56 b) supports this assumption. It is largest for solvent cleaned rutile where 2 ALD cycles are necessary to reach an In$_2$O$_3$ thin film thickness equivalent to one monolayer ($\sim 3$ Å), whereas more than 20 ALD cycles are needed in case the substrate is solvent cleaned anatase, a factor 10 difference. To cover in-situ cleaned rutile with one monolayer equivalent In$_2$O$_3$, 10 ALD cycles
are necessary. However, as the In$_2$O$_3$ thin film approaches bulk thickness, the growth rate per cycle converges at 0.30 Å/c for both conformations and preparation methods.

In conclusion, we suggest that the In$_2$O$_3$ growth rate is conformation and cleaning method dependent in the sub-monolayer domain. However, once the bulk structure is established, growth rates start to align.

5.5: Conclusion

We investigated various thick ALD In$_2$O$_3$ thin films on differently prepared PLD anatase and rutile substrates and rutile crystals in order to study the conformation dependent formation of an interface dipole and to further study the influence of different preparation methods in the process. In addition, we investigated how those factors impact the growth behavior of In$_2$O$_3$.

Our results suggest the formation of a hydroxyl (OH) terminated surface dipole on solvent cleaned TiO$_2$ substrates as consequence of UV light induced surface hydroxylation of oxygen vacancies in the presence of residual water. Additional experiments exclude its origin based on artificial charging effects. The magnitude of the surface dipole is determined to -0.7 eV on solvent cleaned anatase and -0.5 eV on solvent cleaned rutile. The formation of a surface dipole cannot be observed for an in-situ cleaned rutile crystal, pointing out the importance of the presence of residual water during UV light exposure.

The interface dipole at the In$_2$O$_3$|TiO$_2$ heterojunction is climaxing when the In$_2$O$_3$ thin film thickness is equivalent to one monolayer. The corresponding maximum dipole strength, taking band bending effects into account, is identical (-0.96 eV) for both solvent cleaned
substrates. The maximum observed dipole strength for in-situ cleaned rutile is determined to -0.81 eV.

**Figure 56:** Thickness of ALD In$_2$O$_3$ on different conformations (a) and average growth rate per ALD cycle (b). The In$_2$O$_3$ monolayer thickness was set to 3 Å based on an average 2 – 4 Å [17]. The initially overestimated growth rate in part b) converges for all conformations to approx. 0.30 Å/c for thicker In$_2$O$_3$ films. The different growth rate observed initially is assumed to be caused by a more or less surface hydroxylated surface for different substrates.
However, work functions (and interface dipole strengths) of solvent and in-situ cleaned rutile are nearly identical after deposition with 1 ALD cycle In$_2$O$_3$, suggesting the negligibility of the cleaning method and the prevalence of surface hydroxyl groups as anchor points for ALD precursors.

![Figure 57](image.png)

**Figure 57**: Ti 2p$_{3/2}$ core level emission feature for solvent cleaned PLD anatase and rutile and in-situ prepared rutile as a function of binding energy (a). The intensity of the signal decreases as the In$_2$O$_3$ thin film grows in thickness. Energy diagram (not to scale) of the band bending $\Delta $BB observed at the heterojunction interface, increasing the maximum dipole strength $\Delta $D$_{total}$ (b).

The investigation of the growth rate is aligned with previous observations, i.e. dependent on the substrate conformation, surface area (related to the step terrace length and the amount of
under-coordinated step-edge sites) and employed cleaning method. The highest initial growth rate is observed on a solvent cleaned rutile substrate. This is followed by the in-situ prepared counterpart and solvent cleaned anatase. However, the bulk growth rate is determined to 0.30 Å/c.

The results of this study may serve to establish a better understanding of the interface dipole formation at the In$_2$O$_3$|TiO$_2$ heterojunction and how the substrate conformation and employed sample preparation methods influence the dipole strength and growth behavior. The results can further be used to optimize the investigated junction, thus helping band alignment in complex interface structures.

Figure 58: Evaluation of PLD process showing complete substrate coverage with single-crystalline thin film for anatase (a) and rutile (b). The substrate signal is completely attenuated indicating a thin film thickness exceeding 5 nm (typical penetration depth for X-ray radiation used in this study).
CHAPTER 6: SYNTHESIS AND IN VACUO DEPOSITION OF IRON OXIDE NANOPARTICLES BY MICROPLASMA-ASSISTED DECOMPOSITION OF FERROCENE

6.1: Abstract

Microplasma-assisted gas-phase nucleation has emerged as an important new approach to produce high-purity, nanometer-sized, and narrowly dispersed particles. This study aims to integrate this technique with vacuum conditions to enable synthesis and deposition in an ultrahigh vacuum compatible environment. The ultimate goal is to combine nanoparticle synthesis with photoemission spectroscopy-based electronic structure analysis. Such measurements require in vacuo deposition to prevent surface contamination from sample transfer, which can be deleterious for nanoscale materials. A homebuilt microplasma reactor was integrated into an existing atomic layer deposition system attached to a surface science multichamber system equipped with photoemission spectroscopy. As proof-of-concept, we studied the decomposition of ferrocene vapor in the microplasma to synthesize iron oxide nanoparticles. The injection parameters were optimized to achieve complete precursor decomposition under vacuum conditions, and nanoparticles were successfully deposited. The stoichiometry of the deposited samples was characterized in situ using X-ray photoelectron spectroscopy indicating that iron oxide was formed. Additional transmission electron spectroscopy characterization allowed the

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22 Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC. See Appendix A: Permissions. Link to full text: [http://dx.doi.org/10.1063/1.4897165](http://dx.doi.org/10.1063/1.4897165).
determination of the size, shape, and crystal lattice of the particles, confirming their structural properties.

6.2: Introduction

Microplasma synthesis of nanoparticles by homogeneous nucleation in the gas phase has emerged as an exciting new paradigm for plasma processing [112, 113]. The unique characteristics of microplasmas including non-equilibrium thermodynamics [92], high electron density [134] and pD-scaling [112] (p for pressure and D for the plasma length) allow nanoparticles to be produced at atmospheric pressure, while controlling structural aspects such as size, dispersion, agglomeration, purity, composition, and crystallinity [10, 28, 100, 112, 113].

While atmospheric pressure operation is an attractive feature of microplasma-based processes to lower cost and enable scale up, a drawback is that characterization of the as-grown nanoparticle materials by surface sensitive materials analysis techniques such as X-ray photoelectron spectroscopy (XPS) require pristine samples that are not contaminated by exposure to the ambient. This is especially critical for nanoscale materials with high surface to volume ratios. The small size and low power requirements of microplasma reactors facilitate their integration with materials analysis equipment [156]. Here, we present a microplasma reactor integrated with an ultrahigh vacuum compatible vacuum chamber with the goal of in vacuo deposition to enable photoemission spectroscopy on as-synthesized materials.
6.3: Experimental Setup

6.3.1: General Procedure

Ferrocene (FeCp₂) vapor was dissociated in the microplasma to nucleate iron nanoparticles, and directly deposited onto substrates in the vacuum chamber. XPS analysis was used to detect both any unreacted ferrocene precursor and the synthesis of iron (Fe) nanoparticles. This allows optimization of process parameters to achieve complete precursor decomposition. Characterization of the Fe nanoparticles indicates oxidation states corresponding to iron oxide. TEM characterization confirmed the synthesis of crystalline, nanometer-sized particles corresponding to iron oxide. Details regarding the sample preparation can be found in the Appendix.

6.3.2: Microplasma System

The microplasma reactor was built and integrated with a pre-existing ultra-high vacuum compatible ALD reactor connected to an analysis chamber outfitted with X-ray and ultraviolet photoemission spectroscopy (XPS, UPS) and inverse photoemission (IPES). Figure 59 schematically shows the microplasma reactor integrated with the ALD system for synthesis and in vacuo deposition of nanoparticles. The system is separated into three parts.

The first part, the gas injection system, consists of two mass-flow controllers that separately regulate a pure flow of the carrier gas (Ar) and a mixed flow of carrier gas and ferrocene vapor with a total flow rate range of 0-200 cm³/min. The ferrocene vapor was introduced to the microplasma by subliming solid powder from a stainless steel reservoir at 25
°C (room temperature) into the Ar stream. The resulting Ar/ferrocene mixture was further diluted with the Ar carrier gas to control the final concentration. The second part of the reactor consists of the active plasma region.

**Figure 59:** Microplasma reactor integrated with an ALD system connected to a surface analysis chamber. The right side shows the ALD reactor with the attached gas injection system and in vacuo parts of the nanoparticle injector system. A zoomed in version of the in vacuo part of the injector system is shown to the left. A high voltage feedthrough has been used to connect the capillary to positive high voltage. The plasma itself is contained in a quartz tube between the tip of the capillary and the mesh that acts as the ground connection through the sample stage. The whole injection system can be moved in +/- z-direction to allow sample transfer into the ultrahigh vacuum analysis chamber and to enable grounding of the mesh through the sample stage. Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC.
A stainless steel capillary (1/16 ″ OD, 0.005 ″ ID) and a stainless steel mesh were inserted into a quartz tube. Electrical feedthroughs were used to bias the capillary tube at positive high voltage, while the mesh was held at ground potential. Nanoparticles were nucleated in the microplasma and carried by the gas flow for deposition to the substrate, which was mounted on a heatable sample stage.

The entire microplasma setup could be moved within the main vacuum chamber in +/- z-direction enabling physical contact of the mesh electrode to the sample stage to establish the ground connection. We note that this is different than previously reported by Chiang W. et al. where nanoparticles were deposited further downstream of the microplasma by electrostatic precipitation. There, the substrate was biased at very large electric potentials of ~10 kV/cm to aid deposition [28]. In our case, grounding of the substrate could not be avoided due to the design of the sample stage within the vacuum chamber, but nanoparticle deposition was obtained by positioning the substrate close to the microplasma.

6.3.3: Experimental Parameters

Five experiments were performed. The procedure for igniting the microplasma inside the vacuum chamber was as follows: first, pure Ar was introduced at the required flow rate. Then a voltage of +600 V was applied between the capillary tube and the mesh to ignite the plasma. After stable microplasma conditions were established, the voltage was lowered to +450 V. The current was limited to 1 mA via an 80 kΩ resistor in series with the power supply. Finally,
ferrocene vapor was introduced into the microplasma at different concentrations, while keeping
the total gas flow rate constant at 100 cm$^3$/min (Table 6).

**Table 6**: Summary of reaction conditions for in vacuo deposited samples. The roughing vacuum
base pressure during each experiment is also shown. Reproduced with permission from [148].
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<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ar/ferrocene ratio</th>
<th>Deposition time [h]</th>
<th>U [V]</th>
<th>I [mA]</th>
<th>p [mTorr]</th>
</tr>
</thead>
<tbody>
<tr>
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<td>1</td>
<td>415</td>
<td>1.01</td>
<td>189</td>
</tr>
<tr>
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<td>99:1</td>
<td>0.5</td>
<td>425</td>
<td>1.00</td>
<td>190</td>
</tr>
<tr>
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<td>40:1</td>
<td>1</td>
<td>440</td>
<td>1.06</td>
<td>191</td>
</tr>
<tr>
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<td>20:1</td>
<td>2</td>
<td>450</td>
<td>1.10</td>
<td>186</td>
</tr>
<tr>
<td>5</td>
<td>10:1</td>
<td>4</td>
<td>430</td>
<td>0.95</td>
<td>188</td>
</tr>
</tbody>
</table>

**6.3.4: TEM Measurements**

TEM characterization was performed with a TECNAI F20 transmission electron
microscope at the University of South Florida Nanotechnology Research & Education center
(NREC). TEM samples were prepared with identical process parameters as for XPS
characterization except that Cu coated carbon grid substrates were used instead of Si wafers
(“TEM grid”). To determine the nanoparticle structure, the average interplanar spacing (d-
spacing) was obtained by measuring the distance across 10 atomic planes. The resulting lattice
parameters were evaluated using a crystallographic database.
6.4: Experimental Results

6.4.1: Electronic Structure Analysis Fe 2p (XPS)

Figure 60 shows a series of Fe 2p spectra collected from the five samples detailed in Table 6.

Figure 60: Fe 2p emissions of in vacuo deposited samples. The red line corresponds to the binding energy arising from ferrocene. The green line corresponds to the binding energy arising from the deposited iron nanoparticles, respectively. The bottom graph shows a ferrocene SAM control sample. The peak maximum of this ferrocene SAM is shifted to lower binding energies compared to assumed ferrocene throughout the nanoparticle production by 0.25 eV. This can be explained by the different chemical environment both samples were exposed to that resulted in a different interface dipole. Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC.
The increase in intensity of the peaks with increasing ferrocene vapor concentration and deposition time agrees well with the expected increase in the amount of Fe deposited on the surface. In addition, changes in the emission features can be observed. As the ferrocene vapor concentration is increased, the Fe 2p\textsubscript{3/2} peak shifts from 710.7 eV to 708.6 eV and changes from a significantly broadened peak to a superposition of two peaks. The peak shape at lower ferrocene concentrations indicates the presence of two different iron species, Fe\textsuperscript{2+} and Fe\textsuperscript{3+} [3]. It is most likely that the peak at 708.6 eV arises from ferrocene [166] (compare ferrocene SAM control spectrum in Figure 60) and the peak at 710.7 eV arises from the oxide at the surface of metallic Fe nanoparticles or from fully oxidized iron oxide nanoparticles. Peak broadening may additionally be explained by a polydisperse size distribution due to a varying length of the microplasma region under vacuum conditions, which affects the particle growth time. Assuming that the XPS analysis shows oxidation, we find that iron oxide nanoparticles are produced at all ferrocene concentrations. However, the top graph in Figure 60 shows high concentrations of pristine ferrocene that can be accompanied by strong satellite peaks [166] and therefore it is not clear if nanoparticles were created. As the ferrocene concentration in the microplasma is reduced, the intensity of unreacted ferrocene vapor decreases and is eventually not detectable at an Ar to ferrocene ratio of 40 to 1. Additionally, a spectrum was collected from a control substrate that was exposed to pure Ar plasma for one hour (i.e. the microplasma was run without mixing in ferrocene). The spectrum shows no observable Fe peaks (compare Figure 60). It can be concluded that ferrocene can be decomposed completely within the microplasma if the concentration is low enough (at least 40/1), e.g. no ferrocene peak can be observed anymore (compare Figure 60). Due to the experimental setup and conditions, carbon residues were most presumably co-deposited during the experiments and therefore can explain the higher than
expected carbon contributions especially in experiment 2 and 3. The control sample also shows that Fe is not produced by sputtering of the electrode materials.

6.4.2: Electronic Structure Analysis C 1s (XPS)

Figure 61 shows the C 1s emissions of the same samples. A broad peak at 284.6 eV is assigned to carbonaceous contaminations derived from the control sample (peak maximum shown by red line).

![Carbon C 1s emissions. The bottom spectrum was measured on the control sample (no ferrocene in the microplasma). After mixing in ferrocene (upper four spectra) a new emission feature arises, indicating the deposition of ferrocene fragments, in addition to varying amounts of unreacted ferrocene. Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC.](image-url)
The deposited samples show that the introduction of ferrocene shifts the C 1s peak maximum to a higher binding energy (285.2 eV, $\Delta$BE = 0.6 eV). This shift in binding energy indicates the presence of different carbon compounds. This is in agreement with the Fe 2p spectra in Figure 60, which indicate the co-deposition of some non-decomposed ferrocene with iron oxide nanoparticles for the two least-diluted cases (10/1 and 20/1).

6.4.3: Comparison with Nanoparticles Synthesized via the Atmospheric Pressure Process

Results obtained for the in vacuo deposition were compared to Fe nanoparticles synthesized and deposited at atmospheric pressure and transferred in room air to the XPS instrument (see Ref. [100] for experimental procedure). In addition, a control sample of a ferrocene terminated self-assembled monolayer (SAM) was used to obtain a baseline ferrocene Fe 2p$_{3/2}$ spectrum for comparison. Figure 62 shows the Fe 2p$_{3/2}$ emissions measured on these three samples.

While there is a small difference in absolute binding energies, the spectra obtained from films deposited in vacuo and at atmospheric pressure appear similar. This suggests that both methods lead to oxidized Fe nanoparticles. The comparison with the spectrum for a SAM of ferrocene suggests that complete dissociation of ferrocene was achieved for both synthesized samples. While oxidation of the samples is expected for deposition at atmospheric pressure because of transfer in room air, oxidation for in vacuo deposition is not obvious. An explanation for oxidation under vacuum conditions is suggested by a previous study done by A. Grosvenor et al. who showed that at partial oxygen pressures of only 0.1 mTorr, a flat, bulk iron substrate can
oxidize about 2.3 nm deep within the first 200 seconds of exposure [55]. The total base pressure throughout the experiments conducted in this study was 2.0 mTorr.

**Figure 62:** Comparison between in vacuo deposited (Ar/ferrocene ratio 40/1) and atmospheric pressure deposition and room transfer of Fe nanoparticle films. The bottom spectrum was collected from a ferrocene terminated self-assembled monolayer for reference. Both film deposited spectra show mostly identical features indicating that on both samples the ferrocene was fully decomposed, and that a similar stoichiometry was achieved under vacuum conditions as at atmospheric pressure. Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC.

Assuming a fractional oxygen pressure of 20.9 % in the residual gas (note that this is only an estimate, since it assumes the same pumping efficiency for N₂ as for O₂), we estimate a partial oxygen pressure of 0.4 mTorr, a factor of four higher than reported by Grosvenor et al.
Considering that nanoparticles have a much larger surface to volume ratio than their bulk material, it is reasonable to assume that the nanoparticles can completely oxidize within the timeframe of our experiments. It should be pointed out that the goal of this study was not to produce pure Fe nanoparticles, but rather to prevent an environmental contamination layer forming after the deposition, which is essential for direct in situ characterization of nanoparticle films by photoemission spectroscopy. The elimination of a contamination layer is also essential for the planned integration of such nanoparticles into ALD film structures.

6.4.4: Size, Shape and Species Analysis

Figure 63 shows a TEM image of a typical nanoparticle synthesized in our microplasma setup using the experimental parameters of experiment 2 (see Table 6). The image confirms that the particles are nanometer sized. The particles are larger than those previously reported at atmospheric pressure [28]; this may be the result of the larger microplasma volume at lower pressures which increases the space time for particle growth. The particles are single crystalline, as can be seen by the regular pattern of atoms, and a measurement of the distance across 10 atomic planes reveals a mean interplanar distance (d spacing) of 2.7 Å (compare Figure 64), which can be indexed to the (104) plane of hematite [59]. These results are consistent with the growth of iron oxide indicated by XPS analysis.
6.5: Conclusions

In summary, we have demonstrated that nanoparticles can be synthesized and deposited under vacuum conditions by integrating a DC microplasma reactor with an ALD system. XPS characterization confirms that the samples deposited in vacuum have a similar composition and oxidation state as nanoparticles synthesized under atmospheric pressure conditions with the standard micro plasma technique.

Figure 63: Representative TEM image of an iron oxide nanoparticle exhibiting ordered atomic planes indicative of a single crystal. Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC.
The analysis of the C 1s emissions revealed the presence of aromatic cyclopentadienyl rings or ring fragments from the ferrocene precursor in the deposits.

TEM characterization showed that the deposited nanoparticles are larger than particles produced at atmospheric pressure. The main reason for this difference may be the different synthesis conditions. Future studies are planned to understand how the vacuum conditions may influence particle nucleation and growth, as well as reduce the contamination of the particles due to oxygen and carbon to obtain higher purity materials.

**Figure 64:** TEM cross-section across 10 atomic planes of the nanoparticle indicated in Figure 63 that was used to determine its interplanar spacing d. Reproduced with permission from [148]. Copyright 2014, AIP Publishing LLC.

The presented results demonstrate that microplasma-assisted nanoparticle synthesis is a promising technique for the clean deposition of metal-based nanoparticles for surface analysis experiments. The direct integration of the microplasma setup into an ALD reactor also opens the possibility for the integration of nanoparticles into ALD layer stacks, which promises interesting possibilities for the creation of 1D quantum confinement structures that are integrated into lamellar 2D structures.
6.6: Appendix: Substrate Preparation and Cleaning Procedure

Si wafers cut with a diamond scribe into 2 x 2 cm pieces were used as substrates for nanoparticle deposition. The square pieces were mounted on a sample holder ensuring good Ohmic contact to the sample stage. The contact resistance of the wafer with the sample holder was measured at three locations on each sample and in all cases was less than 10 Ω. After mounting, the Si substrates were cleaned by successively immersing in acetone, methanol, isopropanol and deionized (DI) water, and finally blown dry with nitrogen. The substrates were loaded into the ultrahigh vacuum chamber via a fast entry lock and then into the main chamber. As a final cleaning step, the substrates were subjected to 30 minutes of Ar plasma sputtering (at 5 kV, 15 mA in a 9 x 10^-6 Torr Ar atmosphere) to remove any remaining residual surface contamination.
CHAPTER 7: CONCLUSIONS AND OUTLOOK

7.1: Conclusions

The experiments discussed in this dissertation were enabled by the design and construction of a stop-flow type thermal ALD reactor, which was integrated into a preexisting UHV multi-chamber photoemission characterization system. This was done in order to enable complete in-situ experimentation on ALD interfaces in the interest of keeping ambient contaminations to a minimum. This system was further expanded by the implementation of a DC microplasma based nanoparticle injector system into the ALD reactor. This was done with a proof-of-concept approach in mind, adapting a well-established technique optimized for ambient pressure conditions to the vacuum domain.

Three experimental studies are presented as part of this work. The first two studies demonstrate the in-situ deposition capabilities of the ALD reactor on prototypical Ru, RuO\text{x} and In\text{2}O\text{3} based hetero-interfaces in order to study the electronic structure and band alignment phenomena at Ru(O\text{x})|Au and In\text{2}O\text{3}|TiO\text{2} heterojunctions with photoemission characterization experiments. Particular interest was given to the modularity of the interface dipole formation with varying process parameters in order to enable tailor-designing the band-structure at heterojunction interfaces. The third study focused on the in-situ deposition of nanoparticles into the ALD reactor under clean vacuum conditions. This was demonstrated by using the organo-metallic precursor ferrocene to synthesize iron oxide nanoparticles.
In order to study the Ru($O_x$)|Au heterojunction in the first presented study, the home-built ALD reactor was used to fabricate a number of ALD films with various Ru/RuO$_x$ compositions on Au substrates, by varying the injection parameters in each experiment, i.e. by varying the precursor injection timing. Photoemission characterization of the ALD films was performed in-situ, thus minimizing ambient contaminations, which can alter ALD film surfaces, thus complicating the electronic structure analysis. It was shown that the degree of oxidation is a direct consequence of the injection parameters. If the O$_2$ to Ru ratio was set below 1, the formation of metallic ruthenium (Ru$^0$) was observed, while at ratios above 1 a blend of RuO$_2$ and RuO$_2$/OH was observed. LIXPS work function analysis indicated a strongly physisorbed Ru($O_x$)|Au heterojunction rather than a chemically bond interface. This was expected due to the noble metal character of gold. An injection parameter dependent interface dipole was observed reaching maximum dipole strengths of up to $-0.93$ eV. It was further suggested that the physisorbed nature of the interface is responsible for observed small growth rates of $0.21$ Å/cycle for RuO$_2$ and RuO$_2$/OH and $0.04$ Å/cycle for metallic ruthenium (Ru$^0$). The surface termination of RuO$_2$ was investigated in additional sputter/photoemission characterization experiments. The results indicated the presence of a hydroxyl terminated surface and the homogeneity of the underlying bulk structure.

The In$_2$O$_3$|TiO$_2$ heterojunction was investigated as part of the second study. In$_2$O$_3$ ALD films were grown on PLD anatase and rutile substrates. This was done in order to study whether the interface dipole formation is conformation dependent, and how different cleaning methods can influence the growth behavior of the In$_2$O$_3$ ALD films. We observed the formation of a surface dipole as consequence of UV light induced surface hydroxylation of TiO$_2$ surfaces in the presence of residual water on solvent cleaned substrates. In addition, experiments were
performed to exclude charging artifacts from the observed work function shift that indicated the surface dipole in the first place. The magnitude was different for different conformation with values of -0.7 eV on anatase and -0.5 eV on rutile. For in-situ cleaned substrates, this effect was not observed, indicating the importance of residual water while exposing the sample to UV radiation. We observed an interface dipole formation at the In$_2$O$_3$ heterojunction, reaching maximum strength (-0.86 eV) at an In$_2$O$_3$ ALD film thickness equivalent to one monolayer. The maximum dipole strength for in-situ cleaned rutile was determined to -0.71 eV. To investigate the influence of the cleaning method into the formation of an interface dipole, a solvent and in-situ cleaned rutile sample were subjected to 1 ALD cycle In$_2$O$_3$. Analyzing the work function in LIXPS characterization concluded with the result that the work functions after deposition are nearly identical, thus indicating the negligibility of the surface dipole formation on solvent cleaned substrates. The highest initial growth rate was observed for solvent cleaned rutile (that was terminated by hydroxyl groups prior to deposition due to UV light exposure), followed by in-situ cleaned rutile and solvent cleaned anatase. The different growth rate observed on the same crystal structure (rutile) was attributed to the presence of hydroxyl groups for the solvent cleaned substrate. The differences among the crystal structure were attributed to different step terrace lengths and the different amount of step-edge sites on anatase and rutile. The bulk In$_2$O$_3$ growth rate converged at 0.30 Å/c.

The nanoparticle injector experiments demonstrated that the microplasma approach can be adapted for deposition into vacuum chambers. This finding opened the door to the use of vacuum based analytical techniques for the investigation of microplasma generated nanoparticles. This was demonstrated via photoemission spectroscopy experiments on iron oxide nanoparticles synthesized using ferrocene precursor. Photoemission characterization of the Fe 2p
core level emission features indicated a similar composition than nanoparticles fabricated under ambient conditions. Further analysis of the C 1s emission feature pointed towards the presence of precursor ligand rests (aromatic cyclopentadienyl rings ad ring fragments) present in the deposits. However, characterization of the nanoparticles made with transmission electron microscopy revealed particles larger in comparison with those fabricated under ambient conditions. In summary we concluded that the implementation of the nanoparticle injector system into the ALD reactor was successful and allows for contamination-free deposition and electronic structure characterization of metal-based nanoparticles directly in vacuo.

7.2: Outlook

This dissertation demonstrated the use of an ALD vacuum deposition system integrated with a photoemission characterization system in order to study band alignment phenomena at ALD thin film interfaces. The setup that was built as part of this work enables research on electronic structure phenomena of ALD films enabling a host of interesting future experiments. It would be interesting to further enhance the ALD system with a plasma source to enable plasma-enhanced ALD in addition to the current thermal ALD capability. The ALD reactor is terminated by a 4 inch diameter top flange making attachments like this straight-forward to install. The matching network necessary to operate the plasma can be integrated into the current controller setup. The direct advantage resulting from plasma-based ALD would be the possibility to deposit a wider spectrum of materials. For instance, high activation energy materials like nitrides or carbides whose thermal ALD recipe either does not exist or the growth rate is very low could particularly benefit. The plasma source would also add additional substrate and ALD
film conditioning processes including plasma cleaning and surface passivation. In addition, more precursor reservoirs could be installed into the gas delivery system. Currently four reservoirs, two for precursors and two for reactants, are installed. More reservoirs would allow additional precursors to be used in conjunction, thus allowing more complex multi-layer ALD heterojunctions to be fabricated in a one step process.

With regard to further experiments that would be interesting to perform, ALD is known for having a rich variety of precursors available for each material that can be fabricated. In that light, it could be studied how different precursors relate to the results presented here. For example RuO$_x$, precursor/reactant combinations like cyclopentadienyl ethylruthenium dicarbonyl and oxygen, bis(N,N’-di-tert-butylacetamidinato)ruthenium(II) dicarbonyl and oxygen, (ethylbenzene)(1,3-butadiene)Ru(0) and oxygen, a special RuO$_4$-precursor (ToRuS) and hydrogen or bis-2,2,6,6-tetramethyl-3,5-heptandionato-1,5-cyclooctadiene ruthenium and oxygen could be investigated and their influence of the electronic structure and dipole formation of the resulting films studied.

The same concept could be used to further investigate the electronic structure at the In$_2$O$_3$|TiO$_2$ heterojunctions, where additional precursor/reactant combinations like indium tris-guanidinate and water, cyclopentadienyl indium and ozone, indium chloride and water, indium acetyl acetonate and water/ozone, and others are available. Additionally to the electronic structure investigation, it would be interesting to study how different precursors relate to the growth rates and nucleation behaviors. Furthermore it would be interesting to correlate the properties of the deposited films to other means of sample preparation, cleaning and passivation techniques. By altering the substrate material that was used here including noble metals like Au, Pt, Ir, etc. and oxide corroding materials like Si, Cu, Fe, Al, etc., the chemical nature of the
interface could be studied further, specifically in relation to the transition from physisorbed to covalently bond heterojunction interfaces and how those changes influence parameters like interface dipole strength, band gap, general band alignment, growth rate, etc.

The developed microplasma nanoparticle injection capability could be used for a host of experiments on ALD/nanoparticle structures leading to interesting experiments on electronically isolated nanoparticles. One approach expanding on the presented research as part of this dissertation could use different metallic precursors like nickelocene, cobaltocene, nickel acetylacetonate or combinations thereof to fabricate nanoparticles and study their electronic structure by depositing them onto insulating AlOx ALD layers thin enough to prevent sample charging during measurement yet thick enough to sufficiently decouple the electronic system of the nanoparticles from the substrate.

This research could be expanded into the investigation of lamellar structures of integrated ALD films and nanoparticle layers or to cover larger nanoparticles with sub nanometer thick thin films of various compositions to modulate the band structure of various nanoparticles. Those structures could be used to give insight into the electronic structure and band modulation possibilities in order to optimize those structures for applications such as quantum dot lasers or nanoparticle based sensors.

In the context of device applications a number of interesting experiments are enabled by the developed set-up. The International Technology Roadmap for Semiconductors (ITRS) suggests that tailor-designing heterojunction interfaces (i.e. manipulating their electronic band line-up), is a viable path that can lead to device improvement. However, before novel heterojunctions can become reality in applications, their electronic structure and band modulation capability has to be studied in order to understand process dependent band alignment
phenomena. Parameters like process dependent interface dipoles formation, band gap modulation, ALD film growth rate optimization, thin film stoichiometry, etc. are of particular interest in that context. Keywords like “zero barrier metal gate junction” or “dielectric dipole mitigated contact resistance reduction” are just two examples where the developed experimental capability could contribute to gain key insight into crucial properties of device interfaces. Interesting device-relevant heterojunctions are metal-dielectric junctions (metal = Au, Ag, Cu, Fe, Ni, Sn, alloys, etc.; dielectric =SiNₓ, Al₂O₃, HfO₂, ZrO₂, HfSiO₄, ZrSiO₄, La₂O₃, LaAlO₃, Ta₂O₅, etc.) that have a potential to replace common MOS structures or can be used as tunneling barrier layers to prevent Fermi-level pinning or charge recombination at the interface. In a typical experiment, the metal substrate could be prepared and cleaned under ambient or in-situ conditions, characterized by photoemission spectroscopy and then used to deposit an ALD dielectric material on top. In a sequence of deposition and intermittent photoemission analysis, the electronic structure could be determined to get a precise picture of the electronic band modulation as the ALD film transitions from sub-monolayer thickness to bulk structure.
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