Hard x-ray photoelectron spectroscopy of tunable oxide interfaces

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ABSTRACT
The tunability of the oxygen content in complex oxides and heterostructures has emerged as a key to designing their physical functionalities. Controlling the interface reactivity by redox reactions provides a powerful means to deliberately set distinct oxide phases and emerging properties. We present routes on how to control oxygen-driven redox mechanisms in ultrathin ferro(i)magnetic and ferroelectric oxide films and across oxide interfaces. We address the growth and control of metastable EuO oxide phases, the control of phase transitions of binary Fe oxides by oxygen migration, the in operando determination of NiFe2O4/SrTiO3 interface band alignments, as well as the role of interfacial oxide exchange in ferroelectric HfO2-based capacitors—uncovered by the unique capabilities of photoelectron spectroscopy and, in particular, using hard x-rays.

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I. INTRODUCTION

The last decade has witnessed that physical functionalities of ultrathin solid films are not only controlled by their bulk electronic structure but, to a significant extent, by their interfaces.1,2 In metal oxides, the tunability of the oxygen content represents the crucial degree of freedom, which enables us to design material functionalities beyond, e.g., the property portfolio of semiconductors.3 Whether oxygen ions are present or absent in the lattice can either be a mandatory prerequisite or detrimental for the emergence of oxide properties, and may actually induce new ones.4 If metal oxide thin films are joined in a heterostructure, thermodynamic and electrochemical nonequilibrium conditions may drive atom and charge exchange across their contacting interfaces. Interface chemical reactions will occur in the case of oxygen transport; charge transfer is promoted by compensating different contact potentials.

In particular, with regard to reduction-oxidation reactions, the importance of the choice of oxide substrate materials has typically been downplayed. Only lately, the huge potential of this determining factor was received for the design of oxide functionalities via interfacial oxide exchange, such as magnetic or ferroelectric oxides.5,6 The impact of the presence or absence of oxygen is, however, antagonistic: While oxygen ions are an inevitable part of the complex exchange mechanisms in magnetic oxides and their absence leads to a degrading of properties, oxygen vacancies have been identified to induce ferroelectricity in dielectric oxides.7 Here, a well-balanced presence of vacancies can stabilize a robust
ferroelectric state over thousands of electric field switching cycles. Exploiting the tunability of the oxygen content in the materials themselves and understanding interface formation are versatile strategies in designing new functional properties through controlled interfacial oxygen exchange.

X-ray photoelectron spectroscopy (XPS) has been developed as one of the most powerful tools to explore the chemical composition and electronic structure of solids. While the probing depth of XPS using laboratory x-ray sources is well suited for studying the subsurface region of an ultrathin film (about 3–5 nm), the photoelectron information depth is significantly enhanced to about 20–30 nm by performing spectroscopy in the hard x-ray regime (HAXPES). The strongly reduced photoelectron cross sections at 20 electron information depth is significantly enhanced to about 3 nm, the spectroscopic signatures of oxygen vacancies are of indirect nature though and only become apparent by rigid binding energy shifts is possible down to a few percent, which permits uncovering redox processes by valence changes of oxide phases. The spectroscopic signatures of oxygen vacancies are of indirect nature though and only become apparent by rigid binding energy shifts of core levels, which are caused by changes of the Fermi level position in an altered local electric potential. This approach is also used in the so-called Kraut method, which is successfully applied to derive the band alignment at metal oxide/semiconductor interfaces, provided that there are no chemical reactions. For such samples, the variant of in operando HAXPES becomes applicable, which serves as a powerful tool to determine the band alignment and the chemical state of (oxide) interfaces under operation conditions of an electric device in a single measurement.

This article highlights research examples for which laboratory- and synchrotron-based photoelectron spectroscopy emerged as the key experimental probe to uncover complex oxygen exchange mechanisms in oxide ultrathin films and at oxide interfaces, as schematically depicted in Fig. 1. In particular, emerging interface states and their tunability in ferromagnetic and ferroelectric oxide heterostructures—covering both fundamental aspects and exploring application-relevant devices—are discussed.

II. REDOX-ASSISTED GROWTH AT METASTABLE OXIDE INTERFACES

In Sec. II A, we present selected examples of how laboratory- and synchrotron-based XPS enables stabilizing the physically exceptionally versatile though metastable europium monoxide as ultrathin films in all-oxide heterostructures. EuO is a prototype Heisenberg ferromagnet with a spin-only magnetic moment of \( S = 7/2 \) and semiconducting properties. This rare combination has lead to numerous past and recent works on the fundamental spin-dependent electronic properties. In particular, interfacing EuO to oxides and metals gives rise to emerging quantum states, which origin either from atomic-scale interface growth control or are induced by proximity effects at well-defined interfaces. Recent examples include the emergence of two-dimensional electron systems, interfacial spin-charge conversion, or induced ferroelectric states.

Although being particularly prominent as the Heisenberg model system, the growth of EuO single-crystalline and ultrathin films is exceptionally challenging because Eu\( \text{II} \)O is the metastable suboxide of europium—in contrast to its stable but paramagnetic counterpart Eu\( \text{III} \)O\(_3\). Both a meticulous control over the oxygen backpressure during Eu deposition and the finding that small excesses of Eu metal on hot substrate surfaces are tolerable have enabled the so-called “distillation” growth of stoichiometric EuO on inert substrates. Not surprisingly, growing EuO on oxide substrates further complicates the synthesis because the interface also needs to be taken into account as a potential oxygen source or sink. Hence, the oxygen-related interface thermodynamics and kinetics strongly determine the EuO film and interface properties as a direct consequence of the growth process. To gain a fundamental understanding of the growth-dependent evolution of this metastable oxide interface, the proceeding EuO deposition process and growth-related interface formation are tracked by in situ XPS.

A. EuO/YSZ: A quasi-inert “model” interface?

EuO on yttria-stabilized zirconia (YSZ) is typically regarded as a model system because YSZ (001) and EuO (001) are
lattice-matched, and the interface is usually assumed to be quasi-inert, which should result in both structurally and chemically well-defined film/substrate interface.21 This assumption is corroborated by a thermodynamic Ellingham analysis, which is, however, strictly valid for bulklike systems only.23

Here, we focus on the regime of ultrathin EuO films with thicknesses of a few monolayers deposited by molecular beam epitaxy (MBE). By using *in situ* lab-based XPS (Al Kα), we probe the stoichiometry of the first monolayers of EuO at the EuO/YSZ interface. Without adding any additional oxygen gas, the Eu metal deposition duration was varied between 1 and 40 min at a substrate temperature $T_s = 400$ °C. We developed a lab-based strategy for nondestructive depth profiling, i.e., monolayer-controlled Eu deposition is performed stepwise and alternated with *in situ* XPS analysis.

The corresponding Eu 3d$_{5/2}$ spectra for 1, 2, 5, and 40 min of Eu deposition are shown in Fig. 2(a). For 1 and 2 min, we find a significant ratio of Eu$^{3+}$ contributing to the spectrum. After 5 min, the Eu$^{3+}$ ratio is drastically reduced but still clearly observable, while after 40 min, the spectrum shows a pure Eu$^{2+}$ signal.

Observing Eu$^{3+}$ in the initial phase of the growth process indicates the unexpected formation of Eu$_2$O$_4$ or Eu$_2$O$_3$ at the EuO/YSZ interface. Without adding any additional oxygen gas, the Eu metal deposition duration was varied between 1 and 40 min at a substrate temperature $T_s = 400$ °C. We developed a lab-based strategy for nondestructive depth profiling, i.e., monolayer-controlled Eu deposition is performed stepwise and alternated with *in situ* XPS analysis.

B. EuO/SrTiO$_3$: The well-controllable redox interface

Using the previously acquired knowledge on the EuO/YSZ interface, we extend our study to the well-known “work-horse” of oxide electronics, SrTiO$_3$ (STO). Applying the thermodynamical Ellingham analysis, we learn that SrTiO$_3$ and EuO shall not coexist and that we ought to expect Eu$_2$O$_3$ formation. In order to track the oxygen supply at the EuO/SrTiO$_3$ interface, we deposited the Eu metal at $T = 500$ °C stepwise on SrTiO$_3$ (001) and performed *in situ* XPS after each deposition step.

Contrary to the thermodynamic prediction, we observe Eu 3d$_{5/2}$ spectra dominated by the Eu$^{2+}$ valence, which is associated with EuO in Fig. 2(b). Indeed, only the first interfacial layer forms as Eu$_2$O$_3$. For consecutive growth of further layers, the oxygen supply obviously is sufficiently limited, which enables an epitaxial growth of stoichiometric EuO on SrTiO$_3$.

We argue that this mechanism is due to the limited oxygen mobility of the interface—once an initial layer of the Eu$_2$O$_3$ rich phase is formed. This ultrathin intralayer seems to effectively hinder the oxygen supply from the SrTiO$_3$ substrate. The oxygen conductivity of the SrTiO$_3$ substrate is, however, strongly dependent on temperature: At room temperature, SrTiO$_3$ shows very limited oxygen mobility as the EuO/STO interface forms a two-dimensional electron gas (2DEG) as a result of the local oxygen depletion from SrTiO$_3$ to EuO.17 Performing higher temperature studies (at and above 700 °C), we were able to show only highly oxidized Eu$_2$O$_3$ forms. Obviously, the oxygen mobility now exceeds a critical value, and both film and SrTiO$_3$ serve as a permanent source of oxygen for EuO oxidation. This tunability of interfacial oxygen supply enables performing oxide on oxide growth of two reactive oxides in a well-defined temperature range.

**FIG. 2.** (a) XPS of the Eu 3d$_{5/2}$ core level of EuO/YSZ films synthesized by depositing metal only for several deposition times. (b) Lab depth-resolved XPS of an EuO/SrTiO$_3$ bilayer. (c) Depth profile of a buffered oxide interface system obtained using HAXPES at KMC-1 (BESSY-II). The content of Eu$^{2+}$ increases toward the surface, this is caused by a combination of oxygen mobility and thermodynamic potential through the complex YSZ/ITO interface.
This finding underlines the importance of the oxygen mobility of the film and substrate as active parts of the growth process. Here, we find a temperature-dependent growth window to perform oxide-on-oxide growth of the otherwise reactive oxides EuO and SrTiO$_3$. The interface may even be used to functionalize the system as 2DEG or as a tunnel barrier, depending on the type of oxygen vacancies formed in SrTiO$_3$ by the redox process at low temperatures without oxygen replenishing. On the methodical side, the alternating Eu deposition and XPS analysis enable an extensive pre-characterization prior to synchrotron measurements, e.g., unveiling aforementioned two-dimensional electron gas. Moreover, it highlights the usefulness of a combined lab XPS/MBE infrastructure for the characterization of challenging the synthesis of metastable oxide-on-oxide materials.

C. EuO/ITO: An instable oxygen source and sink

What happens eventually if metastable EuO is to be stabilized on an oxide template, which itself is a very good oxygen ion conductor? A suitable substrate to investigate this aspect is ITO/YSZ, i.e., a “virtual substrate” for which an indium tin oxide (ITO) layer is grown sufficiently thick on lattice-matched YSZ (001) such that the YSZ substrate can be disregarded. The growth is performed by reactive MBE at 400 $^\circ$C using a Eu flux rate of 0.13 Å s$^{-1}$ and an oxygen partial pressure of 1.7×10$^{-7}$ mbar. A 10 nm Al capping is applied after growth to prevent further oxidation.

In order to enable a nondestructive chemical depth-profiling of the EuO film and interface, we here employ hard x-ray photoelectron spectroscopy using variable synchrotron radiation. The HAXPES experiments were conducted at the KMC-1 beamline at BESSY II (Berlin) with the HIKE endstation. We vary the inelastic mean free path $\lambda$ of the emitted photoelectrons as function of the photon energy between 3 (2010 eV) and 9 nm (5000 eV). The results are shown in Fig. 2(c). We study the Eu 3d$_{5/2}$ core-level and normalize the data to the binding energy of Eu$^{3+}$. In doing so, we observe a chemical gradient with a small content of Eu$^{2+}$ at the interface, which increases toward the surface. Using established models, we identify this as a mixed- or bilayer system with 1.2 nm of EuO and the rest of the nominally 4 nm layer consisting of Eu$_2$O$_3$. The thermodynamic Ellingham analysis clearly reveals that EuO on ITO is an unstable phase, unlike YSZ, which is expected to be compatible with EuO growth. We note that at these temperatures, oxygen is extremely mobile in ITO; for samples grown at room temperature, fully reduced In metal is observed at the substrate’s surface (not shown). In this way, HAXPES enables nondestructive chemical depth profiling by varying the probing depth across interfaces and quantifying the different chemical states of the exemplarily highly reactive EuO/ITO interface.

D. Opportunities of redox-assisted oxide growth

The interface-sensitive studies performed by lab XPS and HAXPES show that even on commonly used model substrates like YSZ, which is, e.g., regarded as inert with respect to the formation of Eu$^{3+}$, interfacial redox processes have to be taken into account. Figure 3 summarizes the acquired results, contrasting in (a) the thermodynamical expectations with (b) the spectroscopically acquired results on interface formation of ultrathin film deposition of EuO on (001)-oriented ITO, STO and YSZ substrates, respectively.

Redox-driven interface reactions need to be considered for stabilizing EuO or other metastable materials on any oxide substrate. As summarized in Fig. 4, we performed a study on the growth of EuO onto different oxide substrates, i.e., SrO (5 nm on SrTiO$_3$), YSZ, LAO, MgO, and LSAT. We find that the substrate’s oxygen ion conductivity correlates well with the film thickness after 5 min of Eu deposition. We could show that the Eu distillation condition can be fulfilled on all of these oxides, rendering them eligible for a kinetic (external) oxygen-free growth mode as described for SrTiO$_3$.

FIG. 4. Correlation of oxygen ion conductivity of selected oxide substrates and redox-grown Eu oxide film thicknesses.
This interface-sensitive study performed by lab XPS shows that even on the commonly used model substrate YSZ, which is regarded as inert with respect to the formation of Eu$^{3+}$, interfacial redox processes have to be taken into account. This circumstance has to be considered for growing EuO or other metastable materials on any oxide substrate and may even be used as a route to stabilizing oxide phases otherwise not accessible by the standard phase diagram.

III. THERMAL PHASE CONTROL OF OXIDE INTERFACES

Albeit being a classical—if not the most ancient—magnetic material, current research on iron oxide Fe$^{x}$O$^{y}$ thin films actively continues developing due to its applications in a broad range of fundamental and technological fields. Functional properties of binary iron oxides thereby range from insulators to conductors and from ferromagnets to antiferromagnets. The prospect of a controlled interconversion between different iron oxide phases, and hence, the deliberate setting of magnetic and/or electrical properties, may open up novel possibilities in oxide electronics. One route toward such tailored reduction-oxidation reactions is by employing an oxide substrate as a - thermally controllable—source or sink of oxygen.

In the following, we will discuss mechanisms that enforce the reduction of magnetite Fe$_3$O$_4$ thin films toward lower oxidations states and finally toward Fe metal. Using the depth- and elemental sensitivity of HAXPES allows us to explore the thermally induced chemical transitions between different phases of iron oxide thin films. The information depth for samples illuminated by hard x rays at a photon energy of 4 keV is approximately 20–25 nm, which enables to capture spectroscopic information from the bulk as well as the buried oxide interfaces. All data presented in this chapter was recorded at the HIKE beamline at BESSY II (HZB Berlin, Germany) using a photon energy of 4 keV.

To introduce the relevant material properties, magnetite Fe$_3$O$_4$ crystallizes in an inverse spinel structure with Fe$^{3+}$ occupying the octahedral site, whereas the tetrahedral sites are comprised of a mixture of Fe$^{2+}$ and Fe$^{3+}$ cations. The structure orders magnetically at a Curie temperature of $T_C = 860$ K. Fe$_3$O$_4$ has half-metallic conducting properties and undergoes a metal-to-insulator (“Verwey”) transition at $T_V = 120$ K, which is recognized as a sensitive fingerprint for the Fe$_3$O$_4$ phase stoichiometry. Details on the growth of Fe$_3$O$_4$ films on SrTiO$_3$(001) and YSZ(001) substrates by pulsed laser deposition (PLD), as well as their throughout structural and magnetic characterization have been published elsewhere.

A. As-prepared Fe/STO: The unexpected interface

The first challenge is to conclude on the stoichiometry of as-grown Fe$_3$O$_4$ thin films. Here, the Verwey transition can serve as a very sensitive signature of the Fe$_3$-δO$_4$ phase because it can only be detected for δ < 0.045. This upper oxygen detection limit may even be more sensitive than a quantitative stoichiometry analysis by XPS or HAXPES, for which the elemental sensitivity is typically in the order of 1% depending on specific core-level cross section and peak intensity. We note that besides the oxygen content itself, also the structural phase, lattice strain, and domain size can alter the Verwey transition temperature of Fe$_3$-δO$_4$. However, we recently demonstrated that the Fe$_3$O$_4$ thin films grow structurally fully relaxed. This is why we can directly relate the observation of the Verwey transition to the upper oxygen content, which serves as an alternative measure in addition to HAXPES data.

The Verwey transition was recorded for Fe$_3$O$_4$ thin films grown on YSZ and SrTiO$_3$ with thicknesses of 38 and 4 nm via magnetization vs temperature $M(T)$ curves, as shown in Figure 5. Below $T_V$, Fe$_3$O$_4$ transfers from a cubic to a monoclinic structure, which causes a decrease of the magnetization. The magnetization as a function of temperature $M(T)$ of the 38 nm films grown on both YSZ and SrTiO$_3$ drops around 120 K, which is corresponding to the Verwey transition. This observation suggests a bulklike stoichiometry of the 38 nm Fe$_3$O$_4$ films grown on both SrTiO$_3$ and YSZ.

For an ultrathin film of 4 nm thickness grown on YSZ and SrTiO$_3$, the Verwey transition is still detectable but decreases to 60 K, as shown in the inset of Fig. 5. While its detectability indicates a high structural and stoichiometric quality of the Fe$_3$O$_4$ films, the reduced $T_V$ points toward its reduced dimensionality. Indeed, by HAXPES analysis of the Fe 2p spectra, we can extract the formation of a 2 u.c. of the γ-Fe$_2$O$_3$ interlayer between Fe$_3$O$_4$ and the substrates, which reduces the effective Fe$_3$O$_4$ thickness. From a thermodynamic perspective, this finding is unexpected as no driving force for further oxidation of Fe$_2$O$_3$ shall exist according to an Ellingham analysis—at least for bulk Fe$_2$O$_3$ and substrates. Once more, we find an oxide interface behaving opposite to theoretical predictions—which, in turn, opens up novel possibilities for its thermal tunability via the substrate’s oxygen supply, which we explore in the following.

B. Tuning iron oxide phases by postannealing

To record the thermally induced phase transition from Fe$_3$O$_4$, HAXPES experiment on the above samples were conducted in the
following manner: Fe 2p core-level spectra were recorded during stepwise postannealing of the samples between temperatures of 25–700°C in UHV, and each step was stabilized for 20 min. Moreover, to test whether the Fe 2p spectra are recorded at quasiequilibrium, a film of 4 nm was annealed at 600°C for 90 min, and HAXPES Fe 2p was recorded every 30 min. No changes in peak position or -shape appear in the spectra.

Figure 6(a) depicts Fe 2p core-level spectra of the as-grown Fe₃O₄ films. To identify the Fe valency, the experimental spectra were compared to reference data of FeO, Fe₂O₃, and Fe₃O₄. The emergence and position of satellite peaks yield clear indication for the presence of Fe³⁺ and/or Fe²⁺, see Fig. 6(a). The satellite peaks of FeO and Fe₂O₃ phases have binding energies $E_B$ of 715.5 and 719 eV, respectively. On the other hand, the satellite peaks of Fe₃O₄, which has a mixed oxidation state of Fe²⁺ and Fe³⁺, merge and thus disappear, as apparent for the 38 nm film grown on SrTiO₃ substrate in Fig. 6(a). For 38 nm thick Fe₃O₄, consequently, we find that the two satellites are merged. Moreover, the Fe 2$^{3/2}$ peak is composed of the Fe³⁺ peak and a shoulder that refers to Fe²⁺. We conclude on a bulklike stoichiometry of 38 nm thick Fe₃O₄ films. For 4 nm films grown on SrTiO₃ and YSZ substrates, we observe that the Fe³⁺ satellite peak appears accompanied by a decrease Fe²⁺ peak shoulder at the Fe 2$^{3/2}$ peak. Both observations suggest the formation of an interfacial FeO phase in addition to Fe₃O₄.

For films annealed at $T_{\text{anneal}} = 400\degree C$ in UHV-atmosphere, as shown in Fig. 6(b), the films with thicknesses of 4 nm and 38 nm grown on STO substrates show the appearance of a satellite peak at $E_B = 715.5$ eV, which indicates the formation of a FeO and partial Fe₂O₃ phase. However, for film grown on YSZ, the satellite peak intensity at $E_B = 715.5$ eV is stronger and indicates the full reduction to FeO. On the other hand, for films annealed at $T_{\text{anneal}} = 700\degree C$ in UHV-atmosphere as shown in Fig. 6(c), the 38 nm film grown on STO shows a partial reduction to FeO, whereas the 4 nm film grown on STO shows a full reduction to FeO indicated by the intensities of the satellite peaks. Surprisingly, the 4 nm thick film grown on YSZ is fully reduced to Fe metal.

C. Beyond the standard phase diagram: A thermodynamic discussion

The previous results unveil the strong differences between YSZ and STO substrates in their affinity to be chemically reduced. However, the formation of interfacial $\gamma$-Fe₂O₃ is observed for both systems, Fe₃O₄/STO and Fe₃O₄/YSZ. Figure 7 summarizes the resulting heterosystem before and after annealing. The mechanism for the formation of the interfacial $\gamma$-Fe₂O₃ phase between Fe₃O₄ films and STO and YSZ substrates remains to be discussed.

Taking into account the thermodynamic properties of all constituents, SrTiO₃ has a lower Gibbs free energy of formation $\Delta G^\circ_F = -1588.4$ kJ/mol compared to Fe₃O₄ ($\Delta G^\circ_F = -1015.4$ kJ/mol). Therefore, STO is not expected to oxidize Fe₃O₄. However, oxygen vacancies perturb the formation energy for TiO₂-terminated STO to 461.5 kJ/mol.

Consequently, the formation of an oxidized $\gamma$-Fe₂O₃ intralayer may be explained by the oxygen diffusion from the STO substrate due to the reduced surface formation energy by oxygen vacancies of TiO₂-terminated STO surfaces, which enables the migration of oxygen from STO into Fe₃O₄. We note that this mechanism may simultaneously lead to the formation of reduced Ti³⁺ at the STO interface, which is the key prerequisite for the formation of a redox 2DES. From bulk thermodynamics, the formation enthalpies of Fe₃O₄ and YSZ have similar values. Therefore, no clear expectation of which phase may reduce the other can be drawn. It should be noted, however, that since YSZ is such a good oxygen ion conductor, any formation of additional oxygen vacancies (concomitant with reduction of Zr) at the interface will be followed by a rapid redistribution, making the concentration of excess oxygen vacancies at the interface quite small.

Additionally, YSZ is known to be a good electrolyte because of its high oxygen conductivity, which is influenced by the doping level as well. Therefore, oxygen can diffuse from the outer atmosphere through the YSZ substrate and cause the formation of an
Fe₂O₃ intralayer. Therefore, the oxygen conductivity of YSZ is a key factor for the formation of an oxidized Fe₃O₄ intralayer. However, the perturbation of oxygen vacancy concentration caused by this redistribution within the substrate crystal plays a negligible role.

To conclude, we studied the effect of annealing in different oxygen pressure and the emerging redox processes of Fe₃O₄ inter- faces. A thermodynamics modeling allows to understand phase transformations between Fe₂O₃, γ-Fe₂O₃, and FeO through the oxygen migration across interfaces with oxide substrates SrTiO₃ and YSZ. This finding convincingly demonstrates the important role of the oxide substrates STO and YSZ as oxygen scavengers or suppliers. In this way, alternative opportunities emerge to control interface and thin-film functionalities of all-oxide heterostructures.

IV. BAND ALIGNMENT AT OXIDE INTERFACES

Key parameters of any semiconductor (SC) device are the electronic band alignment and -offsets at the interfaces of a metal-insulator (M/I) heterostructure. HAXPES can serve as an experimental tool to directly extract the valence band (VB) offsets of buried interfaces.¹¹ In addition, also the interfacial chemical state is accessible, which makes HAXPES a unique tool for a thorough interface characterization.⁹ Furthermore, performing HAXPES experiments in operando, i.e., under applied bias voltage, both the band alignment and the chemical state of a M/I device can be determined under realistic operation conditions—and captured in a concurrent measurement.⁷,³⁸ In this chapter, we discuss an Au/NiFe₂O₄/SrTiO₃ heterostructure as a prototype example for an in operando HAXPES experiment, as schematically sketched in Fig. 8.

NiFe₂O₄ directly compares to Fe₂O₄, as both materials adopt the inverse spinel crystal structure. In NiFe₂O₄, divalent Ni cations occupy the Fe⁺² lattice sites of the Fe₂O₄ unit cell. The thereby altered magnetic exchange and electronic correlations turn NiFe₂O₄ into an (also) ferrimagnetic but insulating material, with a similar Curie temperature of about 850 K.³⁹ In Fig. 9(b), the NiFe₂O₄ spectral signatures of the Fe₂p core level spectra thus shows a Fe³⁺-only feature which lacks the Fe²⁺ shoulder, as observed for Fe₂O₄ in Fig. 6(a). With regard to the chemical stability, however, NiFe₂O₄ and Fe₂O₄ strongly differ: the NiFe₂O₄/STO interface turns out to be chemically extremely robust compared to Fe₂O₄/ STO. No signatures of interfacial redox reactions could be observed by HAXPES for NiFe₂O₄.⁴⁰ Thus, the NiFe₂O₄/STO heterostructure serves as a prototype example for a quasi-nonreactive M/I interface, which, in turn, is a prerequisite for an in operando HAXPES characterization.

A. Experimental in operando HAXPES

The design of samples for in operando HAXPES measurements requires metal top electrodes to apply a bias voltage. On the
other hand (in order to adapt to the information depth of the HAXPES experiment), these electrodes need to be structured into different regions which either can be electrically contacted (thick metal pad) or can be probed by HAXPES while applying the bias potential (thin metal overlayer).

Figure 8 sketches a possible heterostructure for in operando HAXPES. Half of the Nb-doped SrTiO3 substrate is covered with a 500μm SiO2 film, which serves as a buffer between the STO back electrode and Au top electrode. On top of STO, a 10 nm NiFe2O4 layer is deposited via pulsed laser deposition. Next, a 4 nm thin Au pad (2×3.6 mm2) is deposited ex situ via electron beam vapor deposition, which overlaps the SiO2 and NiFe2O4/SrTiO3 areas. On top of this thin gold pad, a 40 nm gold finger structure is deposited. The fingers width and distance between the fingers is 0.2 mm, respectively. The top Au electrode is connected to the voltage source and the SrTiO3 substrate is grounded.

In operando HAXPES experiments were performed at beam-line P09 (now P22) at PETRA III (DESY Hamburg, Germany)41 in normal emission geometry using a photon energy of 6 keV. For each voltage step, the electrical current was measured, see Fig. 9(a). As reference data, spectra of a SrTiO3 substrate, a 20 nm NiFe2O4 film and a 50 nm Au film were recorded.

B. Chemical stability of the NiFe2O4/STO interface

In order to determine the band alignment of the Au/NiFe2O4/SrTiO3 heterostructure in operando, the layers and interfaces need to be chemically stable—not only thermodynamically but also under applied bias voltages during the HAXPES measurement. Figure 9(b) displays the Fe 2p core level for varying applied voltages, whereby the on-potential spectra had been shifted on the binding energy (BE) scale on the zero voltage Fe 2p3/2 position. No spectral changes of the core levels are observed. In particular, at the low binding energy flank of the Fe 2p3/2 peak, no shoulder of a possibly emerging Fe2+ component can be identified, and also the position of the Fe3+ satellite peak remains unchanged. Hence, NiFe2O4 can be assumed to be chemically stable during the in operando HAXPES measurement.

For each voltage step, the electrical current was observed to check whether the sample had not been shorted. A positive applied voltage refers to a direction where negative charges move from SrTiO3 to NiFe2O4, while a negative applied voltage refers to a direction vice versa. The resulting I–V curve is shown in Fig. 9(a). We find a symmetrical and nonohmic response indicative of a M/SC/M structure. Although NiFe2O4 is expected to be insulating,
the growth of NiFe$_2$O$_4$ on SrTiO$_3$ introduces defects like dislocations or mosaicity due to the large lattice strain.\(^3\,^4\) NiFe$_2$O$_4$, therefore, electrically acts as a semiconductor. In general, throughout the entire in operando HAXPES measurement process, the sample was electrically and chemically stable, as shown in Figs. 9(a) and 9(b).

C. Band alignment analysis via HAXPES

In a simple but powerful model used in semiconductor physics, the valence band (VB) offset $\Delta E_v$ at the interface of two SCs A and B is simply determined by the energy difference of their VB maxima $E_v$, $\Delta E_v = E_v^A - E_v^B$. The same relation holds for the Schottky barrier height $\Phi_b$ of a metal/SC interface; here, the metal valence band maximum is given by the Fermi energy, $\Phi_b = E_F^M - E_v^{SC}$.

In an (oxide) heterostructure, however, the VBs of the different materials are overlapping and thus the VBs of the individual layer often cannot be directly recorded by HAXPES. Therefore, an indirect method is typically applied, which relates a core level binding energy position to the actual position of the valence band. This so-called "Kraut model" assumes flatbands and chemically stable interfaces.\(^13\) If these conditions are fulfilled, it can be used to determine the band alignment and the band offset at the interfaces of (oxide) heterostructures, here Au/NiFe$_2$O$_4$/SrTiO$_3$.

According to Kraut’s model,\(^13\) the measured energy difference between any core level peak maximum and the VB maximum of a reference material $A$ is taken as a constant value, also if material $A$ is part of a heterostructure. Thus, binding energy changes of the core level should directly reflect the same changes at the VB maximum, $$(E^v_{cl})_{\text{ref}} - (E^v_{cl})_{\text{het}} = (E^A_{cl})_{\text{het}} - (E^A_{cl})_{\text{ref}}.$$ (1)

Due to the element selectivity of HAXPES, specific core levels can be related to the individual layers of a heterostructure and hence the VB position of the individual layers can be determined. The experimentally not accessible valence band maximum $(E^A_{cl})_{\text{het}}$ is now substituted by the difference of the equivalent core level binding energies relative to the reference sample, $$(E^v_{cl})_{\text{het}} = (E^v_{cl})_{\text{ref}} - [(E^v_{cl})_{\text{ref}} - (E^v_{cl})_{\text{het}}].$$ (2)

Now, the VB offset $E_v$ or Schottky barrier height $\Phi_b$ between different materials A and B, here Au/NiFe$_2$O$_4$ and NiFe$_2$O$_4$/SrTiO$_3$, becomes experimentally accessible by using Eq. (2).

For the determination of the band alignment of the Au/NiFe$_2$O$_4$/SrTiO$_3$ model sample, the core level binding energies of the Au 4f$_{7/2}$ level for the Au top electrode, the Fe 2p$_{3/2}$ and Ni 2p$_{3/2}$ level for NiFe$_2$O$_4$, and the Ti 2p$_{3/2}$ and Sr 3d$_{5/2}$ levels for the SrTiO$_3$ layer are analyzed. As reference samples an uncovered SrTiO$_3$ substrate, a 20 nm NiFe$_2$O$_4$ film and a 50 nm Au film are used. The Fermi level $E_F$ of Au was used as binding energy reference and set to zero. As depicted in Fig. 9(c), the VB edges $E_v$ of the SrTiO$_3$ and NiFe$_2$O$_4$ reference samples are determined by fitting.\(^42\)

In Fig. 9(d), the resulting band alignment is shown. The conduction band positions $E_c$ are calculated by adding the bandgap $E_g$ to the VB offsets $\Delta E_v$. For SrTiO$_3$, a bandgap of $E_g = 3.25$ eV is assumed\(^43\) and for NiFe$_2$O$_4$ the calculated majority and minority, bandgaps of $E_g = 2.7$ eV and $E_g = 2.3$ eV are used.\(^44\) The bias dependent band alignments diagrams for $U = 0$, 6 V, $-6$ V of the Au/NiFe$_2$O$_4$/SrTiO$_3$ heterostructure are shown in Fig. 9(d), with the corresponding $I$–$V$ curve depicted in Fig. 9(a).

We find the spectrally determined $\Delta E_v$ at the NiFe$_2$O$_4$/SrTiO$_3$ interface being independent of the applied voltage, while $\Phi_b$ at the Au/NiFe$_2$O$_4$ interface strongly changes. Thus, the electrical transport characteristics of the Au/NiFe$_2$O$_4$/SrTiO$_3$ heterostructure are mainly governed by the Au/NiFe$_2$O$_4$ interface. For $U = 0$ V, the Fermi level $E_F$ is located in the bandgap of NiFe$_2$O$_4$ and close to the conduction band $E_v$ of SrTiO$_3$. Due to its Nb-doping, SrTiO$_3$ is electrically conducting. For small voltages, NiFe$_2$O$_4$ acts as a barrier, and only small currents are expected, which fits well with the observed nonohmic, symmetrical $I$–$V$ curve in Fig. 9(a). At $U = -6$ V, the Fermi level $E_F$ is located in the conduction band of NiFe$_2$O$_4$ and SrTiO$_3$. Thus, there is a conducting path established, which is also observed in the $I$–$V$ curve. In the case of $U = 6$ V, the Fermi level $E_F$ aligns with the valence band edge of NiFe$_2$O$_4$ and lays in the bandgap of SrTiO$_3$. Thus, again a conducting channel is established, which is confirmed by the $I$–$V$ curve in Fig. 9(a).

From the above experiments, an element-specific quantification of band alignments of a complex oxide heterostructure was realized, which confirms the results of electrical $I$–$V$ measurements. In that, in operando HAXPES is a powerful spectroscopic tool to probe multilayer devices under realistic operation conditions.

V. INTERFACE OXIDE EXCHANGE IN FERROELECTRIC CAPACITORS

Sections II and III discussed mechanisms by which controlled oxygen supply by oxide substrates can be utilized to deliberately set ferro(i)magnetic oxide properties of ultrathin films. On the other hand, ferroelectricity in dielectric HfO$_2$-based compounds is mainly introduced by the absence of oxygen, introduced either by doping or directly by oxygen vacancies.\(^45\) Ferroelectric (FE) capacitors based on simple metal–FE insulator–metal (MIM) structures are envisioned as efficient nonvolatile memory devices.\(^46\) Since its discovery around 2010, HfO$_2$-based ferroelectric materials, in particular, Hf$_6$Zr$_{12}$O$_{27}$ (HZO), emerged as most promising candidates due to their outstanding CMOS compatibility.

In practice, however, performance instabilities, such as the so-called wake-up, imprint, and fatigue effects, are still poorly controllable and currently hamper its application in commercial FE memory devices.\(^47\) The common feature of these issues is the emergence of excess oxygen vacancy defects located within the ferroelectric HfO$_2$-based layer with an increased density at the electrode interfaces. Thus, the control of the oxygen defect density within the HfO$_2$-based layer and at its interfaces is currently of major interest.

It has become evident that the choice of the metallic electrode material in MIM capacitors plays a crucial role, in particular, because the interface chemical state modulates the oxygen exchange across the interface—which can either act passively or rather as a source or sink of oxygen. Hence, the material choice can either increase or reduce the defect density at the HfO$_2$ interface and...
exploiting the tunability of oxygen vacancy density is a major aspect in current MIM design. HAXPES as an element-selective, depth-sensitive, and nondestructive analysis tool serves as an ideal probe for the emerging interface chemistry. All HAXPES data presented in this section had been recorded at the beamline P22 of PETRA III (DESY Hamburg, Germany) using a photon energy of 6 keV.49

Figures 10(a)–10(c) schematically depicts three MIM structures for which oxygen exchange mechanisms across the interface was explored by HAXPES. Their specific preparation conditions by either physical vapor deposition (PVD)45 or/and atomic layer deposition (ALD)50 were taken into account for discussion of the spectroscopic results, as, in particular, the oxygen supply before or during HfO2 layer growth significantly alters the interface properties. Moreover, all three capacitors devices had been characterized electrically by polarization-voltage (P-V) curves,45,51 and hence a direct relation between the interface chemical properties and ferroelectric state of the MIM structures can be drawn.

A. Oxygen scavenging by TiN electrodes

For TiN/HfO2/TiN capacitors, the interface properties strongly depend on the specific PVD growth parameters: Fig. 11 depicts the Hf 4f core levels recorded from two samples for which either no or 2 SCCM gaseous oxygen was provided before and during the HfO2 layer growth. For a direct comparison, the rigid binding energy shift between the two measurements was corrected, and both spectra were subtracted from each other. This differential spectrum (shaded blue area) reveals a double peak structure with the same energy splitting as the Hf 4f doublet but shifted by 600 meV to lower BE values and with an intensity ratio of about 5% compared to the main Hf 4f doublet. This feature is assigned to a spectral contribution of a Hf3+ valency in agreement with the literature,52 and its intensity strongly decreases with the amount of supplied oxygen during the growth process.53

For the N 1s core level shown in the inset of Fig. 11, we also compared the differential spectra and found an enhanced spectral weight at the lower binding energy side for the sample without additional oxygen supply. This contribution can be assigned to the presence of HfN.54 Further, the peak located at $E_B = 397.5$ eV is assigned to TiN and the peak fit at $E_B = 396.7$ eV can be related to TiN$_x$O$_y$ contributions.55 In analogy to the Hf 4f spectrum, the formation of the HfN related component is found to decrease the amount of oxygen provided during the growth process.53
The emergence of Hf\textsuperscript{IV} spectral weight in the Hf 4f core level may either be interpreted as HfN contribution or as an indirect signature of positively single and double-charged oxygen vacancies, V\textsuperscript{+} and V\textsuperscript{2+}. From angular dependent HAXPES measurements (not shown), the Hf\textsuperscript{IV} contribution can be located at the interface between HfO\textsubscript{2} and the bottom TiN electrode. As the HfN component is observed in the N 1s core-level spectra, an interfacial HfN formation seems likely. However, oxygen vacancies are also known to be enhanced at the interfaces. Thus, both contributions may contribute to the Hf\textsuperscript{IV} component.

At this point, we conclude that without additional oxygen supplied during the PVD growth, the TiN electrode can exchange nitrogen and oxygen with the HfO\textsubscript{2} layer during the rapid thermal annealing process, which results in the formation of a TiO\textsubscript{2}/HfN interface layer, as schematically depicted in Fig. 10(a). The incorporation of nitrogen in the HfO\textsubscript{2} may, in turn, change the vacancy features at the interface as discussed by Baumgarten et al.\textsuperscript{56}

B. Interface stabilization

What happens at the TiN/HfO\textsubscript{2} bottom interface if additional oxygen is supplied before and during PVD growth, and what are the consequences for the defect distribution in HfO\textsubscript{2}? From the previous results, we expect an interface exchange of oxygen and nitrogen dependent on the gradual increase of oxygen dosage.

In Fig. 12, the Ti 2p core level of samples prepared under different oxygen flows reveal contributions of several chemical species, namely, TiN, TiN\textsubscript{0.5}O\textsubscript{2} suboxides,\textsuperscript{57,58} and TiO\textsubscript{2}. The increase of the oxygen flow during growth leads to a significant increase of the spectral weight of the TiO\textsubscript{2} component, starting from a small spectral weight at 0 SCCM to a \textasciitilde 1:1 ratio of TiO\textsubscript{2} and TiN for 2 SCCM. From angular-dependent HAXPES measurements (not shown), it can be concluded that the TiO\textsubscript{2} contribution is located on top of the TiN bottom layer.

Since the TiO\textsubscript{2} peaks already appear for the amorphous HfO\textsubscript{2}/TiN system (not shown) and thus are not related to the rapid thermal annealing crystallization process, an oxygen scavenging from HfO\textsubscript{2} can be excluded. Rather we conclude on the formation of a TiO\textsubscript{2} interlayer between the TiN bottom electrode and HfO\textsubscript{2}. The TiO\textsubscript{2} interlayer thickness has been calculated from the TiO\textsubscript{2}/TiN intensity ratio, taking into account the reduction of the TiN thickness at the expense of the TiO\textsubscript{2} growth (see Ref. 53 for a detailed description). The resulting self-limiting layer growth is depicted in the inset of Fig. 12.

From the above HAXPES experiments, we propose the following chemical processes, which strongly determine the interface properties of TiN/HfO\textsubscript{2}/TiN capacitors. The oxygen supply before HfO\textsubscript{2} growth generates a TiO\textsubscript{2} interface layer, which is self-limiting at about 3.5 nm. This layer effectively stabilizes the interface and prevents the exchange of oxygen and nitrogen. TiO\textsubscript{2} itself is chemically very stable and thus not expected to supply oxygen to the HfO\textsubscript{2} layer. Moreover, the interface stabilization by a TiO\textsubscript{2} buffer offers the possibility to design the defect properties of the atop HfO\textsubscript{2} layer deliberately by specific growth parameters.

C. Oxygen supply by IrO\textsubscript{2} electrodes

Finally, we explore the possibility of supplying oxygen into ferroelectric HfO\textsubscript{2} by an adjacent metal electrode. IrO\textsubscript{2} electrodes have been utilized as oxygen supplier in IrO\textsubscript{2}/PZT/IrO\textsubscript{2} ferroelectric MIM structures.\textsuperscript{59} Due to the resulting option to control the oxygen vacancy concentration in PZT, the ferroelectric performance of such MIM structure could be significantly optimized. The same effect was anticipated for IrO\textsubscript{2}/Hf(Zr)O\textsubscript{2}/IrO\textsubscript{2} MIM structures by increased controllability of HZO-related defects.

From the chemical perspective, IrO\textsubscript{2} readily supplies oxygen because it is an unstable compound and can be easily reduced to metallic iridium at elevated temperatures.\textsuperscript{52} Moreover, the choice of different annealing atmospheres has been found to crucially impact the IrO\textsubscript{2} composition and on the crystallization anneal process.\textsuperscript{60} In Fig. 13, the Ir 4p and the O 1s core-levels are displayed. The Ir 4p emission around 495 eV shows different binding energies for annealing of the IrO\textsubscript{2}/Hf(Zr)O\textsubscript{2}/IrO\textsubscript{2} in an oxygen atmosphere (OA) compared to forming gas annealing (FGA) (FG: 90% Ar, 10% H\textsubscript{2}). The OA Ir 4p\textsubscript{1/2} level appears at 800 meV higher binding energy, indicating a chemical shift. The IrO\textsubscript{2} top electrode is reduced to metallic Ir by the FG ambient, whereas the oxygen atmosphere, in turn, stabilizes the IrO\textsubscript{2} electrode. In addition, the metallic FG Ir electrode shows an oxygen content at a binding energy of 533 eV, which is related to oxygen unbound to Ir (see the inset).\textsuperscript{50}

The emergence of metallic Ir electrodes containing unbound oxygen is of special interest to control the ferroelectric behaviour of the Ir/HZO interface during electrical switching of the MIM device. In the inset of Fig. 13, two spectra are displayed for which...
the FGA-annealed MIM device either had been electrically switched back and forth $10^6$ times (FGA-E6) or is electrically still untreated (FGA-P). A comparison reveals a modification of spectral weight in the O 1s component. The intensity of the unbound oxygen component at 533 eV decreases, while an additional component at 531 eV appears. This emission can be related to IrO$_2$. Thus, the application of the electrical switching pulses seemingly induces a chemical reaction at the interface. Such a reaction is most likely induced by charge injection into defect states at the interface. Whether this is accompanied by an oxygen migration across the interface cannot be concluded from the current HAXPES results and requires further investigations.

The emergence of the IrO$_2$ component, as shown in Fig. 13 can be directly related to a changed band alignment at the interface. As discussed in Sec. IV, binding energy shifts of core levels can be used as a measure of the binding energy shifts of the VB maximum relative to the Fermi level. Here, the Hf 4f binding energy shift is used as a relative measure of the interfacial band alignment. Figure 14 shows the Hf 4f spectra of the OA and FGA samples, compared to samples annealed without top electrode [see Fig. 14(c)]. From the Hf 4f binding energies of the samples without the top electrode, the band alignment at the bottom electrode is deducible. The IrO$_2$ top electrode of the OA sample shows a small shift of 130 meV toward lower binding energies [Fig. 14(b)], whereas the Ir top electrode of the electrically untreated FGA and FGA-P sample show a shift of 320 meV toward higher binding energies [Fig. 14(a)]. After $10^6$ switching cycles (FGA-E6); however, the Hf 4f level has shifted back to the same binding energy as observed for the IrO$_2$ OA sample, see Fig. 14(b). This coincides with the appearance of the IrO$_2$ component at the interface and directly reflects the change from an Ir-related band alignment toward an IrO$_2$ related one. This shows the strong relation between interface chemistry and band alignment and again highlights the capability of HAXPES to address both.

VI. SUMMARY

In summary, oxide interfaces between (ultra-)thin films and substrates had been shown to offer exciting possibilities to set functionalities deliberately by a controlled oxygen exchange. The element-sensitivity of soft- and hard x-ray photoelectron spectroscopy allows to disentangle the specific mechanisms of how adjacent materials affect each other through, e.g., chemical reactions, ion diffusion, or charge transfer, which may be related to electronic band bending or defect formation. In addition, the depth-sensitivity of HAXPES has been shown to be indispensable to probe these phenomena in a nondestructive manner at hidden interfaces and in real multilayer devices. In this regard, we presented spectroscopic results on emerging interface states and their tunability for selected ferro(i)magnetic and ferroelectric heterostructures—covering fundamental aspects and exploring application-relevant devices. The ability to tailor functional thin film properties will be key for future applications, e.g., in oxide...
electronics, which require full control over these complex electronic ground states.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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