Surface Science Studies of Metal Oxides Formed by Chemical Vapour Deposition on Silicon

PATRIK KARLSSON
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Abstract

For an electronic device well-designed interfaces are critical for the performance. Studies of interfaces down to an atomic level are thus highly motivated both from a fundamental and technological point of view. In this thesis, a surface science approach has been employed to study the formation of interfaces in systems relevant for transistor and solar cell applications. Surface science methodology entails ultra high vacuum environment, single crystalline surfaces, submonolayer control of deposited material, surface sensitive spectroscopy and atomic resolution microscopy.

The primary experimental method for characterization is electron spectroscopy. This is a family of very powerful experimental techniques capable of giving information on the atomic level. Additionally, studies have been performed using scanning tunnelling microscopy. Combined these two methods can provide an atomic level characterisation of the geometric and electronic properties of the surface.

The emphasis of this work is placed on ultra thin TiO$_2$ and ZrO$_2$ films grown on silicon substrates by means of ultra-high vacuum metal-organic chemical vapour deposition. ZrO$_2$ has also been grown on SiC and FeCrAl. Deposition has been performed with different process parameters. The interface region of each film has been characterised. The band alignment, a most important issue with regard to the development of new transistor devices, for the ZrO$_2$/Si(100) system has been explored. Decomposition pathways of the metal organic precursors have been studied in detail. Changing process parameters is shown to alter both the precursor decomposition pathway and the nature of the interface region, thus opening the possibility to tailor the material function.

The titanium dioxide films grown in situ have shown to be excellent models of nanostructured electrode materials. In this spirit, interfaces of model systems for the solid-state dye-sensitized solar cell have been studied. Links between device performance and interface structure have been elucidated.

Keywords: chemical vapour deposition, high-k, metal oxides, silicon, dye-solid interface, metal organic, electron spectroscopy, scanning tunnelling microscopy

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List of papers

This thesis is based on the following papers. Reprints were made with permission from the publishers: Elsevier, American Institute of Physics and American Chemical Society. Reprinted material is copyrighted.


III CVD of TiO$_2$ on Si(111), SiO$_x$/Si(111) and TiO$_2$: Substrate and temperature dependence, P. G. Karlsson, J. H. Richter, M. P. Andersson, J. Blomquist, M. K.-J. Johansson, H. Siegbahn, P. Uvdal and A. Sandell, in manuscript.

IV Ultra-high vacuum metal organic chemical vapor deposition of ultrathin ZrO$_2$ films on Si(100) and Si(111) studied by electron spectroscopy, P. G. Karlsson, J. H. Richter, J. Blomquist, P. Uvdal, T. M. Grehk, A. Sandell, in manuscript.

V Initial stages of ZrO$_2$ chemical vapour deposition on Si(100)-(2x1) from zirconium tetra-tert-butoxide, P. G. Karlsson, E. Göthelid, J. H. Richter, A. Sandell, in manuscript.


VII Ultrathin ZrO$_2$ films on Si-rich SiC(0001)-(3x3): Growth and thermal stability, P. G. Karlsson, L. I. Johansson, J. H. Richter, C. Virojanadara, J. Blomquist, P. Uvdal, and A. Sandell, in manuscript.

IX Surface chemistry of HfI₄ on Si(100)-(2x1) studied by core level photoelectron spectroscopy, A. Sandell, P. G. Karlsson, J. H. Richter, J. Blomquist, P. Uvdal, in manuscript (submitted to Surface Science).


Comments on my own participation

The papers presented here are based on teamwork. I had the main responsibility for experiments, data analysis and manuscripts in paper II, III, IV, V, VII and XI. In paper I, VI, VIII, IX, X, and XII I took part in the in the experimental work and participated in the evaluation of the data.
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<tr>
<td>AFM</td>
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<td>DSSC</td>
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<td>LDOS</td>
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<td>MOSFET</td>
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<td>STM</td>
<td>Scanning Tunnelling Microscopy</td>
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<td>TTIP</td>
<td>titanium(IV) isopropoxide</td>
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<td>XAS</td>
<td>X-ray Absorption Spectroscopy</td>
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<td>ZTB</td>
<td>zirconium tetra-tert-butoxide</td>
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1. Introduction

The function of electronic devices is heavily dependant on the properties of the included interfaces. For an electronic device, such as a transistor or a solar cell, much of the interesting processes take place at an interface. Many models, even advanced ones, describing the characteristics of electronic devices assume perfectly sharp transitions between two different materials. The interface region between two different materials is thus often approximated to be infinitesimally thin, and the materials are given their bulk properties on each side of a sharp interface. The research community is aware that sharp interfaces often are crude approximations. For solid on solid material combinations, the existence of an extended interface region can often be proven by microscopy methods. It is, however, far from trivial to study the properties of a buried interface region on the molecular level.

Due to their technological importance transistors and solar cells have been studied intensively. There is a continuous technological drive for new solutions that improve the performance, lower the production costs and increase the stability of these types of devices. Consequently, the functionalities of new material combinations in electronic devices are being investigated.

From a technological standpoint the most cost effective, fastest and most adequate method to test a new material combination (or manufacturing process) is to actually fabricate the electronic device and measure its performance. However, such methods do not give detailed knowledge of interface region on the molecular level.

Electron spectroscopy is a family of very powerful experimental techniques capable of giving information on the molecular level. Great effort has been put on fundamental research and instrument development within this field. Many techniques have become well established and mature. Especially the use of photoelectron spectroscopy (PES) has widened over recent years and at present more and more attention is directed towards using advanced PES to characterise systems of explicit technical importance. The possibility to link properties on the molecular level to the actual performance of the device is very attractive from both a technological and a fundamental point of view.

In this thesis model systems of metal oxides on silicon substrates have been studied. The thin-film metal oxides have been grown in an ultra high vacuum environment on silicon substrates by metal organic
chemical vapour deposition. The properties of the extended interface regions have been probed by electron spectroscopy methods. Precursor decomposition in the initial stages of the growths has been examined in detail using a combination of photoelectron spectroscopy and scanning tunnelling microscopy. Changing process parameters is shown to alter the nature of the interface region. This opens the possibility to tailor the material function.

The titanium dioxide surfaces grown in situ are furthermore excellent substrates for other model experiments. Dye-solid interfaces for solar cell applications have been studied on the molecular level. The focus was in this case to further develop the understanding of the solid state dye-sensitized solar cells (DSSC). Novel types of materials have been examined and our results suggest that the relative size between the molecules in the junction has an effect on the efficiency of the cell.

1.1 The MOSFET
1.1.1. Basics of MOSFETs

The Metal Oxide Semiconductor Field Effect Transistor (MOSFET) is the dominant component in logical circuits and computer memories today. Lilienfeld and Heil proposed the principle of the surface field-effect transistor in the early 1930’s [1,2]. In 1960, Kahng and Atalla proposed and demonstrated the first MOSFET using a thermally oxidised silicon structure [3]. Basically, the MOSFET can be described by two diodes connected back-to-back controlled by a capacitor. That is, the current from one diode to the other is controlled by the voltage over the capacitor. In this case the poles of the capacitor consist of a subset of the diodes and a metal (or highly conducting material) plate. The insulating dielectric material is usually SiO₂. A simplified sketch is presented in figure 1.
Figure 1. A simplified sketch of the npn-MOSFET.

The example in figure 1 is given for an ideal (i.e. $V_{BS} = 0$) npn-transistor connected to voltage supplies. The current flowing from source to drain is dependent on the voltage applied on the drain and gate. Consequently, if the drain voltage is kept at a constant negative value the voltage applied on the gate controls the current from source to drain. Hence, the transistor can function both as a switch and signal amplifier.

In more detail, if the gate is negatively biased the electrons (minority charge carriers) in the p-type region will be repelled and holes (majority charge carriers) will be attracted. This state is called accumulation. The current from source to drain will be very small since it has to pass a diode biased in the reverse direction. On the other hand, if a large enough positive bias is applied to the gate, electrons (minority charge carriers) will be attracted and holes (majority charge carriers) will be repelled. Consequently, a negatively charged sheet is produced at the semiconductor-insulator interface. The state is called inversion. The charge sheet is often denoted the channel and can be viewed as a temporary n-type material. Hence, current can be viewed to flow from source to drain in a chain of n-type material.

1.1.2. The MOS-stack

A subset of the MOSFET is the Metal-Oxide-Semiconductor stack (MOS-stack). The MOS-stack can be seen as a variable capacitor, i.e. the capacitance for an alternating current is dependent on the applied direct current bias. The capacitance per unit area has its maximum value in accumulation and is for the ideal interface given by equation 1.
\[ C_o = \frac{\epsilon_{\infty}}{d} \]  

(1)

In equation 1, \( \epsilon_{\infty} \) is the permittivity for the dielectric material and \( d \) is the thickness of the dielectric material. The capacitance per unit area has ideally its minimum value in inversion. Except for the channel a depletion region, i.e. a region lacking mobile charge carriers, exists when the MOS-stack is in the inversion state. The depth of the depletion region, \( W \), is partly dependent on the doping and for strong inversion the depth of the depletion region has reached its maximum value, \( W_m \). The total capacitance, \( C \), is the series capacitance of the oxide capacitance, \( C_o \), and the semiconductor depletion-layer capacitance, \( C_j \).

\[ C = \frac{C_o C_j}{C_o + C_j} \]  

(2)

For strong inversion equation 2 reduces to equation 3.

\[ C_{\text{inv}} = \frac{\epsilon_{\infty}}{d + \left( \frac{\epsilon_{\infty}}{\epsilon_r} \right) W_m} \]  

(3)

In equation 3 \( \epsilon_r \) is the permittivity of the semiconductor. How the capacitance varies is important for the characteristics of the MOSFET. One of the most used methods to characterise the MOS-stack is to plot the (frequency response) capacitance vs. voltage (CV-curve). Contaminations and non-ideal interfaces can severely alter the features of the CV-curve.

1.1.3. Device scaling

Two MOSFETs can be combined to form an inverter, which is the basic building block for digital circuits. If the two MOSFETs are complementary, meaning that one is n-channel and the other is p-channel, the power consumption can be reduced considerably. This technology is called CMOS and has the attractive feature that only one transistor is on at a time. At a steady logic state the power consumption equals the leakage current through the transistor that is in the off state. However, changing the polarity of the device consumes power. The power and time needed to switch the polarity of the device is roughly proportional to the amount of charge that has to be redistributed. It is consequently advantageous to reduce the dimensions of the MOSFET because in a first approximation a smaller MOSFET becomes faster and consumes less power. Additionally more transistors can be fitted onto a chip allowing for more complex logical circuits.

Scaling of devices is not straightforward. It is important to realise that it is, to a large extent, the strength of the electrical fields that determines the characteristics of the device. The approach most widely used so far is called constant-field scaling [4]. Basically, the dimensions and volt-
ages are reduced by a scaling factor so that the internal electrical fields are the same as for a larger device with good characteristics. However, it is not possible to scale down the gate voltage proportionally, partly because a voltage bias is always needed to reach flat band condition (i.e. compensate for band bending due to work function differences). A consequence of this is that the capacitance per unit area for the MOS-stack has to be increased. Reducing the thickness of the gate oxide can increase the capacitance per unit area. For SiO₂ gate oxides the thickness has reached 12 Å [5]. At these dimensions direct tunnelling dramatically increases the leakage current and therefore reduces device reliability and performance. A new gate dielectric material with higher permittivity, often denoted high-κ material, would theoretically allow for a physically thicker film giving adequate capacitance per unit area.

1.1.4. High-κ materials
In lattice polarizable materials a high permittivity is obtained by a physical displacement of one or more atoms in response to an applied electric field. The response is frequency dependent and a suitable gate dielectric material must be able to respond at high frequencies. Metal-oxides that have high permittivity bulk properties and adequate frequency response can be found for group IVB metal-oxides, e.g. TiO₂, ZrO₂, HfO₂. The research community has put great effort into producing a well functioning MOS-stack using group IVB metal-oxides and other high-κ materials [6].

Actual MOSFET devices with high-κ dielectrics have been demonstrated in laboratory environment. In 1997 Campbell et al. [7] published a study of MOSFETs fabricated using TiO₂ as the gate dielectric. Chemical vapour deposition (CVD) of TiO₂ was used to produce the thin film. The device suffered partly from low mobility in the channel, which was discussed in terms of interface states.

As mentioned previously, a CV-curve is often used to characterise the MOS-stack. Various types of microscopy methods are also widely used. Element specific measurements using photoelectron spectroscopy methods are however difficult to perform on a buried interface. Therefore, only model systems can be considered when using these methods. In spite of the difficulties mentioned above, due to the technological importance of the MOS-stack and the power of photoelectron spectroscopy methods, an increasing number of model systems have characterized by photoelectron spectroscopy methods.

Fulton et al. [8] have performed photoelectron spectroscopy studies of the TiO₂/Si interface and claim that the band alignment of TiO₂ and Si is not optimal for the function of the MOS-stack. Another problem concerning the use of TiO₂ is that it is not sufficiently thermodynamically stable on silicon. That is, TiO₂ is not directly applicable in the industrial
manufacturing process since rapid thermal annealing (RTA) to about 1000°C is used. RTA is needed to activate the implanted impurity atoms in silicon and to heal out defects in the crystal created during the manufacturing process [9]. Thus, the industrial manufacturing process must be considerably altered if TiO₂ is incorporated. Such significant changes imply high costs. Other materials that are more thermodynamically stable have caught more attention over the past years. However, the previous intense and still ongoing study of the TiO₂/Si system within the research community makes this an excellent model system for studies of metal-oxides on silicon.

ZrO₂ has been reported to have better thermal stability on silicon compared to TiO₂, and it has been demonstrated that MOS devices fabricated using ZrO₂ as dielectric have most promising electrical characteristics [10,11].

1.2. Dye-sensitized solar cell

1.2.1. Introduction to solar cells

Conventional solar cells are based on the silicon p-n junction. If the energy of the light is larger than the band gap of the semiconductor electrons in the valence band can be excited to the conduction band, i.e. electron-hole pairs are generated. The charges generated within the depletion region of the junction will be separated by the built-in electrical field. The efficiency of solar cells based on semiconductor technology is adequate for many applications. The production cost is however large; it is expensive to produce pure silicon and the amount of energy required to produce pure silicon and to manufacture p-n junctions is significant. Several alternative types of solar cells have therefore been investigated. One of the most interesting is the CIGS thin film solar cell reaching efficiencies of almost 20% [12].

Another interesting alternative is to harvest solar energy by mimicking nature and use dye molecules. The basic idea is to synthesise a molecule that absorbs a large fraction of the sunlight and use an interface to separate charges. In this way light absorption can be separated from charge carrier transport. Different types of such photoelectrochemical cells have been investigated. In the beginning of the 1990s Brian O’Regan and Michael Grätzel obtained about 7% efficiency with a new solar cell design [13]. This new design, the nanoporous dye-sensitized solar cell (DSSC), showed a huge increase in efficiency for such a photoelectrochemical type of solar cell. The working electrode is made of nanoporous TiO₂ covered with a monolayer of dye molecules. The active area of the nanoporous surface is very large and the cell is therefore able to absorb a large fraction of the sunlight even though there is only a monolayer of dye molecules. The dye molecules are designed to transfer charge into the TiO₂ (conduction band) upon excitation.
and are thereafter left in an oxidised state. An iodide/triiodide redox liquid electrolyte is used to regenerate the oxidised dye molecules. The liquid electrolyte is advantageous since it easily penetrates the pores of the nanostructured electrode.

1.2.2. Solid-state type of dye-sensitized solar cell

The initial results for the DSSC were very promising and the efficiency was increased to 10% in 1993 [14], and to 11% in 2004 [15]. However, some problems remain to be solved before the DSSC can be of any commercial interest. One major problem is the long-term stability. Some of the stability problems such as solvent evaporation and seal imperfections can be attributed to the use of liquid electrolyte. Replacing the liquid by a solid state type of material is therefore an interesting alternative. To successfully make this replacement, first a suitable hole conducting material has to be found and secondly the technical problem to fill all the pores of the nanostructured electrode must be solved.

In 1998 Tennakone et al. [16] published their work on a solid-state photovoltaic cell sensitized with a ruthenium bipyridyl complex. For this cell CuI, a solid-state p-type semiconductor, replaced the liquid electrolyte. The working electrode was nanoporous TiO₂. The choice of materials was partly based on suitable energy level alignments of the pure materials. Also the reasonably large band-gap of CuI (3.1 eV) makes it transparent to visible light, which is important. A schematic representation of the principle of the solid state DSSC is given in figure 2. A method to deposit CuI from solution, filling the inter-crystalline pores of the dye/TiO₂ system, was developed. The performance of the resulting solar cell was lower compared to cells using liquid electrolyte. Still, the maximum power conversion efficiency of about 6% is encouraging. However, the efficiency was reduced for high light intensity and the performance of the device decayed fast with time. The reasons for the reduced performance were not clear. However, filtering out the UV light could reduce the decay of the performance. Tennakone et al. also showed that the CuI/TiO₂ interface, i.e. without the dye, has bad rectifying characteristics. Thus, the dye molecule has an additional function as an insulating layer. From such reasoning, direct CuI-TiO₂ contact will lower the performance of the cell. Recently, O’Regan et al. have reported similar problems for the TiO₂/CuSCN interface [17].
Figure 2. The principle of the solid state DSSC (schematic representation). A photon is absorbed by the dye (1), i.e. the dye is excited. The excited electron is injected into the conduction band of the TiO$_2$ (2), and the hole is filled from the CuI valence band (3). The performance of the CuI/dye/TiO$_2$ cells has not improved considerably since its appearance. It is possible that a fundamental understanding on the molecular level of the CuI/dye/TiO$_2$ system can promote new solutions.

Recently other solid state hole-conductor materials based on larger organic molecules have shown promising results in the dye-sensitized solar cell. Conjugated polymers [18,19,20] and tri-arylamine derivatives [21,22,23] are examples of these hole-conductor materials and energy conversion efficiencies of about 4% have been reached for solar cells using a tri-arylamine derivate hole-conductor [23]. In this case the photo-voltage is even higher than in the liquid electrolyte solar cells. However, the photocurrents are still somewhat lower, which explains the lower total efficiencies.
2. Sample preparation and deposition methods

2.1. Evaporation

Many materials and molecules can be deposited in a highly controlled manner by physical vapour deposition (PVD) methods. The simplest way is to heat the material in an evacuated chamber. If the temperature is high enough atoms or molecules will be evaporated from the source material. Atoms or molecules will be evaporated in every direction and travel at high velocity in straight-line trajectories. A shield with a small opening is therefore often used to prevent unnecessary contamination of the vacuum chamber. Because of the line-of-sight type of deposition uniformity is not always achievable using the simplest PVD methods. Noteworthy is that sputtering methods can improve uniformity properties.

2.2. CVD

Chemical vapour deposition (CVD) is a synthesis process in which the chemical constituents react in the vapour phase near or on a heated substrate to form a solid deposit. CVD has appealing properties including uniform thickness over large areas and excellent conformal step coverage of non-planar devices [24,25]. Deposition is usually thermally activated, but there are examples of other activation methods (e.g. photochemically or plasma based CVD). Thermal activation typically takes place at high temperatures (> 900°C). By using metal-organic precursors the activation temperature can be lowered considerably [26].

Metal-organic chemical vapour deposition (MOCVD) has been used to grow III-V, II-VI and IV-VI semiconducting materials, dielectric materials and metallic films. Some of these processes require two different precursors, others require additional oxidants or reactants and others include precursors that are hazardous (e.g. poisonous or explosive). For optimal stoichiometric control a single source precursor is preferred [26].

The growth rate is limited by either surface reaction kinetics or by mass transport. In the articles in this thesis the MOCVD processes were performed under low pressure and without carrier gas. Consequently
the precursor molecules are transported by molecular diffusion, i.e. effects such as laminar flow can be excluded. The natural process parameters that control the kinetics are sample temperature and precursor partial pressure. The composition of the substrate can in some cases also affect the kinetics [26, 27].
3. Characterisation

3.1. Photoelectron spectroscopy

Photoelectron spectroscopy is a family of methods based on the photoelectric effect. The photoelectric effect was detected experimentally by Hertz in 1887 [28] and explained in detail by Einstein in 1905 [29]. Basically, in photoelectron spectroscopy the sample is irradiated with photons of known energy and the emitted electrons are analysed. In order to analyse the emitted electrons the photoionisation must take place in a chamber with reasonably low pressure. Low pressure is needed because electrons only travel a short distance in air before they lose their energy through collisions with gas molecules. Photoelectron spectroscopy can be used to analyse the electronic structure of gases, liquids and solids. The discussion here will however be limited to solids and molecules adsorbed on solids.

Emission of an electron having its initial energy at the Fermi level of a solid material is only possible if the incoming photon have an energy that is larger than the work function of the material. For emission of electrons with initial energy below the Fermi level the photon energy must be larger than the ionisation energy. If the photon energy is larger than the smallest ionisation energy the irradiated sample will loose electrons by photoemission. If the sample is insulating there will be no charge compensation and the surface will be positively charged. Consequently, for an insulating sample the photon energy required to move an electron out of the sample will increase with time. Photoelectron spectroscopy measurements of insulating samples is therefore troublesome but can be performed, for example by using an electron flood gun. If a conducting sample is grounded the surface charge will be compensated almost instantly. Ultra thin films of insulating material on a conducting substrate are also possible to measure without significant surface charging effects. This is true if the film is thin enough for the electron to tunnel from the substrate through the film in order to compensate charge at the outermost part of the film. The possibility to measure layers of large non-conducting molecules adsorbed on conducting substrates can be regarded analogously.
3.1.1. Core level photoelectron spectroscopy

Molecular core level orbitals are localised to a specific atom and are similar to the atomic orbitals. Additionally, the electron density of states is quantized in nearly discrete core levels having large mutual energy differences. Photoelectron spectroscopy of core levels can therefore give element specific information of a sample. A simplified but illustrative picture of the photoemission process is presented in figure 3. Monochromated soft x-rays of energy \( h\nu \) irradiates the sample (\( h \) is Planck’s constant and \( \nu \) is the frequency of the light). The maximum kinetic energy of an electron emitted from a specific core level to the vacuum is denoted \( E_k \). The electron energy spectrum is analysed with an electron spectrometer. The spectroscopic binding energy, \( E_B \), is simply calculated from equation 5 where \( \phi \) is the work function of the material.

\[
E_B = h\nu - E_k - \phi
\]  

(5)

Figure 3. The figure shows a simplified view of the photoemission process using the energy level diagram for a conducting sample in electrical contact with the spectrometer.

Note that the actual kinetic energy measured by the electron spectrometer will depend on the calibration of the spectrometer. If the spectrometer and sample have electrical contact the Fermi level is an excellent reference for the spectroscopic binding energy scale. For a free molecule, however, the natural energy reference level is the vacuum level. For a molecule adsorbed on a conducting surface in electrical contact with the spectrometer the natural choice of reference level depends on the extent of the surface-molecule interaction. That is, the spectroscopic binding energy levels of a noble gas molecule physisorbed (not chemically bonded) on the surface is most con-
veniently referenced to the vacuum level, and the spectroscopic binding energy levels of a small molecule chemisorbed (chemically bonded) to the surface is most conveniently referenced to the Fermi level. For the general system it is difficult to know the most appropriate reference level before experiments are performed.

As a first approximation the spectroscopic binding energy spectrum directly gives the structure of the core level orbitals. Since each element has its own orbital structure the method is element specific, an example is given in figure 4. Apart from the superimposed signal from oxygen and titanium core levels, the main features of the overview spectrum in figure 4 include the valence band and some additional features discussed in more detail below.

Figure 4. Example of an XPS spectrum measured for a titanium dioxide thin film. The superimposed spectroscopic signatures of oxygen and titanium give this spectroscopic binding energy spectrum for titanium dioxide.

3.1.2. Photoemission in more detail

The exact relation between the electronic structure of the sample and the measured photoelectron spectrum is not straightforward, partly because the core hole is a significant disturbance of the electronic system that is under investigation. Electrons in the close vicinity of a core hole will consequently react on its existence. The maximum kinetic energy, $E_k$, for an electron photoemitted from a core level orbital is limited by the principle of energy conservation. Thus, the maximum kinetic energy can be calculated if the energy difference between the initial and final states of the system participating in an ideally elastic photoemission process is known. For a molecule the system is described by all the molecular orbitals, and for an exact description of the photoemission process from a solid material the system includes the orbi-
tals of the whole sample. For ionisation of a single core electron, the energy of the initial state of the system, $E_i^N$, is given by the ground state including $N$ electrons. The energy of the final state, $E_f^{N-1}$, is given by one core-ionised atom within a disturbed orbital system including $N-1$ electrons. Equation 6 follows from the principle of energy conservation.

$$E_i^N + h\nu = E_f^{N-1} + E_k + \phi$$

Rearrangement and comparison with equation 5 gives the spectroscopic binding energy:

$$E_B = h\nu - E_k - \phi = \left(E_f^{N-1} - E_i^N\right)$$

That is, the spectroscopic binding energy is the difference in total energies of the system having ($N$-1) electrons after the photoionisation and the system having $N$ electrons before the photoionisation.

Calculation of the binding energy (and line shape) from first principles using equation 7 is cumbersome. In a solid material there is relaxation energy due to charge flow from the crystal onto the ion that carries the hole. Also, for core levels in some materials the spectroscopic line does not consist of a single peak due to final state effects. The correct description of these satellite lines requires a lengthy quantum mechanical discussion and is omitted here since it is of little importance for the papers, for a detailed description see e.g. Hüfner [30].

3.1.3. Chemical shift

The analysis of PES experiments does not have to rely on exact theoretical calculations of absolute binding energies to be useful. Instead the binding energy shifts for a specific element in different chemical environments are used. The ability to observe chemical shifts makes core level photoelectron spectroscopy a very powerful technique. Spectra can be analysed using reference sample spectra and relative changes of the spectra after sample preparation. From the ground state orbital energy point of view the chemical shifts originate from different bonding structures. For example, an oxidised atom obtains higher core level binding energies compared to the pure element due to the nature of the bonding. An oxidised atom donates one or more valence electrons completely or partly to more electronegative elements. The core level orbitals for the oxidised atom experiences reduced screening from valence orbitals and will therefore be more strongly attracted by the core. An illustrative example of this first order approximation is given in figure 5.
To calculate the exact magnitude of the measured binding energy shift equation 7 is applied twice. That is, if an element exists in two different chemical states, $A$ and $B$, in a molecule or solid material the binding energy shift $\Delta E_B$ is formally given by equation 8.

$$
\Delta E_B = (E_f^{A(N-1)} - E_i^{A(N)}) - (E_f^{B(N-1)} - E_i^{B(N)}) \quad (8a)
$$

$$
\Delta E_B = (E_i^{B(N)} - E_i^{A(N)}) - (E_f^{B(N-1)} - E_f^{A(N-1)}) \quad (8b)
$$

A consequence of equation 8b is that the direction of the chemical shift also is dependent on the difference between the final states, which can give counterintuitive results considering the ground state electronegativity model.

Complicated calculations of binding energy shifts from first principles (appropriate approximations are always needed) using equation 8 is not always necessary for the interpretation of PES spectra. As previously mentioned reference samples are often used. When calculation of core level binding energy shifts is needed, a procedure employing a Born-Haber cycle is often sufficient for the interpretation of the spectrum. The intention of this procedure is to split the binding energy shift into a sum of energies known from other sources, e.g. energies known from thermodynamic experiments are often used [30,31].

### 3.1.4. Valence band

The intensity in the valence band originates from both localised nearly atomic-like orbitals and non-localised hybrid-type molecular orbitals. For a solid sample, the electron density of states is relatively high for a widespread interval due to the band structure. For metals the electron density of states is
occupied all the way up to the Fermi level. Hence, the binding energy position of the Fermi level can directly be measured for a metallic sample.

Tracking changes in the valence band is of special interest between sample preparations since the probed orbitals are responsible for the chemical bonds in the material. A detailed theoretical calculation is often needed for the interpretation of a valence band spectrum. Combined with theory, angle resolved valence band spectra are used to map the band structure of single crystalline materials. However the valence band spectra can directly give qualitative information of for example the band gap and the existence of filled defect states in the band gap.

3.1.5. Mean free path

The mean free path (often given in units of Å = 10^{-10} m), \( \lambda \), is a measurement of the probability for inelastic scattering. The mean free path is dependant on the kinetic energy of the electron and the material in which it moves. For high photoelectron kinetic energies the mean electron-electron distance roughly determines the mean free path. The mean electron-electron distance is roughly equal for all materials. Hence, a “universal” electron mean free path as a function of kinetic energy, sketched in figure 6, can be used as rule of thumb [30]. Thus, the graph gives a qualitative view of how the mean free path varies with photoelectron kinetic energy and thereby gives a perspective of how the surface sensitivity of a PES experiment can be changed using a variable photon source. However, in detail the cross-section for electron scattering is determined by the dielectric function of the material. Comparing materials with very different dielectric functions the mean free path most probably differ for the same photoelectron kinetic energy. There is also a difference between crystalline and amorphous materials.

![Figure 6. A sketch of the “universal” electron mean free path as a function of kinetic energy.](image-url)
3.1.6. Background subtraction

Extrinsic inelastic scattering occurs when the photoelectron on its way out of the material is scattered by non-localized electrons or electrons localized at other atoms. If the kinetic energy of the photoelectron is high the probability of forward inelastic scattering is high. This implies that a detected photoelectron can have been scattered one or several times, with some kinetic energy loss for each event. The amount of energy loss for each inelastic scattering event can be viewed as a continuous probability function depending on the kinetic energy of the photoelectron and the type of material. As a result of the inelastic scattering the core level photoemission spectra have a seemingly featureless rising background. Several authors have used semi-empirical methods for detailed calculations of background profiles. Calculation of the background profile under a peak shape that have a width of only a few electron volts can however be performed without significant information loss by using Shirley’s method [32]. In Shirley’s method the spectrum is viewed as a series of discrete intensity measurements called channels. Each channel represents a constant spectroscopic binding energy interval. Start and end binding energies for the fit are chosen from “featureless” parts of the spectrum on each side of the peak. If the signal in the \(i\)th channel, \(s_i\), is the sum of a background, \(b_i\), and peak, \(p_i\), Shirley’s method gives:

\[
\begin{align*}
    b_i &= k \sum_{j=i+1}^{N} p_j \\
    s_i &= b_i + p_i
\end{align*}
\]  

(9)

In the above equation (9), \(k\) is a fitting parameter and \(N\) is the number of channels. The numbering of the channels is such that the channel representing the highest binding energy gets the lowest number. Thus, the background rises on the high binding energy side of the peak. The equation system 9 is iterated to find the value of \(k\) and the background intensity vector, \(b_i\) (\(i = 0-N\)). Figure 7 displays an example of Shirley background subtraction.
3.1.7. Photoelectron cross-section

The total relative intensity of a spectroscopic line is partly dependant on the transition probability, i.e. the photoelectron (photoabsorption) cross-section, \( \sigma \). A starting point for the discussion is Fermi’s golden rule. The phenomenon that some spectroscopic lines have more relative intensity than others can be explained by the overlap between quantum mechanical wave functions. In general conceptual terms, a transition rate depends upon the strength of the coupling between the initial and final state of a system and upon the number of ways the transition can happen (i.e. the density of the final states). If it is assumed that the wavelength of the radiation is large compared to the dimensions of the excitation volume (i.e. the dipole approximation) the dipole operator, \( r \), can be used yielding equation 10.

\[
V_{f} = r \left| \begin{array}{c}
\psi_i \\
\psi_f
\end{array} \right| \frac{1}{N} \frac{1}{h} \left( E_{f} - E_{i} - h \nu \right) (10)
\]

In equation 10 \( \psi_i \) is the total initial wave function of the system and \( \psi_f \) is the total final wave function of the system. As the equation is written, the total initial wave function includes \( N \) electrons in ground state and the total final state wave function includes \( N-1 \) electrons in a core excited orbital system plus one photoelectron. The \( \delta \)-function ensures energy conservation analogous to equation 7. Depending on the definition of the spectroscopic core line intensity, the right hand side of equation 10 should be multiplied by the appropriate density of states.

Atomic subshell photoionisation cross sections have been calculated for the pure elements with reasonable accuracy using the dipole approximation. Theory and experiments show that the photoionisation cross
section is very different between orbitals and depends on the energy of the incoming photon.

3.1.8. Signal attenuation

As previously mentioned, the short mean free path, \( \lambda \), for the electron in solid material make PES measurements very surface sensitive. For a pure model sample containing only one element, the probability that a photoelectron in the direction towards the analyser is emitted to the vacuum without being scattered, \( P \), is given by equation 11.

\[
P = e^{-z/\lambda}
\] (11)

In equation 11 \( z \) is the length of the path that the electron will have to travel within the solid material. For photoemission in the surface normal direction \( z \) is the thickness of the material covering the site of the photoionised atom. Since \( e^{-3} \) is approximately 0.05 it is concluded that the atoms situated within three mean free path lengths from the surface is attributed to 95% of the photoemission signal. Measuring the photoelectrons emitted in a direction almost parallel to the sample surface can further increase the surface sensitivity.

The total photoelectron intensity emitted per unit area from the discussed model sample will depend on several factors. To simplify the discussion the following conditions are assumed to be fulfilled: Atomically flat sample surface, constant intensity of the incoming light and normal emission. These properties are included in an experimental factor \( C \). Also contained in \( C \) is the spectrometer transmission function that depends on spectrometer settings and the kinetic energy of the analysed photoelectron. The total intensity, \( I_A \), of a core line from the pure model material, \( A \), is then obtained by integrating over the exponential escape probability, \( P \), multiplied by the atomic density, \( n_A \), the cross section for the transition, \( \sigma_A \), and \( C \), yielding equation 12.

\[
I_A = C_A n_A \sigma_A \int_0^z e^{-z/\lambda_A} \, dz = C_A n_A \sigma_A \lambda_A \quad (12)
\]

If a completely homogenous and flat ultra thin film of a second material, \( B \), is deposited on the material \( A \), the photoelectron intensity of a core line attributed to this material can be calculated analogously:

\[
I_B = C_B n_B \sigma_B \int_0^d e^{-z/\lambda_B} \, dz = C_B n_B \sigma_B \lambda_B \left(1 - e^{-d/\lambda_B} \right) \quad (13)
\]

In equation 13 \( d \) is the thickness of the film. A different experimental factor, \( C_B \), is introduced partly because the kinetic energy of the photoelectrons can be different.
The intensity measured for the core line attributed to material A will be damped due to the overlayer. Since the photoelectrons must travel through an additional layer of material B the attenuated intensity, $I_A^d$, is given by:

$$I_A^d = I_A e^{-d/\lambda_B}$$  

In equation 14 $\lambda_B$ is the mean free path in material B for the electron having the kinetic energy associated with spectroscopic line of material A. Hence, the damping of the substrate signal can be used to estimate the thickness of the deposited overlayer if this mean free path is known.

When comparing different oxidation states of the same element outgoing from a single core level photoelectron spectrum the differences between $\lambda_B$ and $\lambda_B$ and $C_A$ and $C_B$ are small. Using approximations, fruitful equations can be derived combining equation 12, 13 and 14.

3.1.9. Broadening of the line
The core hole has a finite lifetime. From the Heisenberg uncertainty principle this results in a Lorentzian broadening of the line, denoted lifetime broadening. For solid samples, mainly discussed in this thesis, phonons in the lattice give additional Gaussian distributed broadening of the line. Furthermore, the energy of the incoming photons and measured photoelectrons are Gaussian distributed. This gives rise to an instrumental Gaussian broadening. The total line will therefore have the width and shape from a combination of the above. For the symmetric lines discussed in this thesis Voight profiles are used in the curve fitting.

3.1.10. Secondary electrons
A core hole in a neutral atom or ion is not a stable state. After creation, the core hole will decay in about $10^{-18}$-$10^{-15}$ s. In the decay process the core hole is filled by electronic transitions from a shallower core level or valence level. The relaxation energy released in the decay process is transferred to a photon (fluorescence) or to another valence electron. For fluorescence the transition follows the dipole selection rules, i.e. $\Delta l = \pm 1$ and the principle of energy conservation. If a valence electron is emitted in the core hole decay process this is denoted an Auger-like decay. The electron emission decay process is governed by the Coulomb operator and hence does not follow the dipole selection rules. For the lighter elements, Auger-like decay is the dominant channel for the relaxation energy. The Auger-like decay is a secondary process following the creation of a core hole. Hence, the electrons emitted in the process are denoted secondary electrons.

Analogous to the previous discussion around core excitation and binding energies an exact description of the core hole decay process
involves overlapping wave functions of the initial and final states. A more
detailed quantum mechanical description is omitted in this thesis. Approxi-
mately, the maximum kinetic energy of a secondary electron excited in the
process of the filling of a core hole is the binding energy of the core orbital.
Hence, there are Auger lines in photoemission spectra at characteristic ki-
etic energies, e.g. see figure 4 presented previously.

3.1.11. Near edge x-ray absorption fine structure spectroscopy

Synchrotron facilities offer the possibility to tune the photon energy. This
allows for additional spectroscopic methods. A method that can give infor-
mation on the unoccupied states of the sample is near edge x-ray absorption
fine structure spectroscopy, NEXAFS. In NEXAFS transitions from core
levels to unoccupied states are tuned in. At perfect match, i.e. resonance, the
transition can occur. The transitions follow the dipole selection rules. The
photon energy is scanned over an absorption edge, i.e. the radiation is tuned
to match the transitions of choice. The x-ray absorption process produces
core hole excited neutral states.

X-ray absorption can be measured in different ways. For ex-
tremely thin samples the number of absorbed photons can be measured di-
rectly from the intensity of the transmitted light. For a thicker sample a re-
fection setup can be used. Alternatively, the absorption can be monitored
via a secondary process, i.e. by detecting photons or electrons released in the
decay of the neutral core excited state created in the absorption event. Detec-
tion of photons is technically challenging and gives information mostly on
the bulk properties of the sample. Electrons are easily detected and a method
based on electron emission is very surface sensitive.

The detection method used in this thesis is based on secon-
dary electrons. The number of emitted electrons is measured as a function of
the photon energy. Since each x-ray absorption process with high probability
results in a secondary Auger-like decay, the total number of emitted elec-
trons from the sample is proportional to the probability for core excitation. A
detailed theoretical calculation is often needed for the interpretation of a
NEXAFS spectrum measured by monitoring secondary electrons. Since the
synchrotron light is plane polarised NEXAFS can be used to give informa-
tion on the orientation of adsorbed molecules.

A NEXAFS spectrum can be used as fingerprint of a crystal-
lographic phase. A brief discussion around the theory is given below but first
some definitions: In a single crystalline material the atoms are well ordered
in a periodic pattern. A polycrystalline material consists of many small sin-
gle crystalline domains. An amorphous material, on the other hand, lacks
any form of periodicity. In an ordered material every atom has an environ-
ment with high symmetry.
Transition metals have an incomplete shell of d-electrons. Many properties of transition metal compounds can be explained using the crystal-field theory approximation. In crystal field theory the symmetrically distributed ligands are regarded as point centres of electron repulsion around a central atom. In an octahedral symmetry the d-orbitals fall into two sets: Those who point directly towards a ligand (e\(_g\)-orbitals) and the others who point between them (t\(_{2g}\)-orbitals). Consequently, the e\(_g\)-orbitals will have higher energy than the t\(_{2g}\)-orbitals. However, a distinct energy splitting can only be measured if a majority of the probed atoms are in an environment with the same symmetry. Hence, NEXAFS spectra can be used to determine if a sample is crystalline or amorphous. In addition, different crystalline phases of the same transition metal compound can be related to unique NEXAFS signatures [33,34].

3.1.12. Synchrotron radiation

As previously mentioned, synchrotron radiation (SR) light sources are very beneficial for photoelectron spectroscopy measurements. In a SR facility electrons are accelerated to relativistic velocities and thereafter injected into a synchrotron storage ring. A synchrotron storage ring consists of a number of straight sections and bending magnets in a closed circuit. The basic idea of a SR light source is that when an electron is accelerated it emits photons. At each bend the electrons are accelerated to change their direction and will consequently lose some of their energy emitted as photons. The extremely high speed of the electrons is needed for a number of reasons. Most importantly, consider an electron moving at a low non-relativistic speed. If the electron is accelerated perpendicular to its motion photons will be emitted in a wide angular distribution. However, for an electron moving close to the speed of light relativistic effects occur. If this electron is accelerated perpendicular to its motion photons are emitted in a narrow cone in the line of motion. This is because the photons cannot move faster than the speed of light. Consequently, the emitted light becomes extremely focused. Improved performance over the bending magnet radiation can be achieved using insertion devices in the synchrotron, i.e. undulators and wigglers.

The photons produced by the synchrotron are directed into a beam line. The photon energy distribution from bending magnet radiation is continuous and very broad. Many beam lines have a monochromator that can select specific photon energies. The monochromator works with several mirror gratings. Additional mirrors in the beam line are used for focusing the light. The beam line leads the light from the synchrotron to the end station, where the experiments are performed. The majority of the measurements presented in this thesis have been conducted at beam line d1011 [35] at the Swedish National Laboratory Max-lab in Lund.
3.2. Scanning probe methods

Scanning tunnelling microscopy (STM) was developed at IBM in Zürich and the first results were published in 1982 [36]. STM has developed into a powerful tool for surface structure analysis. It also inspired the development of related scanning probe techniques such as atomic force microscopy (AFM).

3.2.1. STM

An instrument for STM has an extremely sharp needle, the tip, which can be moved in three dimensions with extreme accuracy using piezoelectric scanners. If the tip is brought into a few atomic distances from the sample, but never touching it, a quantum mechanical effect called tunnelling occurs. For conducting materials, the wave functions of the tip and the sample will interact over the vacuum barrier. Hence, electrons can tunnel from the tip to the sample and vice versa. If both the tip and sample are grounded the current flowing from the tip to the sample, $I_{nt}$, equals the current flowing from the sample to the tip, $I_{st}$. As a first approximation the tunnelling current can be expressed as in equation 15.

$$I_{nt} = -I_{st} \propto \exp \left(-4\pi d \sqrt{2m\phi} / h \right)$$

In equation 15 $d$ is the distance between the sample and the tip, $m$ is the electron mass, $h$ is Planck’s constant and $\phi$ is the height of the vacuum barrier. If a voltage bias is applied between the tip and the sample a net tunnelling current, $I$, can be measured. As a consequence of equation 15 the net tunnelling current under bias condition typically varies by an order of magnitude for each Ångström change in the distance between the tip and the sample.

The microscope can run in different modes of operation. Constant tunnelling current mode is often used. In this mode the tip is scanned over the surface and its position is recorded. The distance between the tip and the sample is determined by a preset voltage bias and a preset tunnelling current. The tunnelling current is controlled using a feedback circuit that is allowed to change the distance between the tip and the sample. The recorded positions of the tip give a topographic image of the sample surface.

A useful approximation is that the STM image represents the filled or empty local density of states, LDOS. Empty LDOS is probed if the net tunnelling current consists of electrons tunnelling from the tip into the sample (positive sample bias), and filled LDOS is probed if the net tunnelling current consists of electrons tunnelling from the sample into the tip (negative sample bias). The value of the voltage bias determines which specific states are probed. This is because the total energy must be conserved for the tunnelling process.
For the interpretation of STM images there are numerous considerations: The image depends on the nature of the tip (i.e. the shape and material of the outermost part), if the sample is soft it can be deformed during the measurement, it is the LDOS that is measured not the actual topography (adsorbates can be imaged as voids), etc.

The possibility to measure on insulating material can be discussed analogously to the previous discussion given for photoelectron spectroscopy, i.e. thin films can be considered. Additionally the voltage bias must be relatively high due to the band gap.

See paper V in this thesis for examples of STM images.

3.2.2. AFM

The operation of an AFM instrument is similar to that of the STM. Instead of the tunnelling current, the distance between the sample and the tip is controlled by the strength of the atomic forces. To realise sensitivity to small atomic forces the tip is attached to a cantilever. When the tip is in very close proximity or in contact with the sample the cantilever will bend. The bending of the cantilever can, for example, be measured by tracking a laser beam reflected by the cantilever.

In tapping mode the cantilever (including the tip) is driven to oscillate at a very high frequency. If moved close to the sample atomic forces will affect the tip and the oscillation will be damped. Tapping mode uses the oscillation as feedback and is a non-contact technique. In practice, this mode can be used to get a topographic image of any sample regardless of its conductivity and mechanical composition.

See paper XI in this thesis for examples of AFM images.
4. Summary of results

4.1. Titanium dioxide thin-film growth on Si(111) by chemical vapour deposition using the titanium(IV) isopropoxide precursor: Papers I-III

4.1.1 Introduction to the TTIP precursor

Metal-organic chemical vapour deposition of TiO₂ on silicon using the titanium(IV) isopropoxide (TTIP) precursor has been studied for a long time and by numerous techniques, e.g. Taylor et al. (and references therein) [37].

The decomposition of TTIP can be thermally activated (equation 16a and 16b) or hydrolysed (equation 16c) to form the TiO₂ solid deposit and volatile by-products [37].

\[
\begin{align*}
\text{Ti(O-i-Pr)₄} & \rightarrow \text{TiO}_2 + 4\text{H}_2\text{C-CH} = \text{CH}_2 + 2\text{H}_2\text{O} \quad (16a) \\
\text{Ti(O-i-Pr)₄} & \rightarrow \text{TiO}_2 + 2\text{H}_2\text{C-CH} = \text{CH}_2 + 2\text{HO-i-Pr} \quad (16b) \\
\text{Ti(O-i-Pr)₄} + 2\text{H}_2\text{O} & \rightarrow \text{TiO}_2 + 4\text{HO-i-Pr} \quad (16c)
\end{align*}
\]

For a constant TTIP precursor pressure of 4.0 × 10⁻⁵ Torr, Taylor et al. [37] identified three growth mode regimes. A low temperature regime was identified in which the deposition rate increases rapidly with temperature. This behaviour was attributed to reaction-limited deposition, i.e. the growth rate is limited by the rate of precursor decomposition. At intermediate temperature the growth rate has its maximum and is independent of small temperature changes. The growth rate was therefore said to be flux-limited, i.e. limited by the transport of precursor molecules to the surface. The growth rate is then directly proportional to small changes in the pressure. The temperature boundary between the reaction-limited and flux-limited regimes is dependant on the partial pressure of precursor molecules. At high temperatures the growth rate decreases with increasing temperature. This behaviour was discussed in terms of rapid precursor desorption.

Furthermore, the morphologies of deposited films are temperature dependant. This can be discussed in terms of precursor surface diffusion distances and diffusion of decomposition products. The precursor surface diffusion distance is the distance that the precursor can move on the surface before it decomposes. This distance is thought to be longer at lower temperatures. Diffusion of decomposition products is more pronounced at
high temperatures. Included in this discussion are preferential diffusion directions and preferential reaction sites, which are issues that have been further elucidated by our investigations. The same discussion is important for any CVD process intended to give conformal coverage of an irregular surface.

In this thesis includes investigations of CVD mechanisms on the molecular level. It is shown that the adsorption process and decomposition pathway of the precursor molecule are dependant on both surface composition and surface temperature.

4.1.2 Paper I

In paper I the TiO₂ growth on SiOₓ/Si(111) is investigated. The SiOₓ/Si(111) surface was produced by a moderate pre-oxidation of a Si(111)-(7x7) surface in situ. The precursor used was titanium(IV) isopropoxide and the sample was heated to 500 °C during deposition, which is in the flux-limited growth regime [37]. The interface region was probed by electron spectroscopy using synchrotron radiation. The morphology of the resulting thin film was probed by scanning tunnelling microscopy. The results are compared to deposition directly on pure Si(111)-(7x7) at 500 °C previously performed by our group [38]. Pre-oxidation has no dramatic effect on the morphology of the anatase film with respect to the particle size and particle density, but the anatase particles formed upon pre-oxidation are more crystalline in shape, see figure 8. Electron spectroscopy data, however, reveals substantial interfacial differences between the two systems: Pre-oxidation of the surface at 500 °C passivates the surface so that the thickness of the amorphous TiSiₓOᵧ interface layer decreases from 30-35 Å to 15-25 Å. In addition, the formation of interfacial carbon is completely eliminated, as can be seen in figure 9.
Figure 8. STM constant current topographs of titanium-oxide films grown at 500 °C by TTIP deposition on (a) Si(111)-(7x7) and (b) SiOₓ/Si(111). Copyright Elsevier (2003).

Figure 9. Photoemission spectra of the C 1s region for various amounts of TTIP deposited on SiOₓ/Si(111) and Si(111)-(7x7), respectively. Copyright Elsevier (2003).
4.1.3 Paper II

Paper II is a continuation of the study on silicon-metal oxide interfaces. This work elucidates the changes in the Si 2p spectra induced by chemical vapour deposition. Metal-organic chemical vapour deposition growth of titanium oxide on moderately pre-oxidised Si(111) using the titanium(IV) isopropoxide precursor has been studied for two different growth modes, reaction limited growth at 300 °C and flux limited growth at 500 °C. We focus on the Si 2p synchrotron X-ray photoemission spectra and show how these spectra can give detailed information of the two different interfaces. The cross-linking from oxidised Si to bulk Si after TTIP exposure has been found to be very similar to that of SiOₓ/Si(111). However, the results show that the additional oxidation of Si most probably causes a corrugation of the SiOₓ/Si interface. Those conclusions are valid for both growth modes. We furthermore present a model in which the amorphous interface region is described as (TiO₂)ₓ(SiO₂)ᵧ where x and y change linearly and continuously over the interface region. By using the modelled distributions it is demonstrated that a change in the relative intensities of the signals from silicon oxide and silicon can be attributed to (TiO₂)ₓ(SiO₂)ᵧ mixing. The result of model calculations is presented in figure 10. The method can be generalised and used for analyses of other metal-oxides on silicon. For the specific system presented in this work the model implies that the film grown at the lower temperature has the thicker interface of the two systems.

![Figure 10. Calculated Iₓ/S₀ₓ ratios as a function of the nominal amount of oxidised silicon for the mixed interface and the SiOₓ/Si interface. It is readily observed that mixing results in an increased Iₓ/S₀ₓ ratio when the nominal amount of oxidised silicon is equal. Copyright Elsevier (2005).](image-url)
4.1.4 Paper III

In paper III the decomposition of the titanium(IV) isopropoxide precursor has been studied in detail. The surfaces have been probed by photoelectron spectroscopy and x-ray absorption spectroscopy using synchrotron radiation. Scanning tunnelling microscopy has been used to monitor surface topography.

We show that the growth rate depends on both surface temperature and surface composition. The growth rate is faster at surfaces kept at 500 °C (773 K) than at 300 °C (573 K), as can be seen in figure 11. At 300 °C the growth rate is relatively slow on the Si(111)-(7x7) surface, a little faster on the SiOx/Si(111) surface and much faster on the TiO2 surface. At 300 °C surface temperature there is a strong correlation between the stability of surface isopropoxy and isopropyl groups and the growth rate. An increased stability for these intermediates reduces the growth rate. The precursor decomposition pathway depends on the surface. The mechanisms controlling the growth rate are therefore more complex in the initial stages of the growth compared to steady-state growth. When performing film growth at 300 °C starting from clean Si(111)-(7x7) surface the surface composition will change continuously in the initial stages of the growth, which results in an accelerating growth rate with increasing exposure to TTIP. The resulting TiO2 surface is carbon free and in the anatase crystalline phase.

TiO2 island formations are suggested in the initial stages of the growth performed at 300 °C starting from the Si(111)-(7x7) surface. The tendency towards TiO2 island formations can be reduced by pre-oxidation of the Si(111) surface prior to TTIP exposure.
Figure 11. Estimated overlayer thickness as a function of total exposure to the TTIP precursor for three different growth series: Growth at 573 K starting from the Si(111)-(7x7) surface, growth at 573 K starting from a SiOx/Si(111) surface and growth at 773 K starting from a SiOx/Si(111) surface. The numbers given in percent are the anatase part of the Ti L-edge XAS spectra for the different situations.
4.2 Zirconium dioxide thin-film growth by metal-organic chemical vapour deposition using the zirconium tetra-tert-butoxide precursor: Papers IV-VIII

4.2.1 Introduction to ZrO\(_2\) and the ZTB precursor

ZrO\(_2\) has emerged as a possible replacement for SiO\(_2\) as gate material. ZrO\(_2\) has a dielectric constant of about 20, which is five times that of SiO\(_2\). It has been demonstrated that MOS devices fabricated using ZrO\(_2\) as dielectric have most promising electrical characteristics [10,11]. Furthermore, the thermal stability of ZrO\(_2\) makes the material interesting for a variety of application.

Among metal-organic precursors, zirconium tetra-tert-butoxide [Zr(OC(CH\(_3\))\(_3\))\(_4\), (ZTB)] appears particularly attractive. It has a high vapor pressure and decomposes to form ZrO\(_2\) without an additional oxidant at substrate temperatures as low as 300°C [39].

4.2.2 Paper IV

In paper IV the growth of ultrathin ZrO\(_2\) films on Si(100)-(2x1) and Si(111)-(7x7) has been studied with core level photoelectron spectroscopy and x-ray absorption spectroscopy. The films have been deposited at 400°C sample temperature by chemical vapor deposition using zirconium tetra-tert-butoxide as precursor.

On Si(100)-(2x1) the local geometric structure characteristic for tetragonal ZrO\(_2\) (t-ZrO\(_2\)) is clearly observed already at a film thickness of 11 Å and this structure remains up to the thickest film in this study (74 Å), see Figure 12a. It is observed that the Zr-O hybridization within the ZrO\(_2\) unit depends on the chemical composition of the surrounding. This is most likely an effect of the different electronegativities of Zr and Si. On Si(111)-(7x7) the local structure of t-ZrO\(_2\) is not observed until a film thickness of 51 Å is reached, see Figure 12b. The higher tendency for the formation of t-ZrO\(_2\) on Si(100) can be related to the fact that the number of dangling bonds per surface Si atom agrees with the Zr-O valency, whereas the number of dangling bonds per surface atom on Si(111) does not.

The t-butoxy ligands undergo efficient C-O scission on Si(100), leaving carbonaceous fragments embedded in the interfacial layer. In contrast, stable t-butoxy groups are found after small deposits on Si(111). These are consumed upon further deposition. Stable methyl and, possibly, also hydroxyl groups are found on both surfaces within a wide film thickness range.
4.2.3 Paper V

In paper V the initial stages of chemical vapor deposition of ZrO$_2$ from zirconium tetra-tert-butoxide (ZTB) on Si(100)-(2x1) have been studied by Scanning Tunneling Microscopy (STM) and synchrotron radiation excited Photoelectron Spectroscopy (PES). Key STM results are presented in Figure 13. The STM images in conjunction with core level spectra indicate that the surface modifications induced by ZTB are due to carbonization and oxidation reactions. It is proposed that the carbonization reaction leads to a surface reconstruction forming (3x2) patches. Possible structure models are discussed and related to the C-induced Si(100)-c(4x4) reconstruction. The oxidation reaction leads to ZrO$_x$ units surrounded by Si$^{1+}$ species. It is probable that oxidation occur by release of atomic oxygen from the ZTB molecule. STM features are observed that are directly comparable to O$_2$ reaction with Si(100)-(2x1).

Figure 12. Zr 3p x-ray absorption spectra from the deposition of ZrO$_2$/ZrSi$_2$O$_4$ on (a) Si(100)-(2x1) and (b) Si(111)-(7x7).
Figure 13. Filled states STM topographs for (a) the clean Si(100)-(2x1) surface and (b) the surface of the same sample after 0.1 mL of ZTB exposure. The sample was kept at 400 °C during exposure to ZTB. The image of the clean surface (a) shows a low density of A and C-type defects. After exposure (b) two features are repeated over larger areas: Squares or elongated islands along the Si(100) high symmetry directions imaged as depressions (E) and small reconstructions (R). These features are discussed.
4.2.4. Paper VI

For the interface between silicon and gate oxide in the MOSFET the conduction and valence band offsets are important parameters. In a first approximation the conduction band offset determines the limit of the gate voltage that can be applied without unacceptable electron currents through the oxide. In the same approximation the valence band offset determines the limit of the gate voltage that can be applied without unacceptable hole currents through the oxide. Hence, in this respect a large band gap is not enough if the bands are not properly aligned.

In paper VI the band alignment of ultrathin ZrO$_2$ films of different thickness formed on Si(100) have been monitored with synchrotron radiation photoelectron spectroscopy and x-ray absorption spectroscopy. A significant decrease in the conduction band offset is found for increasing film thickness. It is accompanied by a corresponding increase of the valence band offset, as can be seen in Figure 14. The variations are largest in the thickness regime associated with ZrO$_x$-SiO$_y$ mixing. This suggests that it might be possible to tune the band alignment by changing the composition of the ZrSi$_x$O$_y$ layer. The interfacial layer characterized by a lower degree of Zr-O interaction than in bulk ZrO$_2$ and there is no clear evidence for partially occupied Zr 4d dangling bonds.
Figure 14. Valence electronic structure of the ZrO$_2$/ZrSi$_6$O$_y$/Si(100) system as function of film thickness. The vertical lines indicate the ZrO$_2$ (ZrSi$_6$O$_y$) and Si band gaps, respectively. **Left side:** Occupied states as probed with valence photoemission ($h\nu=130$ eV). The original spectra are denoted A, whereas B denotes difference spectra obtained by subtracting the spectrum for the clean Si(100)-(2x1) surface. Spectrum C denotes the spectrum after 4 Å deposition shifted in binding energy in order to match the structure at 3 eV. This gives information about the valence band edge for Si(100)-(2x1), which otherwise is obscured by the surface states. **Right side:** Unoccupied states as probed with O 1$s$ x-ray absorption (XAS). The XAS spectra are related in energy vs. the Fermi level by comparing the XAS photon energy scale to the binding energy scale vs. the Fermi level of the corresponding O 1$s$ photoemission spectrum. *Copyright AIP (2006)*
4.2.5 Paper VII

Silicon carbide is a material suitable for high temperature, high power, high voltage and high frequency devices and sensors. The quality of SiC crystals has improved considerably over the last years. This makes it possible to grow films onto SiC with high quality interfaces. The combination of the two compounds SiC and ZrO$_2$ can be most useful for devices and materials that need to function at high temperatures.

In paper VII the growth of ultrathin ZrO$_2$ films on the Si-rich SiC(0001)-(3x3) surface has been explored with photoelectron spectroscopy (PES) and x-ray absorption spectroscopy (XAS). Exposure to zirconium tetra tert-butoxide (ZTB) at 400°C results in the formation of tetragonal ZrO$_2$. Of special interest is the characterization of the interface formed between the ZrO$_2$ film and the SiC substrate. The Si 2p spectra recorded at different photon energies show that the interface contains Si in various oxidation states. In addition, low BE Si 2p states are observed after deposition, as can be seen in Figure 15. These are assigned to Si species formed by reaction with hydrocarbon fragments of the ZTB molecule. These low binding energy states are not observed upon oxidation using O$_2$. Si in a $+4$ oxidation state is detected in the near surface region. This shows that intermixing of SiO$_2$ with ZrO$_2$ occurs, possibly under the formation of silicate.

Subsequent annealing of the deposited film was performed in order to study the thermal stability of the system. Annealing to 800°C does not lead to decomposition of the tetragonal ZrO$_2$ (t-ZrO$_2$) but changes are observed within the interface region. After annealing to 1000 °C the film breaks up forming a heterogeneous layer. The surface region can be subdivided in regions with t-ZrO$_2$ remnants, metallic Zr silicide and Si aggregates.
Figure 15. Selected Si 2p PES spectra measured using 130 eV photons from the film growth series. At the top relative binding energy positions from references are marked. The SiO$_2$/Si(0001) marker is set relative to the SiC bulk peak position and indicates from left to right the positions for Si$^{4+}$, Si$^{3+}$ (O-Si$\rightarrow$C) and SiC bulk. The ZrO$_2$/Si(111) marker is relative to the Si$^{4+}$ position and indicates from left to right the positions for Si$^{4+}$ ((SiO$_2$)$_x$(ZrO$_2$)$_{1-x}$), Si$^{3+}$ (O-Si$\rightarrow$Si), Si$^{2+}$ (O=Si=Si), Si$^{1+}$ (O-Si=Si) and Si bulk.
FeCrAl is an alumina scale-forming alloy used in high temperature applications such as heating elements and metal-based catalytic converter bodies. The alumina scale that is formed during the oxidation process protects the underlying steel from corrosion. The quality and adhesion of the alumina scale is influenced by the addition of small amounts of Y, Zr and Ti.

In paper VIII the properties of ultrathin ZrO\textsubscript{2} films deposited on a FeCrAl alloy by way of MOCVD at two different substrate temperatures have been investigated. The coatings grown at 400 °C and 800 °C showed clear differences in the chemical composition. At 400 °C the coatings mainly consist of tetragonal ZrO\textsubscript{2} and at 800 °C the coating consists of a mixture of ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, and as can be seen in Figure 16 the mixture entails heavily reduced zirconium species. The Al metal diffuses from the FeCrAl bulk to the metal/coating interface at 400 °C and to the surface of the coating at 800 °C.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{zr_3d_core_level_spectra.png}
\caption{Zr 3d core level spectra obtained for different exposure times and sample temperature. Spectra a, b, d, and e was recorded in a surface sensitive mode with $h\nu = 290$ eV and spectrum c in a more bulk sensitive mode with $h\nu = 900$ eV.}
\end{figure}
4.3 Surface chemistry of the HfI$_4$ precursor on Si(100): Paper IX

Hafnium oxide, HfO$_2$, has emerged as a possible gate oxide material in the next generation of metal-oxide-semiconductor field effect transistors (MOSFETs). Among the merits of HfO$_2$ are a large band gap, high dielectric constant and thermal stability when in contact with silicon.

Atomic layer deposition (ALD) of HfO$_2$ has been accomplished using several different types of precursors. The use of HfI$_4$ as Hf-carrier has been found to result in films with lower degree of contamination compared to when using e.g. HfCl$_4$ [40]. The combination HfI$_4$+O$_2$ allows for ALD of HfO$_2$ at higher temperatures than employed in water-based ALD, which in turn allows for higher deposition rates [40].

In paper IX has the chemistry of HfI$_4$ adsorbed on the Si(100)-(2x1) surface been studied by synchrotron radiation core level photoemission, in UHV. Initially HfI$_4$ dissociate into HfI$_3$ and HfI$_2$ on the surface at 200 K. The dissociation is accompanied by the formation of SiI. Higher exposure leads to the formation of a HfI$_4$ multilayer. The HfI$_3$ and HfI$_2$ species remain on the surface upon heating the multilayer to 690 K, which can be seen in Figure 17. Heating to temperatures between 690 and 780 K results in complete desorption of iodine and concomitant formation of metallic Hf. At higher temperatures Hf silicide is formed.

Deposition of HfI$_4$ at 870 K results in a layer consisting of metallic Hf, probably in the form of particles. A substantial amount, but not all, of the Hf in this film is oxidized by O$_2$ consistent with Hf particle formation. Finally, deposition at 1120 K results in the formation of Hf silicide.

The observation that both HfI$_3$ and HfI$_2$ are stable surface intermediates may prove to be important for the understanding of ALD mechanisms, in particular at lower temperatures. Complete oxidation of Hf will be a critical step in ALD as our results show that metallic Hf particles may form.
Figure 17. L 4d (a), Hf 4f (b) and Si 2p (c) photoemission spectra measured after deposition at 200 K followed by annealing to the indicated temperatures. Hf 4f spectra for the two depositions at 200 K are included in (b) and a Si 2p spectrum for the clean Si(100)-(2x1) is included in (c). The different surface species are labeled. The Si 2p labels refer to clean surface and adsorbate related states.
4.4 Dye-solid interfaces

Research on dye-sensitized solar cell (DSSC) systems has been conducted within “Physics I” and collaborating groups for some time. Three papers connected to the research on DSSC systems are included in this thesis. The three papers represent different levels of approach. Paper X is a study of molecules on surfaces much on the fundamental level. Paper XI is a model experiment with a low contamination level having an explicit technological question at issue. In paper XII advanced characterisation is combined with measurements of device performance.

The titanium dioxide surfaces grown in situ are valuable for model experiments, partly because it is difficult to clean anatase TiO₂ single crystals without turning them into rutile TiO₂.

4.4.1. Paper X

Bi-isonicotinic acid (2,2'-bipyridine-4,4'-dicarboxylic acid), which is sketched in figure 18, is an important ligand in the chemistry of organometallic devices. In paper X the adsorption of a monolayer of the molecule on in situ-grown anatase TiO₂ nanoparticles has been investigated by means of X-ray photoemission spectroscopy and X-ray absorption spectroscopy. Model experiments and quantum mechanical calculations have been used to interpret the results. The bonding geometry is determined. Furthermore, resonant core spectroscopies have been used to study the excited-state-dependent electron transfer from the core-excited molecule to the substrate. For an excitation to the lowest unoccupied orbital, the excited electron is localized on the molecule because of a core-excitonic effect. Excitation to the two following unoccupied orbitals leads to a charge transfer on a low-femtosecond time scale.

Figure 18. Bi-isonicotinic acid (2,2'-bipyridine-4,4'-dicarboxylic acid).
4.4.2. Paper XI

This project, resulting in paper XI, was inspired by the possibility to evaporate CuI in situ and thereby allowing for very pure model systems. We have studied the interfaces of a system that models a solid-state dye-sensitized solar cell. First, a dye-sensitized nanostructured anatase TiO₂ film was prepared in a controlled way using a novel combined in situ and ex situ method. Onto this film CuI was deposited in situ and the dye-TiO₂ and dye-CuI interaction was monitored as a function of the amount of CuI. CuI forms particles, which interact with a fraction of the NCS groups of the dye. This is clearly seen from the S 2p spectra presented in Figure 19. Concomitantly, dye-TiO₂ bond breaking occurs. That is, the very effective charge injection channel provided by the dye-TiO₂ carboxylic bonding is directly affected for a substantial part of the dye molecules. These findings suggest that the deposited CuI displaces dye molecules, leading to a film consisting of a compressed dye layer separated by CuI particles. Furthermore, valence PES data indicate that electronic interaction between the dye and CuI occurs.

Figure 19. S 2p photoelectron spectra for increasing amounts of CuI deposited on the dye-sensitized TiO₂ film. Peak 1 is assigned to dye NCS groups and peak 3 is due to dye NCS groups interacting with CuI. The identity of the other two species (2 and 4) is uncertain. Copyright AIP (2004).
4.4.3. Paper XII

Recently solid state hole-conductor materials based on larger organic molecules than CuI have shown promising results in the dye-sensitized solar cell. In paper XII solid state heterojunctions comprising a dense TiO$_2$ film electrode as an electron conductor, a ruthenium polypyridine complex (Ru(dcbpy)$_2$(NCS)$_2$) as a dye and a triarylamine derivative as a hole-conductor were prepared. The photovoltaic properties as well as the molecular and electronic interfacial structures for heterojunctions based on a series of different triarylamine derivatives were investigated. The results were compared to a system comprising a dye-sensitized dense TiO$_2$ and the hole-conductors dissolved in an organic solvent as well as to a system comprising a dye-sensitized dense TiO$_2$ and tri-iodide/iodide liquid electrolyte. Two of the solid state heterojunctions showed current conversion efficiencies and photovoltages close to those of the system containing tri-iodide/iodide liquid electrolyte, while one system was clearly less efficient. The electronic and molecular interfacial structures of the solid-state heterojunctions were investigated by photoelectron spectroscopy (PES). Different thicknesses of the hole-conducting layer were investigated. The electronic energy levels highest in energy for the dye and the hole-conductors were mapped by valence level PES. Important differences were observed and the results partly explain the trends in efficiency. Differences in the molecular surface structure of the heterojunctions were also observed from the core level PES. Specifically it was found that the smaller hole-conductor is inserted into the dye layer, as sketched in Figure 20.

![Figure 20](image.png)

**Figure 20.** Schematic figure of the position of the different hole-conductors in the molecular interface structures.
5. Populärvetenskaplig sammanfattning

Att på ett effektivare sätt kunna styra flöden av laddning skulle vara nyttigt på många sätt. Till exempel skulle en transistor, som är den viktigaste byggnstenen inom digital teknik, kunna bli snabbare och förbruka mindre energi om den var mindre. Ett annat intressant exempel är färgämnessolcellen, som i dagsläget är väldigt bra på att fånga upp energi från solen, som skulle kunna bli mycket bättre på att ge energi i form av ström.

Att styra flöden av laddning innebär att flytta laddningar från en omgivning till en annan. Det skulle till exempel kunna vara från ett fast material till ett annat eller från en färgämnesmolekyl in i ett fast material.

I fallet transistorn är målet att styra laddningarnas förflyttning genom att lägga på spännings i olika riktningar. På det sätt som den vanligaste typen av transistorer är uppbyggd finns det positioner där laddningarna dras åt fel håll. På dessa ställen behövs det material som isolerar mot ström, dvs en helt annan typ av material mot det som laddningarna rör sig i. För att vidareutveckla transistorn behövs det isolationsmaterial som används idag bytas ut. Väldigt höga krav ställs på potentiella materialkombinationer, bl a måste gränssnittet mellan materialen ha för ändamålet mycket goda egenskaper.

I fallet färgämnessolcellen är målet att snabbt förflytta laddningar, som fått energi från solljuset, bort från färgämnesmolekylen innan energin övergår till värme. Förflyttningen av den energirika laddningen behöver inte bara vara snabb, utan också ske på ett sådant sätt att endast lite energi går förlorad i form av värme.

Både när det gäller transistorn och färgämnessolcellen är det viktigt hur de olika enheterna sitter ihop. Det är alltså inte bara de olika materialen och molekylernas enskilda egenskaper som bestämmer hur effektiv apparat som kan skapas.

När två fasta kroppar av olika material sätts ihop bildas ett gränssnitt, som kan se ut på olika sätt. Det finns ett begränsat antal materialkombinationer där abrupta övergångar är möjliga, dvs där ett material övergår till ett annat från ett atomlager till nästa. Det finns även situationer där de olika materialen blander sig i en gränssnittsregion.

För en molekyl på en yta finns det också olika möjligheter. Till exempel kan molekylen binda kemiskt och ändra form och olika delar av en stor molekyl kan interagera med ytan på olika sätt.

Gränssnitt mellan fasta material kan med fördel studeras genom att skapa en modellsituation där en väldigt liten mängd material stegvis läggs på ett annat. Att utveckla metoder för att på molekylär nivå kontrollerat kunna utföra en sådan preparering har också varit en viktig del av min forskning. Ultratunna filmer i sig är också högst intressanta objekt.


De ultratunna filmer som presenteras i den här avhandlingen har skapats vid låga tryck med hjälp av ovanstående metod. Den kemiska reaktion som sker när en metallorganisk molekyl reagerar på en uppvärmd yta har studerats i detalj. Genom att olika parametrar har använts vid tillväxtprocessen har ultratunna metalloxidfilmer av samma material visat sig kunna ha något olika egenskaper och gränssnitt mot kisel.

Mina studier har bidragit till att öka förståelsen för de system som studerats. Egenskaper hos färgämnessolceller tillverkade i laboratoriemiljö har kunnat länkas till egenskaper på molekylär nivå, vilket är av stor betydelse för vidareutvecklingen mot mer effektiva färgämnessolceller.
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PS Jan, you can write your own below…
7. References

A doctoral dissertation from the Faculty of Science and Technology, Uppsala University, is usually a summary of a number of papers. A few copies of the complete dissertation are kept at major Swedish research libraries, while the summary alone is distributed internationally through the series Digital Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology. (Prior to January, 2005, the series was published under the title “Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology”.)