



Characterization of ultrathin ferroelectric oxide films using X-ray spectroscopy

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Thesis submitted for the degree of Bachelor of Science
Project duration: 4 months

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May 2026

Acknowledgments

I would like to express my sincere gratitude to all individuals who were contributing to the completion of this thesis by constantly offering their academic and emotional support.

First and foremost, I want to thank my supervisor Rainer Timm. I appreciate you welcoming me in your research group and making it possible for me to gain insights on real scientific work performed at big research facilities as the Helmholtz-Zentrum Berlin (HZB) and the MAX IV laboratory. Your strong involvement and your detailed feedback on my project always created a very supportive and insightful environment.

Also, I would like to acknowledge the practical guidance that I received by the Ph.D. students of my research group, Nishant Patel and Eleni Charitoudi, who would always assist me on practical questions and would offer their advice to keep me on the right track.

Last, I want to thank my family and friends. Thank you to my parents for never hindering my big plans of moving abroad and joining this field of ambitious studies. To all my friends, the ones that would sit with me during long days of studying and completing this project and the ones that would distract me from endless academic work on weekends and after hours.

Abstract

Promising advances in the field of ultra low power computing are based on the design of high-density ferroelectric memories with non-destructive readout. In this bachelor thesis, the objective is to study $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ thin films as one of the most popular candidates to replace traditional dielectrics. A thermal annealing procedure is required for the fabrication of these devices, since the ferroelectric phase can only be formed through a phase transition induced through heat and mechanical stress. On the contrary, heat does often promote changes in the stoichiometry and the interface quality. So far, the lack of control over these side effects is limiting the commercialization of the devices. An X-ray absorption spectroscopy (XAS) and hard X-ray photoelectron spectroscopy (HAXPES) study on an in situ annealing experiment are used for monitoring of how the chemical composition and the crystal structure are directly affected by temperatures. This simulates realistic fabrication conditions and serves to improve the understanding on the correlations. For this work two sample structures are being compared. Both the data collected through XAS and HAXPES measurements have mutually shown a transition temperature with a difference attributable to the variation in the sample structure. The alteration of the sample structures after the transition was shown to be irreversible. Additionally, both samples were demonstrated to have undergone electrostatic changes.

Abbreviations

CMOS complementary metal-oxide-semiconductor

HKMG high- κ metal gate

FE ferroelectric

HZO hafnium zirconium oxide

VB valence band

CB conduction band

o-phase orthorhombic phase

m-phase monoclinic phase

t-phase tetragonal phase

EM electromagnetic

XPS X-ray photoelectron spectroscopy

PES photoelectron spectroscopy

XAS X-ray absorption spectroscopy

IMPF inelastic mean free path

HAXPES hard X-ray photoelectron spectroscopy

NEXFAS near edge X-ray absorption fine structure

XANES -ray absorption near edge spectroscopy

RRAM resistive random-access memory

ALD atomic layer deposition

RT room temperature

FWHM full width half maximum

GLS Gaussian-Lorentzian sum

GL Gauss-Lorentz

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1 Introduction

Ever since the beginning of the so called "age of technology" advances in this sector have not slowed down and newest progresses are represented by the development of artificial intelligence, which is gaining more and more importance. It's high efficiency and versatile applications in industrial sector and everyday life tends to overshadow the societal problems that it is bringing along. To ensure its performance large data centers are required which are particularly debated due to their high power consumption.

Before, the way of reducing the power dissipation of electronics was based on the downscaling of the electrical components, most importantly of complementary metal-oxide-semiconductor (CMOS) transistors. Along with that evolution would come an increase in the number of components fitting on integrated circuits. This exponential behavior was already described by Gordon E. Moore in 1965 [1], but it seems like this technique has reached its limitations as further miniaturization of transistors has begun to slow down [2].

To not slow down the progress the More-than-Moore approach introduces new computational systems based on embedded non-volatile memory to imitate a neuromorphic style of computing [3, 4]. That means that both, the memory unit and the processing unit, are combined into one imitating a brain-like structure. With this removal of the data path connecting the units a high writing speed, low power consumption and a nondestructive readout process can be achieved [5]. To support this new method of construction, conventional CMOS transistors have to adapt as well, such that the integration of a new insulating layer with ferroelectric (FE) properties is crucial. Originally the dielectric consisted of SiO_2 , because of its relatively high band gap of $E_g \approx 8.9 \text{ eV}$ or its ease of fabrication, but along with downscaling the devices the width of the gate oxide had to decrease. This on the other hand introduced quantum tunneling and leakage current lowering the device performance. The dielectric was replaced by new high- κ metal gate dielectrics (HKMG) such as HfO_2 based materials [2].

Deposition processes of HfO_2 layers, also referred to as hafnia layers, had already been developed when Böске et al. [6] first discovered the ferroelectric property of such hafnium-based thin films, what made it a promising candidate to pave way for resistive random access memory devices and other ferroelectric components.

Adding a thermal annealing step, essential for the doped HfO_2 -films to crystallize in their ferroelectric phase, to existing fabrication methods is no challenge in itself, however do the increased temperatures promote the diffusion of oxygen into the substrate, which is typically chosen to be formed of a III-V semiconductor [7]. At the interface between the substrate and the HKMG the oxygen tends to bind to the atoms of the semiconductor material and an intermediate oxide layer forms affecting the device performance. Additionally, the transfer of oxygen leaves behind some vacancies in hafnia layer, also classified as oxygen-deficient HZO.

This thesis investigates the properties of these ultrathin ferroelectric oxide films with a focus on their chemical and electronic structure. The thermal conditions are being studied in more detail to identify temperatures required for phase transitions and determine any oxygen vacancies being induced, to better understand the processes taking place on an atomic scale.

2 Theory

2.1 Crystal structures

Identifying the properties of certain materials usually involves the description of atomic structures and motion on microscopic scales. Solids can generally be divided into different subgroups such as amorphous or crystalline ones. The latter one allows for a more simplified investigation because of its high level of periodicity shaping the array of atoms making up the material. Hence, crystals follow the principles of translational symmetry. The positions of the atoms are fixed by the Bravais lattice, a mathematical model with 14 variations in three dimensions due to differences in their point symmetries.

Instead of describing the crystal by each atom individually, one can focus on the smallest volume fraction of the lattice whose repetition perfectly reproduces the macroscopic sample. This fraction is the unit cell. The combination of atoms positioned at each lattice point is referred to as the basis.

A specific crystal has some form of point symmetry when its lattice can be mapped into itself by transformations as rotation about an axis through one of the lattice points, reflection in a plane through a lattice point or inversion through a lattice point. Different lattices that allow for the same point symmetry operations, can be combined to a common symmetry group or system. In Table 1 there are some examples for different symmetry groups and a description of their corresponding Bravais lattices [8].

System	Variation	Features
Cubic	P, F, I	$a = b = c; \alpha = \beta = \gamma = 90^\circ$
Orthorhombic	P, F, C, I	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
Monoclinic	P, C	$a \neq b \neq c; \alpha = \beta = 90^\circ \neq \gamma$
Tetragonal	P, I	$a = b \neq c; \alpha = \beta = \gamma = 90^\circ$

Table 1: Exemplary, four different point symmetry groups are described by their spacial features defining the unit cell. The unique variations making up the group are listed. P refers to the primitive cell with one atom per cell, F stands for face centered with an additional lattice point centered on each side, C refers to the lattice with additional base centered atoms and I to the structures with one additional body-centered point.

Generally, a material can crystallize in different phases, with each one determined by the specific temperature T , the mechanical pressure P_{mech} applied to the sample or the electric field E . For different thermodynamic conditions there is always one stable structure defined by having the lowest free energy G [8]. Whenever two stable phases A and B have the same free internal energy $G_A(T_c) = G_B(T_c)$ at a certain temperature T_c a phase transition is allowed. Although different phases A and B do not necessarily have a great effect on the material properties, there are some phase transitions that can introduce for example new electronic properties [9, 2].

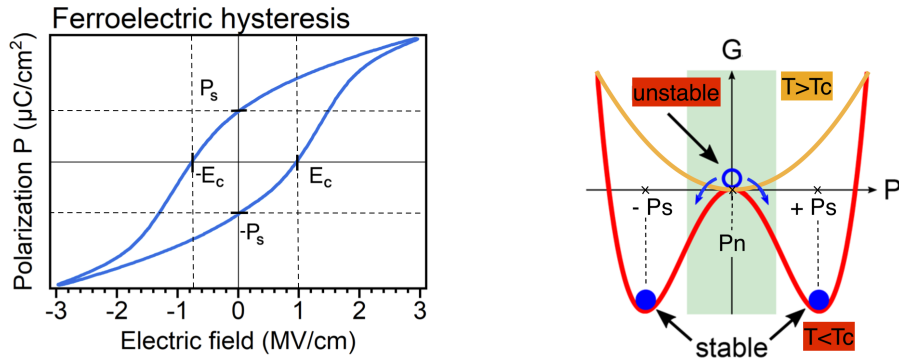
2.2 The electronic structure for atoms in a crystal

The electronic structure of solids differs from the distinct energy levels as found within individual atoms. Due to the tight spacing of the atoms the higher order electronic orbitals overlap. The

distinct energy levels split into several, degenerate sub-levels forming broad energy bands. The energy bands are separated by so-called bandgaps E_g of sizes, which are specific to the material. Solids can then be sorted into different groups, namely metals, semiconductors and insulators, depending on their band gap values and their fraction of occupied states within the highest energy band, the valence band (VB). For the samples studied in this paper all three groups were represented, but the focus was put on the semiconductors and insulators. Both have a fully occupied VB. The next higher energy band is the conduction band (CB) with mostly unoccupied states due to the large E_g acting as a high barrier for possible electronic transitions. The position of the so called Fermi-level determines at which energy the occupation of the states has at 50 % chance of being occupied. The innermost core levels remain distinct since they are highly localized and do not interfere with one another (see Figure 3) [8].

2.3 Ferroelectricity

Ferroelectric materials are characterized by a spontaneous polarization P_s arising from a net electric dipole moment, together with the ability to reversibly switch between two stable polarization states. These properties stem from a specific ionic arrangement within solids, where the center of the positive ions does not coincide with the one of the negative ions. This characteristic can be found in solids with a non-centrosymmetric structure; the Bravais lattice and the basis attached establish a configuration with the absence of any atoms in the center of the cell [2, 9].



(a) The characteristic hysteresis loop shows how there are two stable polarization states accessible in the absence of and external electric field between which one can switch. Adapted from Szyjka [9].

(b) The free energy G has two global minima at polarizations $P \neq 0$ in ferroelectric materials. Adapted from Hoffmann, Slesazek, and Mikolajick [2].

Figure 1

Typically, the ferroelectric state does not uniformly expand over the whole sample, but in reality domains are formed; smaller regions with same polarity along neighboring unit cells. Instead one requires and externally applied field E_0 to switch the orientation of the domains such that they are the same [9]. This behavior is commonly represented by the ferroelectric hysteresis loop (see Figure 1a). One can observe how P_s at $E_0 = 0$ depends on the history of the solid about the previous configuration and E_0 . One can switch the sign of the polarization P by applying

$E_0 \geq |E_c|$. These minimum values $\pm E_c$ are called the coercive field.

Some materials can exist in both a ferroelectric structure and a non-ferroelectric phase, where for example the first can be accessed through a phase transition under certain conditions as mentioned in the previous section.

The free energy G is a quantity that is commonly used to describe phase transitions. It depends on the temperature T and polarization P , and the position of its minimum value determines a stable configuration. Since $G \rightarrow P$, the values for the free energy can differ between polar, or FE-, and non-polar phases and the exact values of G at the minimum determine whether the polar phase is more stable and favorable to the neutral parent structure.

A mathematical description for the free energy according to the Landau theory is

$$G = \frac{1}{2}a(T - T_c)P^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6, \quad (1)$$

with a, b and c being symmetry coefficients distinct to the crystal structure itself [9]. At the Curie temperature T_c , the coefficient $a(T)$ changes signs altering the shape of the energy curve as presented in Figure 1b. The two graphs have different minima at P_n for the orange graph and at $\pm P_s$ as can be seen on the red graph.

At $T > T_c$, the solution of $\frac{dG}{dP} = 0$ corresponding to the absolute minimum of the free energy is located at $P_n = 0$ (see orange graph in Figure 1b). Hence, the energetically most favorable state is a non-polar crystal structure with no net polarization. At $T < T_c$, the shape of the energy curve is altered such that two absolute minima of the function appear at $|P_s| > 0$. The extreme point at $P = 0$ still remains, but it was converted into a local maximum instead, an unstable state for the crystal [9].

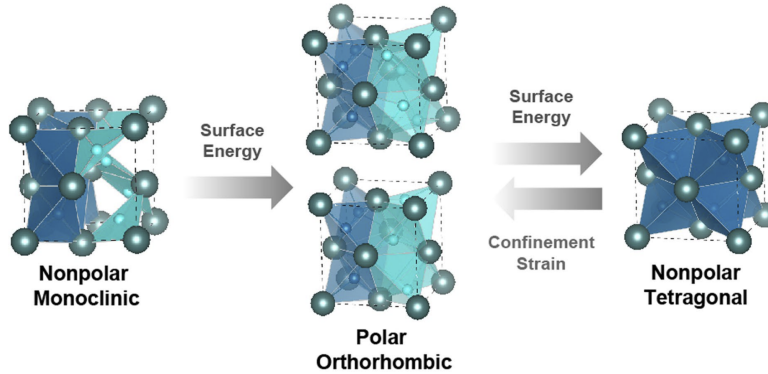


Figure 2: The ferroelectric phase in HfO₂ is the o-phase. This metastable phase can be accessed during the transition from the m-phase to the t-phase. The net dipole moment is due to the displacement of half of the oxygen atoms (cyan). Reproduced from Cheema, Kwon, Shanker, et al. [10].

Traditionally, one would expect only solids consisting of at least three elements to possibly show ferroelectric behavior, but hafnium-dioxide HfO₂ is also demonstrating these properties under certain conditions. The ferroelectric phase in HfO₂ is connected to the orthorhombic phase (o-phase) and to the displacement of half of the oxygen atoms in the Bravais cell that form three

bonds with Hf. The other half forming four bonds with Hf, remain stable (compare to Figure 2) [9, 11]. However, this phase is only classified as being metastable and is only accessed during the transition from the monoclinic (m-phase) to tetragonal (t-phase) phase upon heating. Some form of stabilizing is required and several steps are taken to realize that, as for example the method of fabricating the samples in form of thin films, to lower the temperature, under which the transition takes place. Due to differences in the expansion coefficients among the thin films and the metallic top electrodes additional strain and stress is being introduced to suppress the polar phases. Additionally can doping increase the stability of the o-phase. Introducing elements with the same valency as for example Zirconium atoms, but different dimensions, can change the bond lengths and create distortions of the cells [9, 2].

2.4 X-Ray Spectroscopy methods

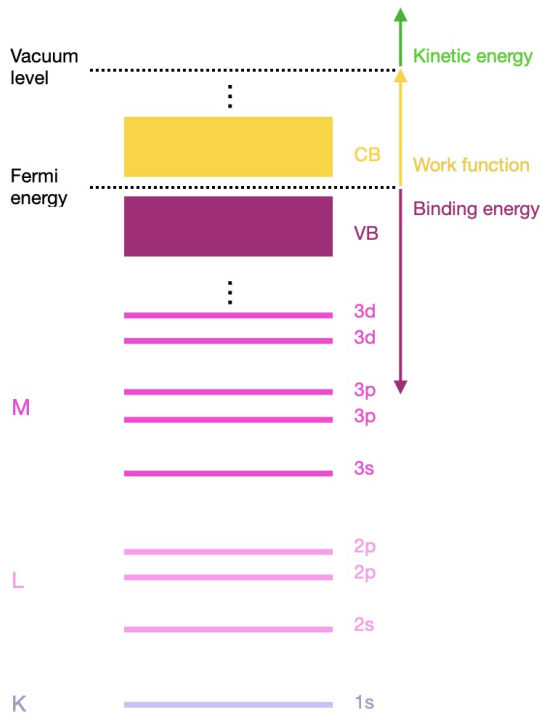


Figure 3: For atoms arranged in a crystal structure the inner most energy levels remain distinct. Less bound levels form energy bands instead. The valence band (VB) is the outermost occupied band and is separated from the conduction band (CB).

orbitals as visualized in Figure 3 can be divided into 3 main sections, that set up energetic relations for the photoelectric effect. States below the Fermi-level E_F are mostly filled and above there are higher bound states to be possibly occupied. Their upper limit is the Vacuum level. Electrons with energy above the vacuum level are basically free and if they are near the surface

Electromagnetic (EM) waves propagating through space with more energy than ultraviolet radiation and less than gamma-rays are classified as X-rays. Their range approximately reaches from 0.5 to 500 keV [12]. The absorption α of radiation with energy E by matter is sensitive to the atomic number of its elements Z and its density ρ as

$$\alpha \propto \frac{\rho Z^3}{E^3}. \quad (2)$$

Hence, the interaction of X-rays with matter carries valid information about the samples, their constituents and electronic structures [12].

That is why several experimental spectroscopy-techniques have been developed based on X-ray absorption, such as the method of X-ray photoelectron spectroscopy (XPS or PES), whose first advancements draw back to Kai Siegbahn in the 1950's [13], or the method of XAS.

2.4.1 X-Ray photoelectron spectroscopy

The main mechanism involved in XPS is the photoelectric effect. The incoming EM radiation can transfer its energy to the electrons occupying the orbitals of the atoms and promote them to higher states. The energetic arrangement of the electronic

of a sample, they could even escape it into the surrounding vacuum. These particles in particular are referred to as photoelectrons, that consecutively can be captured by a detector. The incoming photon energy is then divided into

$$h\nu = E_k + E_b + \Phi, \quad (3)$$

where the binding energy E_b , or BE, is measured with respect to E_F . Φ represents the work function of the material, that is the difference between E_F and the vacuum level and E_k stands for the kinetic energy of the resulting photoelectron.

In XPS the detector measures E_k of the emitted photoelectrons. For a given photon energy $h\nu$ and a specific Φ , dependent on the atomic constituents, the data measured as counts per E_k can then be converted to spectra representing counts per E_b instead. Sharp peaks in the spectra then represent the energies of the individual core levels. The sharp peaks shaping the spectra are uniquely defined by each element on the periodic table just like a fingerprint. They rely on photoelectrons escaping the sample without losing any E_k through other processes like inelastic scattering.

One can increase this fraction of electrons by placing the sample and the detector into vacuum to avoid scattering with air molecules. However, the main cause for inelastic collisions is due to the almost static nuclei. The number of scattering events for an individual free electron increases with its distance to the surface. The inelastic mean free path (IMFP) determines the distance an electron can travel on average before it will transfer part of its E_k due to inelastic scattering. The IMPF depends on several factors as the atomic structure and E_k and can be computed via a complex integral [14]. For example, the IMPF for photoelectrons of energy 100 to 1500 eV is limited to about $\lambda \approx 1$ nm, which is typical for photon energies in the soft X-ray regime as it was used in the early stages of XPS; that is why for the remaining thesis 'XPS' will refer to this method only. As mentioned, the IMPF is only a statistical quantity and is more commonly translated to more physical quantities via the Beer-Lambert law. It is used for discussing attenuation of the XPS intensity by an adsorbate layer of thickness x , and then one typically writes it as

$$I = I_0 \exp\left(-\frac{x}{\lambda}\right). \quad (4)$$

A significant contribution of photoelectrons without E_k loss is exponentially decreasing with x and limits the probing depth to only a few nm [15]. This makes XPS a very surface sensitive method, which limits the selection of samples. Commercial products as used for CMOS transistors typically consist of several layers, whose performance heavily depends on processes taking place at the interfaces of these semiconductor-insulator stacks buried underneath a metal top electrode as found in realistic devices[13].

Since the IMPF λ does increase with E_k in the range of energies as typically caused by HAXPES methods and E_k can be varied with by changing the photon energy $h\nu$ according to Equation 3, probing at higher photon energies also increases the probing depth. One way of producing these high energy photons in the hard X-ray regime as used for HAXPES measurements is by forcing relativistic electrons into a sinusoidal path as it is done in so called synchrotrons.

2.4.2 X-Ray Absorption Spectroscopy

Just like the method of XPS and HAXPES relies on the interaction of EM waves with the electronic structure of atoms, so does XAS. The amount of X-rays absorbed by the sample can be quantified by secondary effects, such as fluorescence, as it was used for the project of this thesis. Fluorescence refers to the process when an incoming photon promotes an electron to an energetically higher level and the subsequent de-excitation of these electrons emitting a new photon, which is then detected. Since the X-rays themselves are more penetrating than the photoelectrons, this method enables to investigate the sample structure at much deeper layers. Also, the information received does not depend on a single photoelectron, such that more information including unoccupied, but bound states, valence states or symmetries is received [13, 16].

A typical XAS spectrum can be scanned over a wide energy range, but the technique of NEXAFS (short for near edge X-ray absorption fine structure) or XANES (X-ray absorption near edge spectroscopy) refer to the cut-outs of the range focusing on the so called edge-features. The edge is located at energies, where $h\nu \geq E_b(\text{level}) + \Phi$, hence each core level produces its own edge feature. For example, the *L2*-edge refers to electrons originating from the second level within the L-shell (compare to Figure 3) being excited to the lowest unoccupied state. Electronic transitions without the excitation of photoelectrons into a state above E_F have to follow certain selection rules [12, 13, 16].

Each level as presented in Figure 3 is uniquely defined by its main quantum number n , its orbital number l and the spin $s = \pm\frac{1}{2}$, where last one is not explicitly included in the diagram. The n indicates the shell an electron occupies (also referred to as K-, L- or M-shell counted from innermost to outer shells). The $l = \{s, p, d, \dots\} = \{0, 1, 2, \dots\}$ is also called the orbital quantum number, and in order for a transition to take place the difference Δl between the initial and final state has to be odd [12]. The orbital number is coupled to the spin s and results in the total angular momentum $j = \{|l - s|; l + s\}$. This creates a so-called spin doublet and accounts for the fact, that apart from the *s*-levels, all other levels appear twice in Figure 3. The spectral lines arising from these restricted transitions are very unique to the type of the absorber atom and are like their fingerprint.

The L2 and the L3 edge of ZrO_2

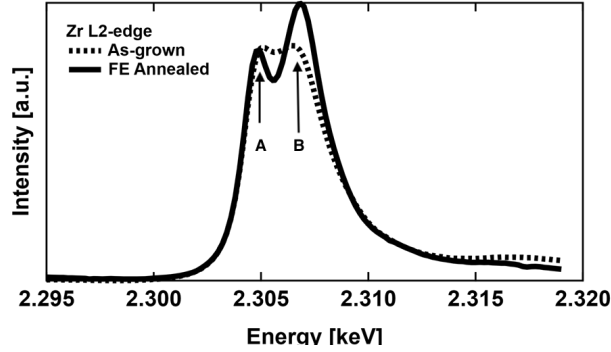


Figure 4: The two graphs are the results of a NEXFAS measurement on two samples (HZO film on an InAs substrate). The As-grown sample was not further heated after fabrication, the other sample (solid line) was exposed to rapid thermal annealing. The two peaks developing after the heating are evidence for increased symmetry in the atomic arrangement. Adapted from Irish [13].

As outlined in the previous section, the ferroelectric phase of HfO_2 is metastable and therefore requires material engineering strategies, such as doping, to achieve stable operation. For this reason, $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (short HZO) thin films are commonly used in device stacks instead of pure HfO_2 .

The accessible phases for the HZO film are the m-phase, at lower temperatures, the t-phase at higher ones, and the o-phase, which was proven to be accessible during the typical transition, but requiring stabilization. The characteristic shape of both L2 and L3 features resembles a doublet peak (compare Figure 4). The ratio of the two peaks is a good indicator for the degree of symmetry about the Zr site and hence the crystallization of the sample. The peak at lower energies is labeled as A and the other peak as B.

For the L2 edge it holds that the presence of subpeaks in A is associated with the m-phase and subpeaks in B with the t-phase due to a lower degree of symmetry about the Zr-sites. The presence of these subpeaks can be observed to interfere with the doublet shape and make it appear like one broad peak. The o-phase observed on the L2-edge is found with a more distinct doublet shape lacking the contribution of smaller subpeaks. Also, the ratio $\frac{A}{B}$ of the peaks is decreased to values below 1.

For the L3 edge B generally remains at higher intensities than A. Again the presence of subpeaks would be evidence for the m- or t-phase and the ratio would be smaller than to 1 for the o-phase [17].

3 Methodology

3.1 Sample structures

Resistive random-access memory (RRAM) stacks typically consist of one or several oxide layers deposited on a semiconductor substrate covered by a metal top contact. The oxide layer is also referred to as the high- κ gate dielectric and forms a thin film between the top electrode and the substrate. The type of thin film investigated in this work has been shown to develop a ferroelectric properties under application of thermal and mechanical stress.

The compared samples were chosen as two variations of RRAM stacks. For both of them high- κ oxide layers were placed between an InAs substrate and a TiN top layer. The common HKMG dielectrics was formed by a Hafniumoxide thin film doped with Zirconium ($\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ or HZO) and an additional, interfacial layer of Aluminiumoxide (Al_2O_3) is located directly on top of the InAs substrate for sample B only. The HZO thin film exhibits the ferroelectric behavior once transitioning into the o-phase.

The HZO and Al_2O_3 layers were grown by atomic layer deposition (ALD) and the top layer was sputtered using physical vapor deposition. They were provided by the group of Prof. Lars-Erik Wernersson, from the department of Electrical and Information Technology at Lund University. The dimensions of the samples and layers are presented in Figure 5.

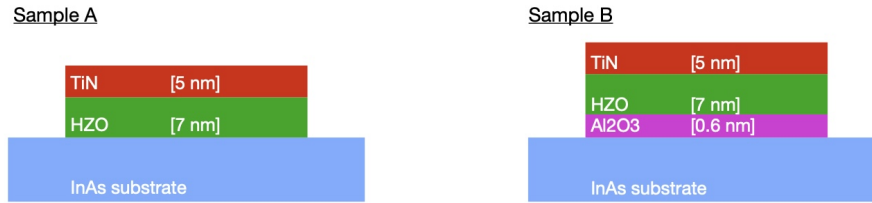


Figure 5: The samples under investigation follow the typical structure of a metal-oxide-semiconductor (MOS) transistor. Sample A is a composition of three layers only, while sample B has an additional Al_2O_3 layer directly on top of the substrate. The dimensions are not to scale.

3.2 Data acquisition at the Beamline KMC-1 with HIKE endstation at BESSY II

In order to better understand the processes taking place on atomic scales, an in-situ HAXPES study was performed. During the measurements, the samples were subjected to a thermal annealing process designed to mimic the thermal conditions commonly used during fabrication. HAXPES allows for tracking possible changes in the interfacial chemistry and correlating them with the annealing temperature. The data was recorded at the Bessy II synchrotron facility in Germany, Berlin, during one week of a so called beamtime.

At a synchrotron facility an electron beam is being accelerated to velocities approaching the speed of light. Magnets are used to steer the beam to follow a circular path. Other arrays of magnets, so called wigglers or undulators, are positioned in linear sections of the ring, perturbing the trajectory of electrons to follow a sinusoidal path. During this process the electrons emit

photons of very small wavelengths, X-rays, in shape of a highly brilliant beam due to relativistic effects at these high velocities [12]. These X-ray beams are guided into beamlines, which differ by their setup of optics guiding and focusing the beam onto a sample and by the detection setup specialized on different types of studies.

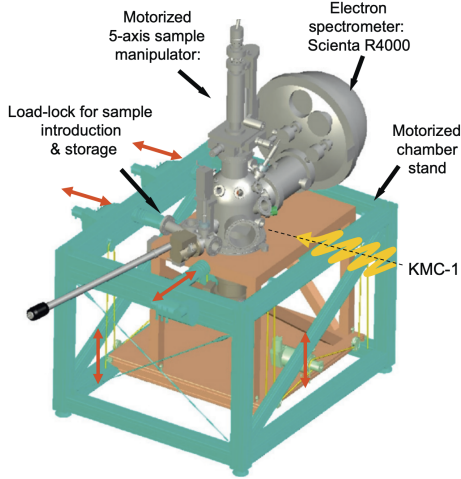


Figure 6: The load-lock, the analysis chamber equipped with a motorized 5-axis sample manipulator and the electron spectrometer are arranged along an array normal to the KMC-1 beamline. Reproduced from Gorgoi et al. [18].

To perform the in-situ annealing HAXPES measurement, the beamline KMC-1 at Bessy II was chosen. The double crystal monochromator setup allows for tuning the beam energies to values within a range of 2 keV up to 12 keV. The specific probing energies chosen for this experiment are 2003 eV and 6009 eV to differ the probing depth. The layers of main interest are the HKMG dielectrics, the semiconductor substrate and their interface. The lower energy setting focuses on the signals originating from the more shallow layers and the high energy setting detects signals from the most buried areas. The HIKE end station is specialized for detecting photoelectrons ejected at high kinetic energies by hard X-rays. It consists of the loadlock, an analysis chamber and the detectors. The first is used to fix and enter the samples, and decrease the pressure before entering the ultra high vacuum (UHV) analysis chamber. The chamber is equipped with a Gammatdata Scienta R-4000 hemispherical analyzer for the HAXPES measurements located at a 90° angle with respect to the

incoming beam. Like that, the data acquisition was performed in normal emission of the electrons and grazing incidence of the photon beam (compare with Figure 6). Additionally, the station has installed a Bruker XFlash [®]4010 fluorescence detector which allowed to obtain the XAS data [19]. Two samples were investigated (compare to Figure 5) to detect the spectra forming around 5 different core levels as summarized in Table 2.

Table 2: In both samples 5 different core levels were recorded at both available settings for the choice of incident photon energy. During the fitting process the data with too bad signal-to-noise ratio was ejected and only the ones specified in this Table were kept.

Core level	Probing energy
Hf 4f	2003 eV
Hf 3d 5/2	6009 eV
As 2p 3/2	6009 eV
As 3d	2003 eV
In 3d 5/2	6009 eV

The HAXPES spectra were recorded with an stepwise increment of temperatures of $\Delta T = 25^\circ\text{C}$ reaching from $T_A = [200^\circ\text{C}; 550^\circ\text{C}]$ for sample A and $T_B = [225^\circ\text{C}; 500^\circ\text{C}]$ for sample

B. Additionally, two scans were performed at room temperatures (RT's) before and after the heating process. The XAS data for comparison was taken over an energy range of $E_{\text{XAS}} = [2170 \text{ eV}; 2370 \text{ eV}]$ with $\Delta E = 0.25 \text{ eV}$ to capture the L2 ($\sim 2315 \text{ eV}$) and L3 ($\sim 2230 \text{ eV}$) edge of Zr at the same temperatures as used for sample B. In total, four physical samples were used throughout the entire experiment, because the transition from HAXPES to XAS measurements required remounting a sample in the endstation and two structures, A and B, were to be probed by both techniques. Thus, while different physical samples were measured, they can be grouped into two pairs corresponding to sample A and sample B, respectively.

3.3 Fitting Process

A spectrum from XPS is typically a combination of several features. However, when processing the data to draw qualitative conclusions, one is typically only interested in individual features. The way to handle this is by deconstructing the full spectrum into its components. Generally, the different sources for these components can be grouped into peaks from primary core level excitation, a background from inelastic scattering processes and additional peaks from secondary excitations. In the following mathematical concepts are being introduced that were used to correctly model the shape of the features and recover the different elements that as a whole reproduce the recorded data.

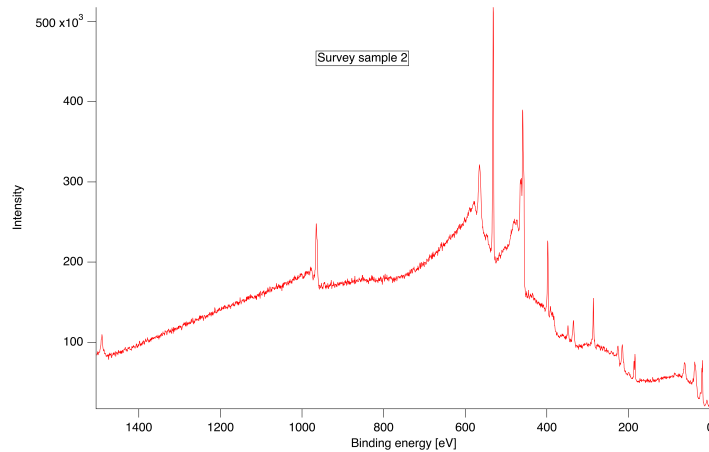


Figure 7: The survey spectrum of sample 2 is a scan over a wide range of binding energies to get an overview over the the contribution of all different components making up the sample. It was taken at photon energies of 2003 eV.

Background subtraction to isolate peaks

The first step of the peak fitting process is typically formed by the background subtraction. The background contributions can be explained as follows.

A peak corresponds to E_k detected from electrons originating straight from its core-hole excitation before depositing any energy through inelastic scattering processes. Electrons that scatter before reaching the surface boundary of the sample on the other hand, contribute to counts towards lower E_k . The XPS spectra are typically displayed with respect to E_b , such that the inelastically scattered electrons form the background towards higher energies. Hence, each peak

carries an additional background signal on its higher E_b -side along with it. The resulting background can be approximated as being shaped similar to a step.

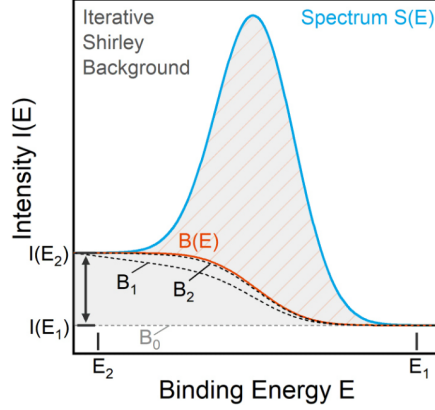


Figure 8: The iterative Shirley background has a step-like nature and is converging after only a few iterations.

A wide energy range spectrum from this experiment of sample 2 is shown in Figure 7. One can observe how the approximation of a staircase background seems to fail at high E_b s. However, since fitting peaks is done on excerpts around individual peaks, the background can still be approximated as resembled by a step. This model follows a logic physical reasoning and is executed by setting it proportional to the integrated intensity of the spectrum [20]. In this way a step naturally forms under the center of the peaks. The mathematical model is called the Shirley background, or even more refined, the iterative Shirley background.

The algorithm performing the computation of the background is an empirical method, which is affected by the selected positions for a starting energy E_1 and an end point E_2 limiting a range about a peak or a selection of peaks. The method requires to set the intensity $I(E_1) = 0$ by subtracting a baseline $B_0 = I(E_1)$. The shape of the background within this range is set by

$$B_n(E) = \frac{A_x}{A_{total}} \Delta I_{1-2}. \quad (5)$$

The subscript n keeps track of the count of the iterations, such that $B_{n-1}(E)$ is the resulting background from the previous iteration. ΔI_{1-2} is the difference between the intensities at the start and end point as

$$\Delta I_{1-2} = I(E_2) - I(E_1). \quad (6)$$

The A 's denote different areas with A_{total} being the total area under the graph found by taking the integral

$$A_{total} = \int_{E_1}^{E_2} [I(E) - B_0 - B_{n-1}(E)] dE. \quad (7)$$

Finally, A_x refers to the area from E_1 to a point E . Hence,

$$A_x = \int_{E_1}^E [I(E') - B_0 - B_{n-1}(E')] dE'. \quad (8)$$

The iterative method naturally converges after only a few n repetitions [20, 9].

One could also force both ends of a peak to be even in intensities by connecting them with a linear function and subtracting it. One needs to be aware that this version of a background subtraction will lead to different results affecting especially the intensity ratios as when applying the (iterative) Shirley method. Generally, the linear background is classified as being wrong, because of its lack of including physical processes [21].

Choosing the correct line shape

The peaks shaping the XPS and HAXPES spectra can be described as being the zero energy-loss signals of photoelectrons and are located on top of the scattered background signal. Naively one would think that these features recorded from photoelectron emissions should be distinctly positioned at one particular energy and have an infinitely sharp line shape, but several physical processes involved in the creation and detection lead to a line broadening of the signal. To reproduce the original data envelope a mathematical algorithm is commonly being used, which iteratively based on an initial guess tries to reproduce the spectrum [21].

The intrinsic peak shape has a Lorentzian profile. When a photoelectron is being created through absorption of X-rays, the empty state is referred to as a core hole. Different processes can consequently fill the core hole again with a new electron from higher energy states. The period in between the photo electron escaping its original energy level and the de-excitation of the core hole itself follows an exponential decay specified by a certain lifetime distinct to the energy levels. The Heisenberg uncertainty principle relates the lifetime $\Delta\tau$ of the core hole to the energy range ΔE for the corresponding peak as

$$\Delta E * \Delta\tau \geq \hbar. \quad (9)$$

Hence, the $\Delta\tau$ for a core hole level is conversely proportional to the range of frequencies resulting in a finite peak signal with a specific full width at half maximum (FWHM). This phenomenon is called lifetime broadening and reduces the assumed infinite sharpness of the peaks to their natural linewidth [13, 21].

The instrumental uncertainties stemming from for example the monochromator or the analyzer can affect the resolution, which is captured as an additional line-broadening of the spectrum. Additionally can randomness of imperfections within the sample alter the line shape. These effects behave as Gaussian functions and require to be accounted for [22, 21, 9].

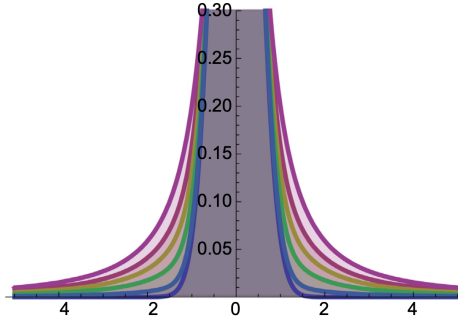


Figure 9: A typical peak shape resulting from an applied GLS function with varying mixing parameter $m = [0, 0.1, 0.3, .5, 0.7, 1]$ and the corresponding graphs having increased wings or tails with higher m s. Reproduced from Jain, Biesinger, and Linford [22].

A proper convolution of the Lorentzian and Gaussian function is called a Voigt curve or function, however can the combination of the two characteristic shapes be approximated in various ways. For this thesis the Gaussian-Lorentzian sum (GLS) was chosen to resemble the Voigt function. As proposed by the name the function is a sum of both functions with each contribution altered by a weighting factor or mixing parameter m , which varies from $m_{min} = 0.0$ for a pure Gaussian function as shown in Figure 9 (the narrowest/ blue line), up to a $m_{max} = 1.0$ for a purely Lorentzian profile (the outermost/ purple line)[22].

For this thesis, peak fitting was performed using IGOR Pro 8. The fitting algorithm approximates the experimental data by minimizing the figure of merit based on the following parameters motivated by the underlying physical principles discussed in the previous sections:

- Area
- Position
- FWHM
- Gauss-Lorentz ratio (GL ratio)
- (Asymmetry and Asymmetry-Translation)
- (Doublet Ratio and Doublet Shift)

For the analysis presented in this paper, the asymmetry could be set to zero since the peak fitting was focused on the components from the non conducting layers. The parameters referring to the doublets specifically, were also set to zero when treating peaks from the s -orbitals or when the narrow scan only included one part of the doublet pair. The area depends on the number of photoelectrons detected. This quantity then again is affected by various parameters, such as the number of sweeps used during measurement or density of the sample. Generally, it was kept as a floating parameter with broad boundaries, since it varies a lot between different spectra. The peak position is used to determine the corresponding core level and chemical state of the element. For the fitting the GL ratio= 0.3 and the doublet parameters were set according to values as reported in literature. The floating parameters included in the figure-of-merit minimization were the area, position and FWHM.

4 Results and Discussion

4.1 The effect of annealing on the crystal structure in the hafnia layer from XAS measurements

The method of XAS is fast way of getting an overview over structural changes taking place within a sample. The data produced with it does not require much processing, instead can the raw data be taken as it is. Comparing it among different samples, temperature steps or with literature allows to connect obvious differences to transitions between accessible crystal phases. For this, specifically the L2 and L3 edge of Zirconium bound as ZrO_2 were probed. In Figure 10 the spectral changes for both samples are shown.

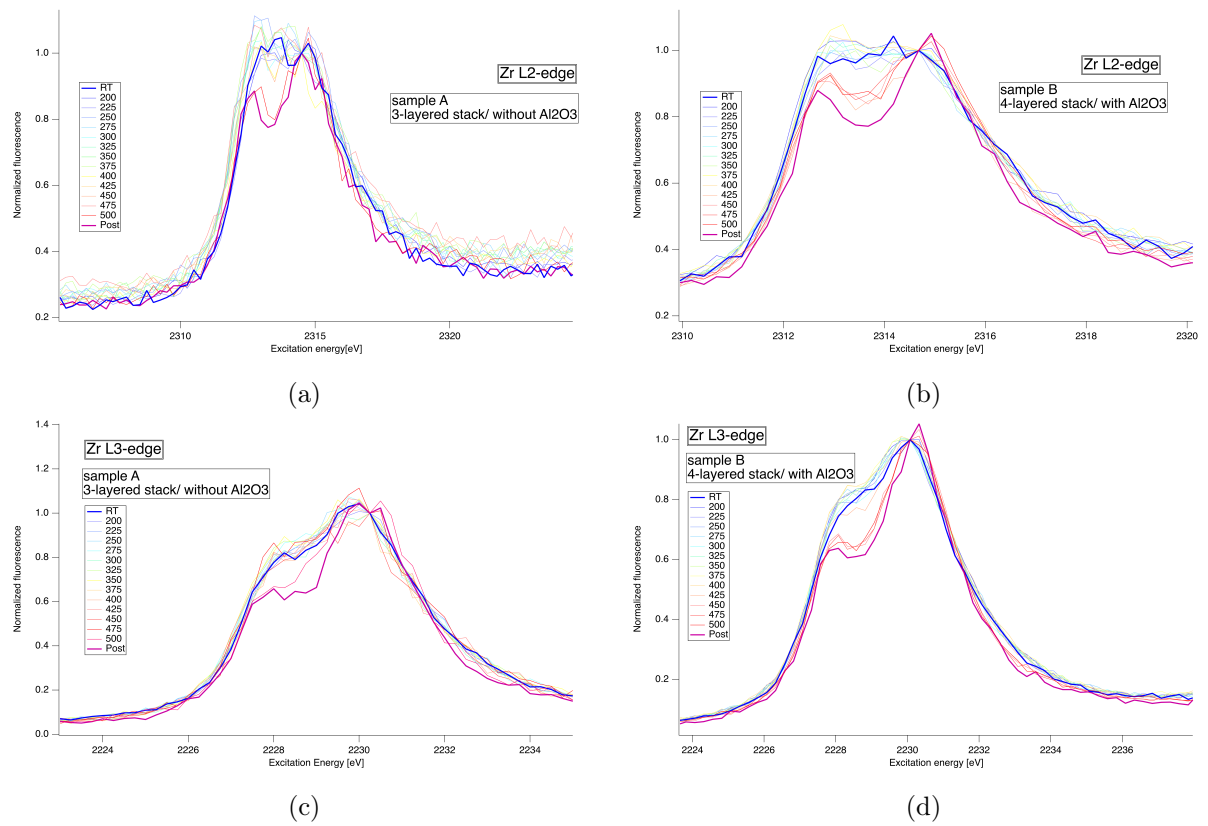


Figure 10: The XANES spectra to the left were taken on sample A and the ones to the right are spectra taken using sample B. The upper row is comparing two L2 spectra and on the bottom row one can see two L3 spectra.

From existing studies on similar RRAM-samples including a HZO thin film it is known and was expected for the samples to undergo a phase change from m- to the FE o-phase [23]. Since the phases are distinctly identified by their symmetry group and the structural arrangement of the atoms (see Table 1), it is possible to follow the transition process through XANES data.

In the spectra we can see a strong increase of the absorption signal at around 2312 eV for the L2 edge and at around 2227 eV for the L3 edge. In Figure 10a and 10b we see a rather broad peak at lower temperatures, which splits into two more distinct peaks at increased temperature, which also remain upon cooling. Similarly, in Figure 10c and 10d, a broad, asymmetric peak

evolves into two more distinct peaks upon heating.

Since discrete features are a measure of the symmetry, one can assume for the thin film in the the samples to be found in its m-phase, the point group with a lower degree of symmetry, or with a lack of a long range order, such as in a amorphous or polycrystalline thin film.

Hence, in both samples a transition between phases can clearly be observed. For sample structure A, on the left, this transition seems more drastic and temperature lies around $475^{\circ}\text{C} < T_{02} < 500^{\circ}\text{C}$. For sample structure B on the other hand, the transition seems to be less abrupt. The doublet shape is adapted more and more in a continuous transition starting already around temperatures of $400^{\circ}\text{C} < T_{03} < 425^{\circ}\text{C}$ and 450°C .

The phase established through the annealing process remains even when the sample was brought back down to room temperature. This demonstrates that the different shape of the spectra is not only due to the sample temperature, but instead indicates an annealing-induced irreversible change of the crystal structure. This last measurement at Post (heating) also shows the most distinct doublet shape throughout all four spectra and can be related to the adaption of the o-phase, maybe in combination with the t-phase.

From the XAS data one can identify at which temperatures a phase transition took place. For the further analysis HAXPES data will be examined to reveal possible connections to changes of the chemical composition of the film or electronic changes at the interface.

4.2 The identification of the film and interface composition as a result of the XPS fitting process

In order to obtain information on chemical composition from the HAXPES data, we need to discuss their fitting process.

A typical choice when investigating the chemical environment of the FE-hafnia layer is the Hf 3d core level. The components summing up to the fitting pattern, which was then verified by both samples and used on the different temperature steps, can be seen in Figure 11.

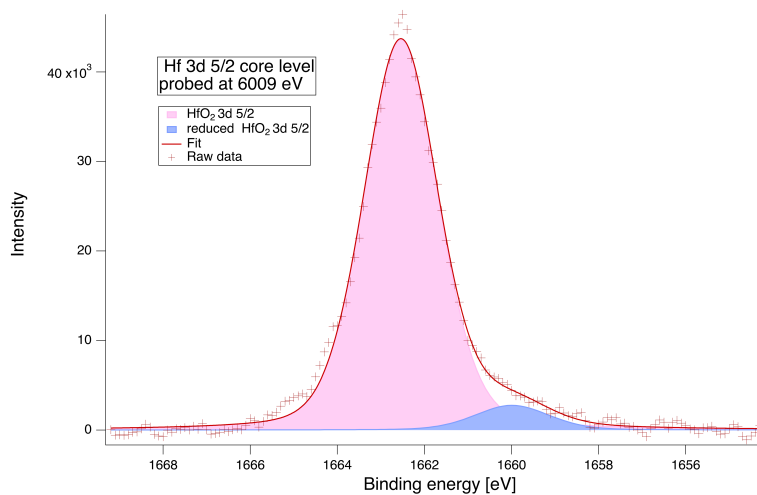
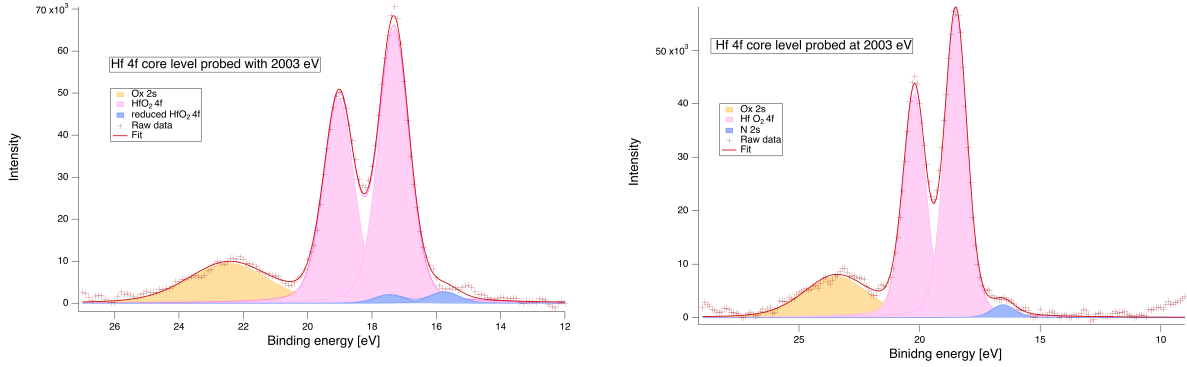


Figure 11: The spectra of the Hf 3d 5/2 core level were reproduced by fitting two components. A bulk peak from $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ (pink) and a suboxide peak (blue). This spectrum corresponds to sample A at $T = 200^{\circ}\text{C}$.

The spectrum consists of a bulk peak from $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ located at ~ 1662.5 eV in good accordance to existing measurements [24], and a smaller peak at lower binding energies of ~ 1660.1 eV for both samples.



(a) One version of the Hf 4f fit included 3 components including a oxygen peak, the bulk doublet and a doublet from Hf in reduced form, from left to right.

(b) The same data as in a) could also be reproduced by fitting the N 2s singlet instead of the suboxide state.

Figure 12: These spectra correspond to sample A at room temperature (RT) before annealing.

The second Hafnium core level under investigation is the Hf 4f doublet. The fitting process though, turned out to be not so straightforward. Two reasonable alternatives of component compositions reproducing the data were identified as can be seen in Figure 12.

The main doublet comes from Hafnium predominantly bound in a $\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$ configuration. Due to oxygen vacancies, the Hafnium exists in different oxidation states causing each causing an additional peak at lower binding energies. In existing literature they are observed with a core level shift of -1.2, -2.1 or -3.3 eV depending on the order of oxidation [25]. Only one additional suboxide was used for fitting in Figure 12a with lower intensity (blue doublet). However, there is another core level located around this position possibly interfering, namely the N 2s level. This component would also be a valid choice considering the TiN top electrode (see again the blue component in Figure 12b).

Although both versions of this spectra on their own seem valid, for the further analysis the one presented in Figure 12a was chosen. Comparing to the Hf 3d spectrum (see Figure 11) makes it clear, that there has to be some reduced Hf present in the samples, so they have to appear along with all different Hafnium core levels. The main peak of the bulk doublet was then found to appear at $E_b \approx 17.3$ eV and the suboxide component with a shift of ~ -1.5 eV.

Using HAXPES instead of XPS was especially important for this study such that the probing depth could be increased to reach the buried layers and interfaces. The analysis of the interfaces with the InAs substrate can be carried out by tracking possible changes in the As and In core levels. Specifically for this paper fitting processes were performed on 3 different spectra presented in the following paragraphs.

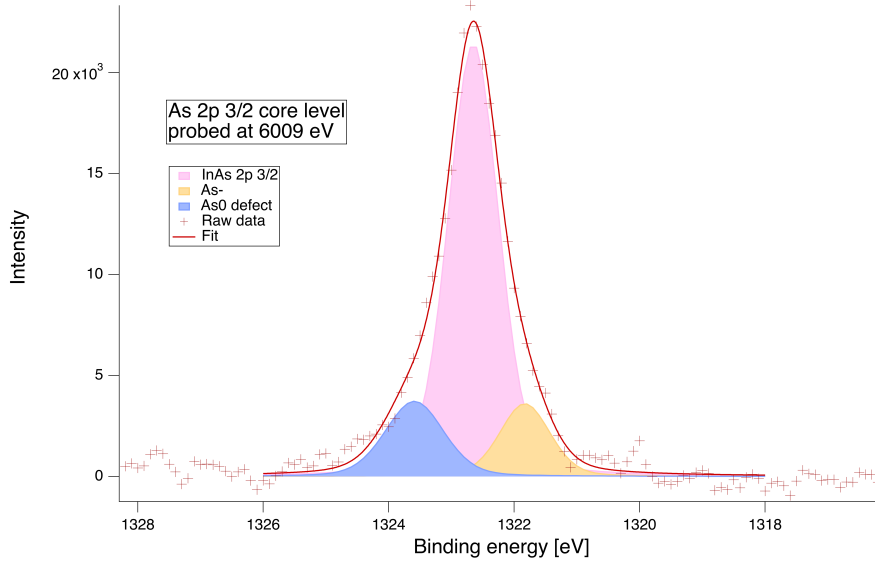
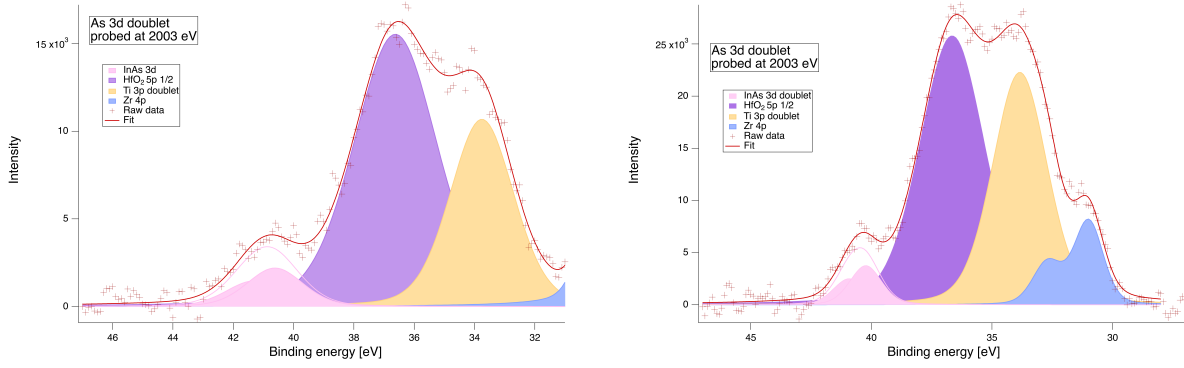


Figure 13: The energy range around the E_b of the As 2p 3/2 peak (pink) seems to include several components of lower intensity on both sides. The one (blue) on the higher energy side comes from a defect state As⁰ and the origin of the contribution overlapping on the lower energy side could not be identified. This spectrum corresponds to sample A at RT before annealing.

In the spectrum presented in Figure 13 one can see a main peak at $E_b \approx 1322.7$ eV and two smaller components creating shoulder-like shapes at $E_b \approx 1323.6$ eV. and $E_b \approx 1321.8$ eV. The component at lowest energies (yellow) could not be identified and is referred to as As⁻ contrary to known oxidation states positioned at higher energies. The difference between the other components amounts to ~ 1.2 eV and typically oxides are observed at even higher energies at about 1325 eV. Instead the component is assigned to result from a defect state As⁰. It was expected that the heating process might promote oxygen flow and induce the formation of interfacial oxide layers. When comparing the data to existing literature [26], it seems as if there was no oxide recorded in both samples.

Complementary to this data, a less bound core level of As, the 3d doublet, was measured with the incident X-rays at lower energies. One can observe the effect of this choice in the spectra and how different components overlapping in this energy region show up at higher intensities whenever they belong to less buried layers of the stacks.

Figure 14 shows again two slightly different fits. In this case Figure 14a corresponds to the spectra recorded over a smaller range as it was done for sample A. The extended spectrum was then chosen when changing to sample B. One can clearly see how the energy range used for sample A ends in the middle of a component (see also Figure 20 in the Appendix). By that, one was prevented from using the iterative Shirley method for the background subtraction as done on the spectra from sample B. The start E_1 would have forced the half-measured peak to zero. Instead a linear background was chosen to approximate the background by aligning the graph with the obvious background signal towards higher E_b 's such that the signal on the low E_b limit remained above zero. When comparing the effect of temperature induced changes between the samples one should keep this difference in the data processing in mind.



(a) The spectrum for sample A was limited to an energy range such that it ended in signal contribution of the Zr 4p doublet (blue). The most interesting component for this project is the As core level (pink), such that other components as the individuals making up the Ti 3p doublet were not further resolved. Here $T = 200^\circ\text{C}$.

(b) The extended range as it was measured for sample B clearly shows the Zr 4p contribution towards lower E_b 's. Here $T = 225^\circ\text{C}$.

Figure 14

The spectrum is generally dominated by photoelectrons originating from the Hf 5p 1/2 level and the Ti 3p doublet, which were not resolved into their individual doublet components or smaller contributions. The signal for the Arsenic core levels in comparison is much lower and the ratio of the noise fluctuations to the original signal is accordingly higher as well, which makes a qualitative analysis more difficult. It was chosen to not fit the defect state separately as done and mentioned in other experiments [27], since its intensity would lie within the error due to the noise as suggested by the complementary data of As 2p and it does not relate to oxygen vacancies. The As 3d peak was found to appear at $\sim 40.3\text{ eV}$ in sample A and $\sim 40.2\text{ eV}$ in sample B.

Lastly, chemical environments of In as the second constituent of the substrate were analyzed. The core level measured consequently was the 3d 5/2 peak. By different papers it was proposed for the bulk to be found around 444.06 eV [28]. From both samples in this data set a peak position at $\sim 444.2\text{ eV}$ obtained.

Just as it was initially assumed for the Arsenic core levels, one could have expected some oxide peak interfering with the bulk peak with a energy shift of about $+ 1.03\text{ eV}$ [28]. As can be seen in Figure 15 there was no contribution measured, which makes sense considering there was no oxide formation found in As. Taking the highly fluctuating noise into account, as it can be observed on the regions at zero intensity, it clear that a possibly existing small contribution would just fall within this error.

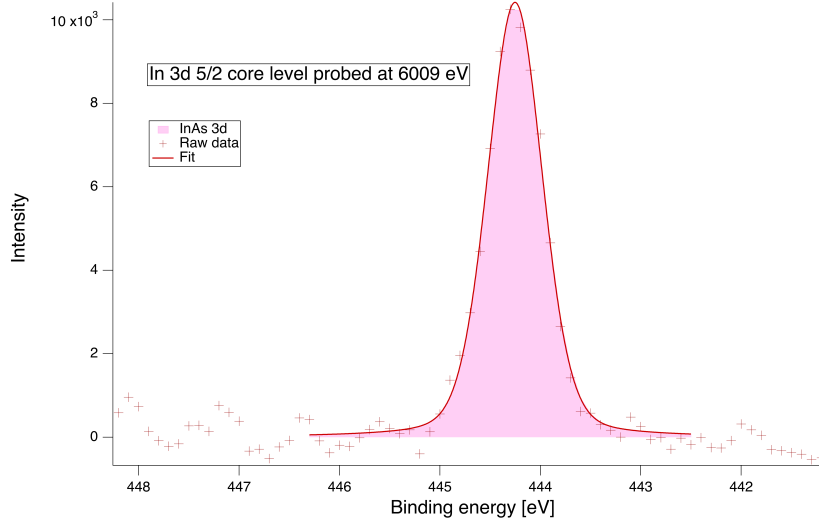


Figure 15: The narrow scan of the In 3d 5/2 peak was fit with a single component.

4.3 Structural and electronic changes of the thin film and interface upon annealing

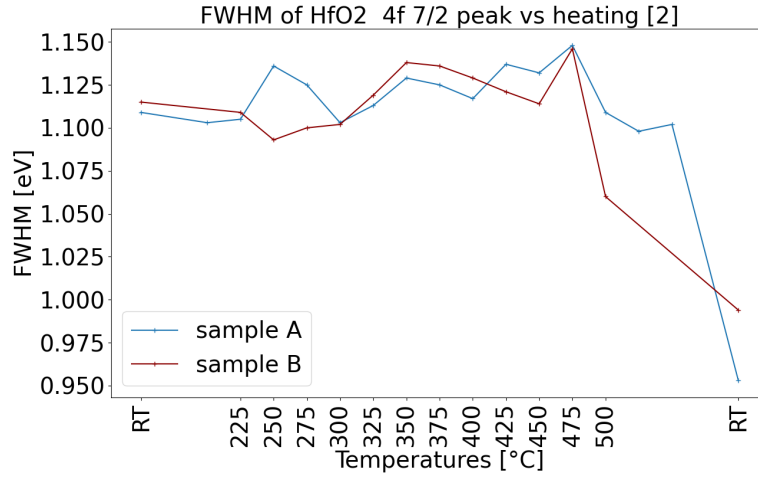


Figure 16: The width of the Hf 4f 7/2 peak has undergone a similar change in both samples of a sharp decrease at temperatures higher than 475°.

Analyzing the values for the FWHM of the peaks upon annealing is a way of determining the possible existence of additional sub-components forming or increasing, which have not been resolved individually. In Figure 16 one can observe how the width of the Hf 4f peak in both samples remains more or less constant in the beginning of the measurements around a value of ~ 1.12 eV. A similar existence of different turning points as observed from the XANES analysis can be identified from these two graphs. After about 475° the peaks seem to rapidly decrease in their width for sample B. This is earlier as observed for sample A, where the jump in width takes place between the last measuring point of $T = 550^\circ\text{C}$. Generally, a smaller FWHM is a measure for a higher degree of order or periodicity within the sample on an atomic scale. It indicates a possible crystallization of the thin film into one of its accessible crystal lattices upon

annealing. This conclusion is in good accordance with the results obtained and presented on the XAS method.

Furthermore, it is worth to go back to the BEs of the peaks, whose values were already mentioned as a result of the fitting process. The BEs as stated correspond to the average of the positions over all temperature steps. However, this parameter was kept floating as mentioned in the Methodology section. It had the freedom to vary within certain boundaries such that its optimal value could be determined through the fitting algorithm.

As can be observed in the graphs presented in the Appendix, the BE's did shift during the heating process. The most obvious change in the BE's of a single core level was observed in the data of the Hf core levels in both samples (compare to Figure 21 and 22 in the Appendix). The change in the numerical values is presented in Figure 17.

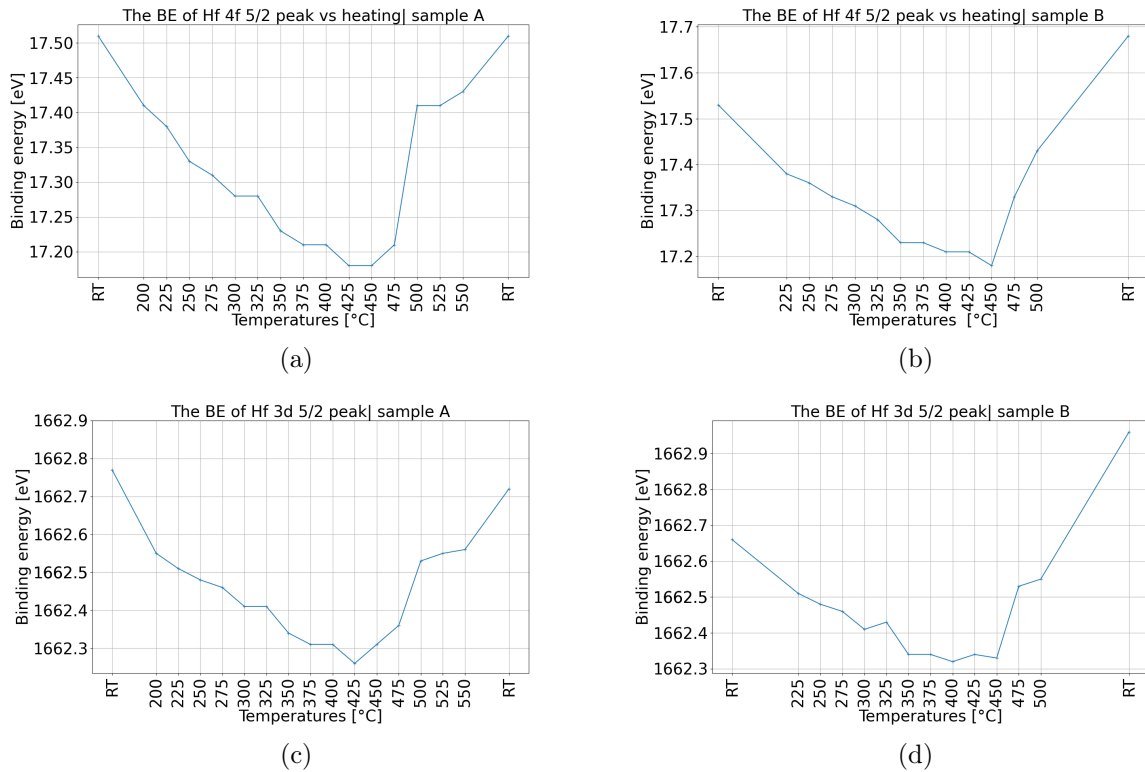


Figure 17: The graphs represent the changing binding energies for the Hf 4f 5/2 core level in a) for sample A and b) measured on sample B. The graphs of the second row show the same quantity but measured for the Hf 3d 5/2 core levels, again with sample A on the left and sample B on the right.

Starting the measurements at room temperature (RT), the change in BE seems to decrease continuously and almost linearly, until the heating passes a threshold of $475^{\circ}\text{C} < T_A < 500^{\circ}\text{C}$ for sample A and $450^{\circ}\text{C} < T_B < 475^{\circ}\text{C}$ for sample B. The evolution of the core level energy changes suddenly after this threshold, such that the smooth shift turns into a rapid increase or jump towards opposite energies. Also, the change seems more abrupt in sample A, which can most clearly be seen at the jump from 475°C to 500°C in Figure 17a, but the same jump of

smaller height appears also in Figure 17c. The fact that the temperatures fall into the same region as the transition temperature observed in the XAS data suggests that the phenomena must be connected. Additionally, this hypothesis is supported by the fact that the transition appears to take place at lower temperatures and that the sample B seems to undergo a smoother phase change from both, the HAXPES and XAS data. Also, one should consider that within each group of the samples A and samples B the composition remains the same and all were put under the same conditions for the XAS and XPS part of the measurement, but in reality there might still be differences in the temperature of a few degrees caused by variations in the heating kinetics due to the physical difference of the actual samples.

In sample A (see Figure 17a and 17c) the peak positions end up being the same comparing the room temperatures before and after the annealing process. They are located for the 4f level at

$$E_{b-RT1} = E_{b-RT2} = 17.51 \text{ eV}$$

and for the 3d level

$$E_{b-RT1} = E_{b-RT2} = 1662.7 \text{ eV}.$$

For sample B instead the BE jumps to higher values remaining still after the annealing with

$$E_{b-RT1} = 17.53 \text{ eV} \quad \& \quad E_{b-RT2} = 17.68 \text{ eV}$$

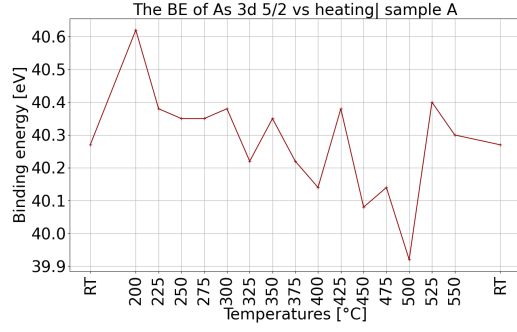
and

$$E_{b-RT1} = 1662.7 \text{ eV} \quad \& \quad E_{b-RT2} = 1663.0 \text{ eV}.$$

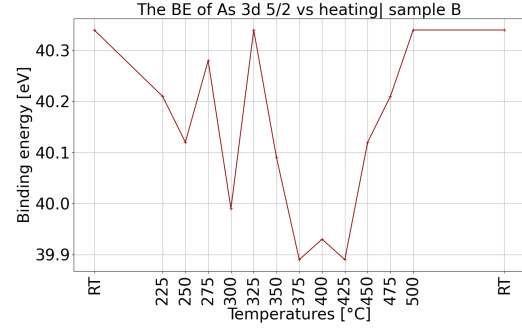
This observation of the difference in the positions of the BE's seems similar to the results obtained in the XAS data, where the phase change remains even throughout cooling the samples down again. The samples were chemically and irreversibly altered through the annealing process.

A common shift of peaks could also be induced by charging effects across the sample shifting the Fermi level and all core levels along with it. This requires a similar shift of the same amount being reproduced by all other components in the sample.

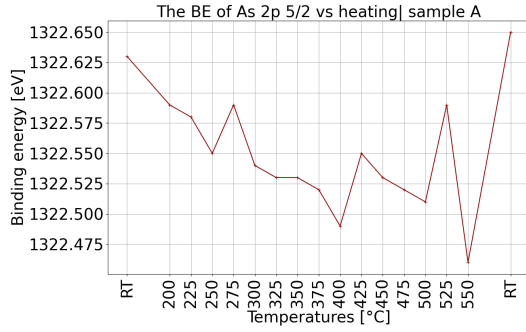
Looking at the spectral analysis from the Appendix suggests that there is a slightly smaller, but still visible shift in the As 2p levels (compare to Figure 23 in the Appendix). Looking at the As 3d levels (Figure 24 in the Appendix) does also justify why the fitting process was required for a quantitative analysis. By the bare eye it is hard to sort which changes are due to which component. Lastly, the In 3d peak is showing a shift identifiable from the side lines of the peak (compare Figure 25 in the Appendix). These observations are quantified in the Figures 18 and 19.



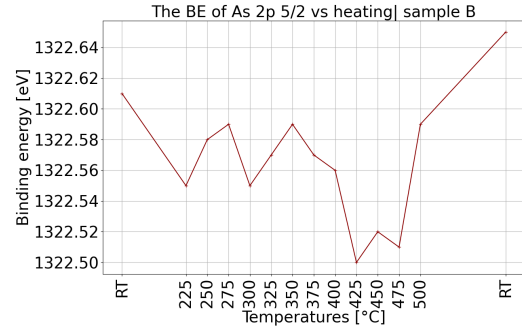
(a)



(b)



(c)

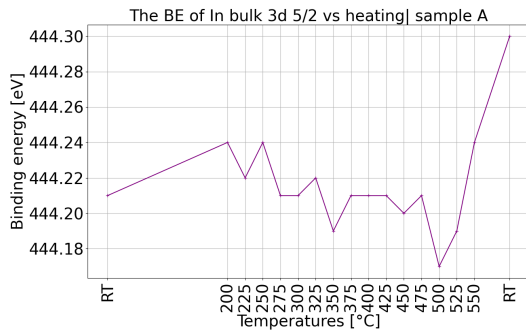


(d)

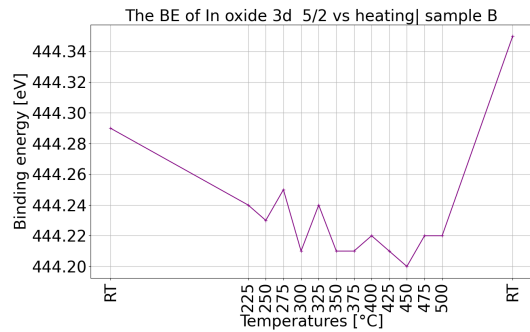
Figure 18: The change in the position of the As 3d 5/2 peak is being displayed in a) and b) for sample A and B, respectively, and of the As 2p 5/2 peak in the bottom row for the same samples.

The change in position for the Arsenic core levels is less smooth, but instead affected by a lot of fluctuations. It is hard to make any statements or comparison to the Hafnium observations. One could say that all four spectra exhibit the same jump at high temperatures. Also, the assumed jump is of order $\Delta E_b \approx 0.4 \text{ eV}$ for the 3d 5/2 peaks, but only about $\Delta E_b \approx 0.15 \text{ eV}$ for the 2p peaks.

The trend captured in the Indium spectra in Figure 19 seems much more similar, but again the range over which the BE shifts are not the same as for the Hf data. They are only about $\Delta E_b \approx 0.1 \text{ eV}$.



(a)



(b)

Figure 19: Along with the heating process a change in the binding energy for the In 3d 5/2 core level was observed both for sample A (a) and B (b).

The change is not constant across all measurements. In general, the binding energy shifts more for the Hf core-levels and less for the In and As 2p core-levels. The As 3d core level too noise to identify a real trend. This might indicate that there is a certain shift of the electrostatic potential for the entire sample as visible at the substrate. The oxide layer experiences an additional shift due to the formation of an electric field, or charge layer, across the semiconductor-oxide interface. One can conclude that the cause for ΔE_b must be a combination of charging effects and an alteration of the stoichiometry of the samples caused by a phase transition into the FE o-phase.

4.4 The influence of a thin alumina barrier

The main difference between the samples is the difference in the changing or transition temperatures observed in various results. First the XAS spectra show how the samples without the Al_2O_3 layer undergo changes only at much higher temperatures, whereas the samples B and D already experience these changes about $50^\circ\text{C} - 75^\circ\text{C}$ earlier. As suggested by the analysis on the BE of the Hf core levels, which reproduced the clearest results out of all elements, the difference in BE is even greater when comparing the final to the initial state of the samples.

It seems as if the Al_2O_3 layer promotes a transition at lower temperatures already, which is important for the processing of ferroelectric devices. The thermal conditions do not need to be as extreme, which would reduce the energy consumption of the fabrication. Additionally, the InAs substrate is sensitive to heat and lowering temperatures during production takes away thermal stress from the III-V semiconductor ensuring its state to remain of higher quality. These type of semiconductor-alloys provide a high electron mobility [23], such that their quality is a decisive factor for the operating mode of the RRAM-devices.

5 Conclusion and Outlook

The aim of this work was to successfully investigate the temperature induced phase transition to the ferroelectric o-phase of the HKMG dielectric, a HZO ultrathin film. A clear phase transition as expected was demonstrated through the XANES data. It suggests a permanent alteration of the sample stoichiometry that remained stable even after the heating process, when the sample had returned to room temperature, suggesting that the final state of the samples is the FE o-phase. Similar transition temperatures and again, a permanent alteration of the samples were also observed on the HAXPES data, where the initial and final measurements representing similar thermal conditions do not coincide. The data analysis of the HAXPES measurements required peak fitting to identify the chemical environment of the samples and revealed the presence of possible oxidation or defect states.

A similar trend of change observed across all elements in the HAXPES data points to an additional alteration of the electrical potential through charging effects. However, the effects were observed to take place on slightly different scales, such that one needs to separate the effects into a general shift of the Fermi-level and an additional change in the electric potential due to a dipole forming at the interface.

The XPS spectra have shown that there was no significant oxygen transfer as often promoted by increasing temperatures. Some reduced HfO_2 as revealed through fitting the Hafnium core levels proposes the presence of oxygen vacancies in the layer, but did not seem to change during the process. Hence, there was no formation of an oxide interface in between the InAs substrate and the gate oxide recorded as initially expected.

The effect of the additional Al-oxide layer was discovered to adjust the transition temperature to lower values, such that the final phase is being induced at even lower temperatures. This behavior could be utilized to optimize fabrication processes toward more energy efficient and more gentle on the sensitive substrate ones.

The purpose of the in situ annealing experiment was to mimic real conditions as used during device fabrication. In this experiment the heating process was running over several hours, hence over quite a long period, but industrial methods can be performed over a much shorter period. The similarities of the environments could be increased by changing to a rapid thermal annealing procedure instead.

The obtained results are very promising, as they indicate that ferroelectric phase transition can occur without detrimental interface oxide formation. However, further work is required to understand the electronic changes in more detail.

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A Additional Figures

A.1 Comparison of the As 3d spectra of sample A and B

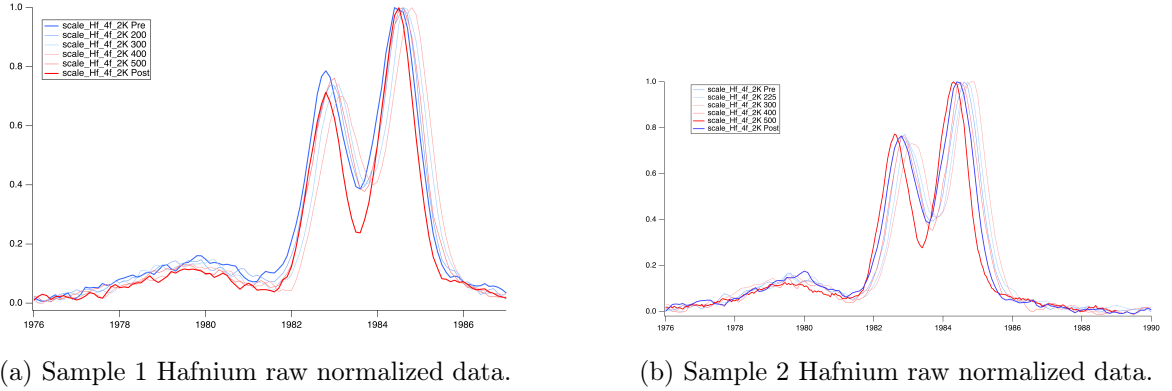


Figure 20: The range of the same core levels was different for both samples, such that the energy range used in sample A (red curve) cuts off a contribution as suggested by the spectrum from sample B and the clear shoulder at around $E_k \approx 1970$ eV.

A.2 Effect of sample temperature, as seen in the HAXPES raw data

Hafnium

4f

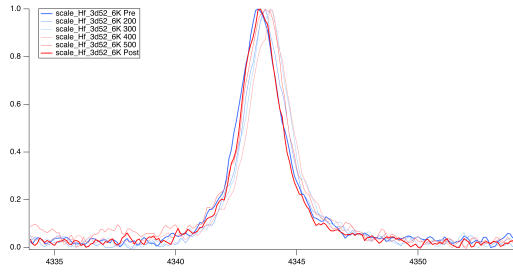


(a) Sample 1 Hafnium raw normalized data.

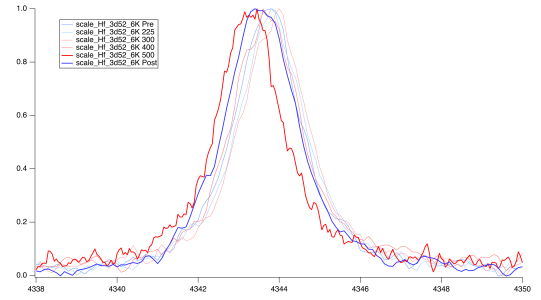
(b) Sample 2 Hafnium raw normalized data.

Figure 21

3d 5/2



(a) Sample 1 Hafnium raw normalized data.

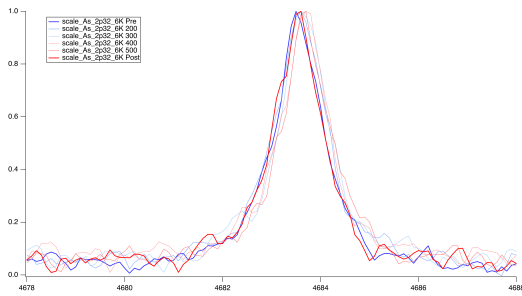


(b) Sample 2 Hafnium raw normalized data.

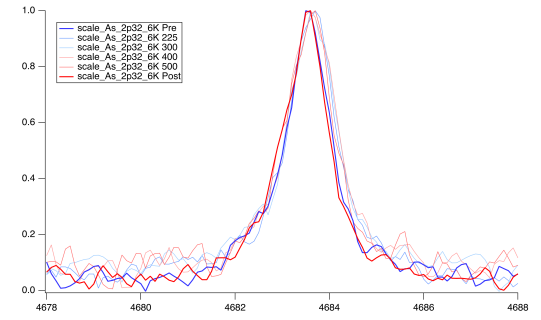
Figure 22

Arsenic

2p 3/2



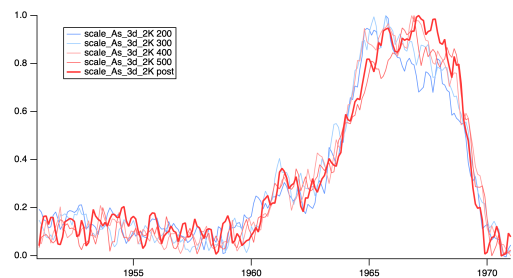
(a) Sample 1 Arsenic raw normalized data.



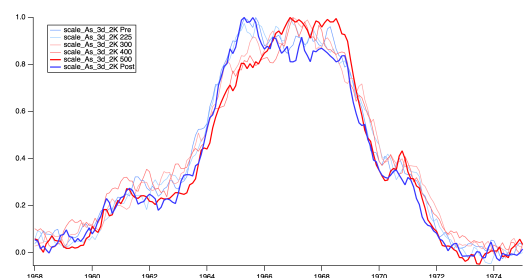
(b) Sample 2 Arsenic raw normalized data.

Figure 23

3d



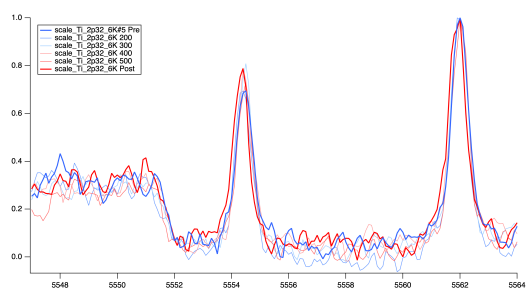
(a) Sample 1 Arsenic raw normalized data.



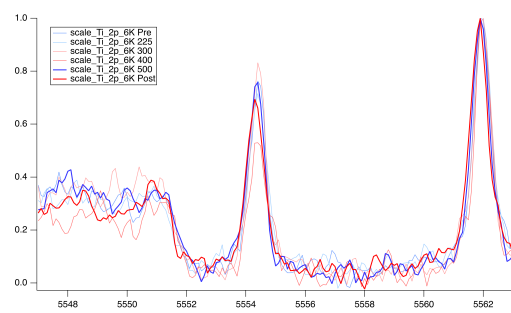
(b) Sample 2 Arsenic raw normalized data.

Figure 24

Indium 3d doublet



(a) Sample 1 Indium doublet raw normalized data.



(b) Sample 2 Indium doublet raw normalized data.

Figure 25