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Understanding and tailoring oxygen ion motion for ultra-low power control of magnetism

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Understanding and tailoring oxygen ion motion for ultra-low power control of magnetism

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Beatrice Bednarz
Mainz, June 27, 2026

Dedicated to

all those people who engage for a climate neutral,
peaceful and just world for everyone.

”Utopien sind der Magnet, der Menschen von der Zukunft her anzieht [...]
Wenn wir die Perspektive umdrehen und von einer wünschenswerten Welt von morgen zurück
auf die Gegenwart blicken, können wir Wege identifizieren, die zu diesem Morgen hinführen.”
(Neubauer/Repenning 2019, 245f)

Abstract

Digitization and artificial intelligence are increasingly shaping our everyday lives. However, their rapid adoption comes with a steep rise in energy consumption. At the same time, the climate crisis is accelerating dramatically. Consequently, it is crucial to further improve the energy efficiency of information and communication technologies, ensuring that their power demand can be met by renewable energies. A promising approach is the use of magnetic materials, which allow for non-volatile, ultra-low power switching between states. The energy consumption to manipulate the magnetic states can be minimized by using electric fields. Since no current is flowing, this avoids ohmic losses.

In this thesis, voltages were applied across an ionic liquid placed on top of the magnetic stack. This enables particularly high electric fields. Thereby, oxygen ion migration was induced which modifies the properties of the underlying magnetic layers. The resulting magnetic changes were characterized using anomalous Hall effect and superconducting quantum interference device measurements.

For Co/PtMn bilayers, this work revealed that ionic modulation can be used in such coupled ferromagnet/antiferromagnet thin films to rotate the ferromagnetic magnetization from an in-plane toward a stable out-of-plane direction while preserving the exchange bias. To achieve this rotation, a mere reduction of the demagnetization energy by decreasing the Co thickness – through oxidation or thinner growth – was shown to be insufficient. However, voltage-driven oxygen migration increases the perpendicular magnetic anisotropy via Co-3d O-2p hybridization. This was identified as the main driver of the magnetization rotation. When the order of ferromagnetic and antiferromagnetic layer is inverted, the out-of-plane magnetization of Co remains unchanged under gating, while the exchange bias can be tuned. Notably, this indicates that oxygen ions penetrated 6 nm metallic PtMn to reach the Co/PtMn interface.

To better understand voltage-induced oxide depth profiles and maximum penetration depths in metals, tantalum was investigated as a model system due to its smooth growth. It was capped with HfO₂, a good oxygen conductor. By X-ray reflectivity and X-ray photoelectron spectroscopy characterization, oxygen was shown to advance as fully oxidized layers with a sharp metal-oxide interface of a few Å. Overall, oxygen ions penetrate to depths of up to 4 nm into the Ta film at gate voltages as low as -3 V. This penetration depth can be highly relevant for magnetic applications with ultrathin functional layers, where buried layers and interfaces may be reached. To initiate the oxidation, a threshold electric field of approximately -2.8 MV/cm (corresponding to approximately -1 V gate voltage), is required, with higher fields needed as the oxide layer thickens. The primary source of the mobile oxygen ions is most likely the ionic liquid, while oxygen within the HfO₂ plays a minor role. Consistently, thinner HfO₂ capping layers increase oxygen penetration due to the enhanced electric field.

These results advance the understanding of ionic-liquid-gating-induced oxygen migration in metallic and magnetic thin films and support the design of next-generation energy-efficient magnetic devices.

Zusammenfassung

Unser tägliches Leben wird zunehmend durch Digitalisierung und künstliche Intelligenz geprägt. Ihre schnelle Verbreitung führt allerdings zu einer rasanten Zunahme des Stromverbrauchs. Gleichzeitig beschleunigt sich die Klimakrise dramatisch. Daher ist es essenziell, die Energieeffizienz von Informations- und Kommunikationstechnologien weiter zu verbessern, sodass ihr Stromverbrauch durch erneuerbare Energien gedeckt werden kann. Ein vielversprechender Ansatz ist dabei die Nutzung von magnetischen Materialien, da sie ein nichtflüchtiges, energieeffizientes Umschalten zwischen Zuständen ermöglichen. Dabei kann der Energieverbrauch minimiert werden, indem elektrische Felder zur Kontrolle der magnetischen Zustände verwendet werden. Da keine Ströme fließen, werden so Ohmsche Verluste vermieden.

In dieser Arbeit wurde eine ionische Flüssigkeit auf die magnetischen Proben gegeben, durch welche die Spannungen angelegt wurden. So können besonders hohe elektrische Felder erreicht werden. Dadurch wurde die Bewegung von Sauerstoffionen induziert und somit die Eigenschaften der darunterliegenden magnetischen Lagen kontrolliert. Die resultierenden magnetischen Veränderungen wurden mit Hilfe von anomaler-Hall-Effekt- und SQUID-Messungen charakterisiert.

Am Beispiel von Co/PtMn konnte gezeigt werden, dass die Bewegung von Sauerstoffionen es ermöglicht, in solchen Ferromagnet/Antiferromagnet Dünnschichten die Magnetisierungsrichtung vom Ferromagneten aus der Ebene heraus in einen stabilen senkrechten Zustand zu drehen. Dabei konnte die Austauschwechselwirkung zum Antiferromagneten erhalten werden. Eine alleinige Reduktion der Cobalt (Co)-Dicke durch Oxidation oder dünneres Wachstum ist dabei nicht ausreichend, um die Magnetisierung aus der Ebene herauszudrehen. Allerdings führt die Sauerstoffmigration durch Co-3d O-2p Hybridisierung auch zu einer größeren Grenzflächenenergie, welche die Magnetisierungsrichtung aus der Ebene heraus in die Senkrechte zieht. Es wurde gezeigt, dass dies der dominante Effekt für die Rotation der Magnetisierung ist. Durch das Tauschen von Ferromagnet und Antiferromagnet bleibt die senkrechte Magnetisierungsrichtung des Ferromagneten unter Spannung stabil und die Austauschwechselwirkung kann modifiziert werden. Bemerkenswert dabei ist, dass die Sauerstoffionen dafür durch 6 nm metallisches PtMn gelangen konnten, um die Co/PtMn Grenzfläche zu erreichen.

Um die feld-induzierten Sauerstoff-Tiefenprofile in Metallen besser zu verstehen, wurde als Modellsystem Tantal (Ta) untersucht, da sich Ta durch sehr glattes Wachstum auszeichnet. HfO_2 wurde als isolierende und passivierende Schicht auf das Ta gewachsen, da es gleichzeitig eine natürliche Oxidation des Ta verhindert, aber unter einem elektrischem Feld Sauerstoff hindurchleitet. Durch Röntgenreflektometrie- und Röntgenphotoelektronenspektroskopie-Messungen konnte gezeigt werden, dass die Oxidation des Ta anhand der Bildung vollständiger Oxidschichten verläuft. Die Grenzfläche von Metall und Oxid ist dabei nur wenige Å breit. Der Sauerstoff erreicht hier Tiefen von bis zu 4 nm bei Spannungen von nur -3 V. Solche Eindringtiefen können für magnetische Anwendungen mit ultradünnen Funktionsschichten von großer Bedeutung sein, da so auch tieferliegende Schichten und Grenzflächen erreicht werden

können. Um die Oxidation zu initiieren, ist ein elektrisches Feld von mindestens $-2,8 \text{ MV/cm}$ (etwa -1 V) notwendig. Je dicker die Oxidschicht, desto größer das benötigte elektrische Feld für eine weitere Oxidation. Die Hauptquelle der Sauerstoffionen ist höchstwahrscheinlich die ionische Flüssigkeit. Sauerstoff aus dem HfO_2 spielt dabei eine untergeordnete Rolle. Dementsprechend führen dünnere HfO_2 Beschichtungen aufgrund des höheren elektrischen Feldes zu einer stärkeren Oxidation.

Diese Resultate tragen zu einem tieferen Verständnis der Feld-induzierter Sauerstoffmigration in Metallen und magnetischen Dünnschichten bei. Damit liefern sie wertvolle Grundlagen für das Design der nächsten Generation energieeffizienter magnetischer Technologien.

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List of abbreviations

AFM	antiferromagnet
AHE	anomalous Hall effect
AI	artificial intelligence
ARXPS	angle-resolved X-ray photoelectron spectroscopy
DC	direct current
DMI	Dzyaloshinskii-Moriya interaction
DOS	density of states
DRAM	dynamic random-access memory
EAL	effective attenuation length
EB	exchange bias
EDL	electric double layer
EELS	electron energy loss spectrum
EM	electromagnet
FM	ferromagnet
FWHM	full width at half maximum
GDP	gross domestic product
GHG	greenhouse gas
HPLC	high pressure liquid chromatography
ICT	information and communication technology
IL	ionic liquid
ILG	ionic liquid gating
IMFP	inelastic mean free path
IP	in-plane
ITO	indium tin oxide
ITU	International Telecommunication Union

MOSFET metal–oxide–semiconductor field-effect transistor

MTJ magnetic tunnel junction

OHE ordinary Hall effect

ORSO Open Reflectometry Standards Organisation

OOP out-of-plane

PMA perpendicular magnetic anisotropy

RAM random-access memory

RF radio frequency

RSF relative sensitivity factor

RSS residual sum of squares

SLD scattering length density

SOC spin-orbit coupling

SQUID superconducting quantum interference device

SRAM static random-access memory

XPS X-ray photoelectron spectroscopy

XRD X-ray diffraction

XRR X-ray reflectivity

We live in a time of polycrises [1, 2, 3]. One of the most far-reaching is global warming. A recent publication in the journal *Global Environmental Change* from July 2025 concludes that “Meeting climate targets now requires the carbon intensity of GDP to decline 3 times faster than the global best 30-year historical rate (−2.25 % per year)” [4]. If we fail to do so, we might reach global average surface temperatures of more than +3 °C above the pre-industrial levels by 2050 [4]. This would lead to significant adaptation challenges [5]. The resulting and increasingly urgent need to act led to a joint climate call of the German Meteorological Society and the German Physical Society [6], which has been joined by the German Chemical Society and the “Verband Biologie, Biowissenschaften und Biomedizin in Deutschland” by December 2025. They remind that already now the number and severity of the extreme weather events increases drastically, also in Germany, with increasing damage to private and public property. If we fail to reduce greenhouse gas emissions soon, this will increase the threat to well-being and lives of people worldwide. In some regions of the world, days with a combination of such high temperatures and high humidity that it becomes impossible to survive outdoors could occur even before 2050 [6]. Therefore, it is the duty of all of us worldwide, who have the education to understand and the possibilities to act, to take action against climate change. Or, in the words of Albert Einstein: “Those who have the privilege to know have the duty to act.”

The well-known sectors with high potential for reducing greenhouse gas (GHG) emissions are, of course, electricity, heating and mobility. For these sectors, established technological solutions already exist. Solutions for decarbonization have also been proposed for many industrial processes. Nevertheless, there are many more areas which need to be considered in order to achieve climate neutrality and remain within Earth’s carrying capacity [7].

One of them is information and communication technology (ICT), encompassing all devices which can “retrieve, manipulate, store, transmit, or receive information in digital form” [8]. This includes end-user devices such as mobile phones and computers, as well as data centers and the entire infrastructure required for the transmission or processing of data. A recent study concluded that “the global average consumption of web surfing, social media, video and music streaming, and video conferencing could account for approximately 40 % of the per capita carbon budget consistent with limiting global warming to 1.5 °C, as well as around 55 % of the per capita carrying capacity for mineral and metal resources use, 20 % for freshwater eutrophication, and over 10 % for particulate matter, ecotoxicity, and fossil resources use” [9].

It should be further noted that the overall electricity consumption of ICT is increasing steadily. According to the international energy agency, the global electricity consumption of data centers “has grown at 12 % per year over the last five years”, reaching around 415 TWh in 2024 [10]. Marlmödin et al. estimated, that the total use stage electricity consumption, mean-

ing “the electricity consumed when running networks and data centers and charging equipment, but excluding the electricity used for raw materials acquisition, production and end-of-life treatment”, has increased from approximately 700 TWh in 2007 to approximately 900 TWh in 2020 globally [11]. This was already more than 1.5 times the annual electricity consumption of Germany (528 TWh in 2024) [12]. Although forecasts of future ICT electricity consumption have high uncertainty, there is agreement that it will most likely continue to increase significantly, not least because of the boom of artificial intelligence (AI) [10, 13, 14].

At the same time, as ICT is closely linked to digitization, it also offers great potential for increasing resource efficiency and mitigating GHG emissions. Charfeddine et al. summarized some of the most important potential benefits: Smart energy consumption and smart buildings can enable energy savings as well as help stabilize the electricity grid while transitioning to 100 % renewable energies. Also the transportation sector and manufacturing industry show promising potentials for energy and GHG emission savings [8].

For the future development of ICT, it is essential that its positive potentials outweigh its negative impacts on climate and environment, so that it ultimately contributes to a net reduction in CO₂ emissions. Achieving this will require the elimination of GHG emissions across the ICT lifecycle and strengthening the sector’s environmental sustainability. For this purpose, the International Telecommunication Union (ITU), which is the United Nations specialized agency for ICT, has issued recommendations to guide ICT organizations in setting net-zero targets and developing appropriate strategies [15]. Due to the high energy consumption of ICT, the decarbonization of electricity generation is of fundamental importance. In parallel, reduction, avoidance and removal of residual GHG emissions, as well as improving energy efficiency are required. To reduce the negative impact on the environment, the demand of fresh raw materials for electronic devices must furthermore be reduced [8, 9]. When assessing opportunities to improve energy efficiency, it is crucial to consider the entire ICT value chain, from wafer and circuit fabrication to networks and data centers [8, 9, 14]. In addition to approaches such as more energy-efficient water cooling [16], improvements in energy efficiency can be achieved through more efficient software or hardware [17]. In this thesis, we focus on the goal of more efficient hardware.

Two major approaches addressing current challenges in ICT energy efficiency are diminishing idle power losses and more energy-efficient computing architectures. The first, idle power consumption, refers to the power consumed even though the system is not performing any task, e.g. due to leakage currents [17, 18]. For example, for the large language model “BLOOM”, the consumption attributed to idle power losses was estimated to be about 2/3 of the power required additionally for active training [17]. The second research approach, aiming for more energy-efficient computing architectures, is particularly necessary when the memory is accessed excessively, as “transferring data from DRAM to the processing unit through the cache hierarchy takes about two orders of magnitude more energy than performing a floating point operation on the processing unit once the data has arrived” [19]. Two important approaches in this direction are neuromorphic computing [20] and, more general, in-memory computing architectures [19]. Neuromorphic computing aims to mimic the brain, which can learn using dramatically less energy than state-of-the-art AI [20, 21, 22]. This makes neuromorphic computing a highly promising approach considering AI’s rapidly increasing energy demand [14].

Magnetic materials play a central role in tackling these challenges, both by intrinsically reducing idle power losses and by enabling novel computing paradigms. This research area, known as *spintronics*, thus contributes to improved energy efficiency for both data storage and processing [20, 23, 24]. One key advantage is that magnetic states are inherently non-volatile due to magnetic hysteresis, so no idle voltage is required to keep a state. Additionally, switching between states can be achieved very fast and at ultra-low power, while the devices exhibit high endurance [24, 25, 26]. In fact, the energy required to write a bit of magnetic memory has caught up with conventional random-access memory (RAM) [24, 27, 28]. In addition, static

random-access memory (SRAM) and dynamic random-access memory (DRAM) are volatile, so a voltage has to be applied to keep the information. This poses a significant disadvantage in terms of energy efficiency during operation compared to the non-volatile magnetic memories [28]. Furthermore, magnetic memories based on voltage control, like the magnetoelectric spin-orbit (MESO) device [29], were proposed to allow for switching energies as low as 1–10 aJ per bit [27, 29]. This is more than two orders of magnitude lower than for conventional RAM.

When switching from the conventional von Neumann architecture, in which memory and processing are separated, to in-memory computing, the energy required for data movement can be saved. This can be very significant especially for memory-intensive applications. For an associative processing task, Jarollahi et al. demonstrated a reduction of energy consumption of three orders of magnitude for hardware based on magnetic tunnel junctions (MTJs) compared to a software-based approach [30]. Compared to a classical hardware-based approach – specifically, a field-based approach using content-addressable memory – the MTJ-based chip requires almost 90 % less energy [30]. Improvements of a similar order of magnitude were also demonstrated by Ma et al. for single texture pattern matching [31].

In this thesis, I investigated the voltage control of magnetization using the ionic-liquid gating technique. Compared to current-controlled manipulation, voltage control allows for particularly low power consumption required for the manipulation of magnetic properties [25, 32, 33, 34]. Additionally, voltage gating provides access to a continuous range of magnetic states, enabling applications such as neural networks [21]. The voltages were applied using an ionic liquid (IL). ILs are molten salts that enable the application of extraordinary large electric fields [35, 36]. Therefore, they can induce the movement of mobile ion species inside a magnetic stack. This ion motion allows for reversible and low-power control of magnetic properties, such as the magnetic anisotropy [37, 38], exchange bias (EB) [39, 40] and Dzyaloshinsky-Moriya interaction (DMI) [41, 42]. The underlying theoretical concepts are discussed in **Chapter 2**. Details on the experimental methods and the IL gating setup which I built in Mainz can be found in **Chapter 3**.

For the manipulation of the EB, research has mainly focused on systems with a constant magnetization direction [39, 43, 44]. However, controlling anisotropy while retaining the EB is also highly desirable, e.g. for applications such as programming 3D magnetization sensors which require partly in-plane (IP) and partly out-of-plane (OOP) anisotropy. As part of this thesis, I demonstrated the stabilization of OOP magnetization in a previously IP magnetized sample while retaining strong OOP EB. These results are presented in **Chapter 4**.

In **Chapter 5**, the control of EB while retaining a stable OOP anisotropy was investigated. By demonstrating the manipulation of the EB, I also illustrated that it is possible to move oxygen ions through 6 nm metallic PtMn to modify the PtMn/Co interface. Aiming to enhance the effect even further raised the question how the oxygen distribution inside the PtMn looks like after IL gating as a function of gate voltage.

In **Chapter 6**, I therefore studied the oxygen distribution inside a metallic layer as a function of the IL gate voltage and thickness of the HfO₂ capping layer. As a model system, Ta was investigated because of its very smooth and uniform growth [45, 46].

Finally, the results are summarized and open questions and possible research directions are discussed in the Conclusion and Outlook in **Chapter 7**.

Theoretical background

In this chapter, we will discuss the fundamentals of magnetism which are required to understand the following results. We will start with an overview over the different classes of magnetism and then look at the microscopic origin of this magnetism. To understand the magnetic properties of thin film magnetic layers, we will then introduce the thermodynamic description of magnetism. In this framework, we will discuss the energy contributions which determine the magnetic structure of the materials investigated in this thesis. This allows us to understand the formation of magnetic domains and the response of magnetic materials to an external magnetic field.

2.1 The richness of magnetism

Magnetism is one of the fundamental properties of materials. The different types of magnetism can be generally classified via the induced magnetization $\mathbf{M}$ as a response to an external magnetic field $\mathbf{H}$. The proportionality factor is called magnetic susceptibility χ . It is defined as $\mathbf{M} = \chi \mathbf{H}$ [47, 48]. Additionally, the total magnetic moment $\mathbf{m} = \int_V \mathbf{M} dV$ of a magnetic material with volume V represents its overall magnetic direction and amplitude.

All materials exhibit *diamagnetism*, reflected by a negative magnetic susceptibility $\chi < 0$. It corresponds to an induced magnetic moment which opposes the direction of the magnetic field. Classically, it can be understood as a consequence of Lenz's law. However, the true origin lies in quantum mechanics [47]. Diamagnetism is usually a very weak effect. Materials, where this effect dominates the response to an external magnetic field, so called *diamagnets*, include e.g. water and benzene [47].

The behavior in an external magnetic field usually looks very different, if the material has unpaired electrons. Each electron has a magnetic moment consisting of a spin and orbital contribution (see Chapter 2.2). If an atom or molecule has unpaired electrons, the magnetic moments of the electrons add up to a net magnetic moment which is different from zero. In an external magnetic field, this net magnetic moment aligns with the field, causing a positive magnetic susceptibility $\chi > 0$. Typically, it is significantly larger than the diamagnetic negative susceptibility. Depending on the strength and type of interaction between the net magnetic moments of neighboring atoms, this can lead to different types of magnetism, which will be discussed in the following.

If the interactions between neighboring atoms are weak, their magnetic moments behave largely independently. This results in *paramagnetism*. Its characteristic is, that the magnetic moments of the atoms or molecules are unordered and the overall magnetic moment of the ma-

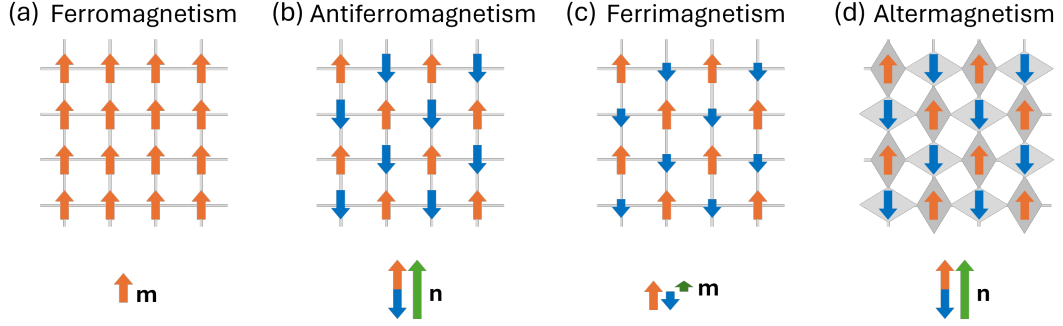


Figure 2.1: Different types of collinear magnetic ordering. (a) In the case of ferromagnetism, all spins are aligned in parallel, represented by the orange arrows. Their direction and amplitude can be represented by the total magnetic moment $\mathbf{m}$. (b)–(d) For antiferromagnetism, ferrimagnetism and altermagnetism, two spin sublattices are present (orange and blue). For collinear magnets, the spins on the two lattices point in opposite directions. For ferrimagnets, an overall magnetic moment remains. For antiferromagnets and altermagnets, the spins fully compensate each other. The direction of the magnetization is characterized by the Néel vector $\mathbf{n}$. For altermagnets, additionally to the spin, also the electronic bands differ between the two sublattices, indicated by the rhombi.

material becomes zero when no external magnetic field is applied [47].

Both, dia- and paramagnetism, are linear effects, so the magnetization changes proportionally with the applied external magnetic field and vanishes when no external field is applied. In contrast, when the interactions between the magnetic moments of different atoms become larger, long-range magnetic order appears even when no external magnetic field is applied. This allows for a panoply of different magnetic ground states. Figure 2.1 gives an overview over some of these states, including the ones discussed in this thesis. In Figure 2.1 only the spin magnetic moments are depicted. The physical origin, why a certain order of spin magnetic moments becomes stable, will be discussed in more detail in Chapter 2.3.

In *ferromagnets* (*FM*s), all spins are aligned in parallel (Fig. 2.1 a) [48]. This results in a strong magnetic moment $\mathbf{m}$. *FMs* are the typical material for fridge magnets, but are also central for many technological applications like motors, actuators, sensors and magnetic recording [48].

AFMs [48, 49] show two or more sublattices with opposing magnetization. A simple case of a collinear antiferromagnet with two sublattices is represented in Figure 2.1 b. Each sublattice has a magnetization $\mathbf{M}_i$ whereby $\mathbf{M}_1 = -\mathbf{M}_2$. Therefore, the total magnetic moment is zero. To characterize the magnetization direction in *AFMs*, the Néel vector $\mathbf{n}$ is defined as $\mathbf{n} = (\mathbf{M}_1 - \mathbf{M}_2)/(2|\mathbf{M}_1|)$. *AFMs* are a common type of magnetic ordering in nature. They occur in many different variations, with different arrangement of the two sublattices, with nonmagnetic spacer atoms in between the magnetic atoms and also with more sublattices and canted moments. *AFMs* can also be imitated by growing thin ferromagnetic layers on top of each other with spacer layers in between, such that the magnetic layers order antiferromagnetically with respect to each other. Such materials are called *synthetic AFMs* [50]. Because of the fully compensated magnetization, *AFMs* are considered a promising candidate for future applications in spintronics. They allow for high bit packing densities and large stability against external fields [51]. Additionally, the antiferromagnetic ordering of the spins causes large energies which can lead to ultra-fast switching in the THz regime between different magnetic states [52].

Similarly to *AFMs*, *ferrimagnets* [48, 53] possess two sublattices, but without fully compensated magnetization $|\mathbf{M}_1| \neq |\mathbf{M}_2|$ (Fig. 2.1 c). This combines the advantage of easy detection

and manipulation of the net magnetic moment, like in FMs, together with the ultra-fast switching dynamics, like in AFMs. Additionally, the net magnetic moment can be tuned, and in some ferrimagnets even inverted, by tuning the temperature or composition [53].

Recently, a new class of magnetic materials was found, called *altermagnets* (Fig. 2.1 d) [54, 55]. These materials possess two sublattices with fully compensated magnetization, like AFMs, but with different electronic structures of the two sublattices. This leads to a broken time-reversal symmetry, which causes effects like an anomalous Hall effect, which would conventionally only be expected in FMs and not in AFMs.

This was just a small glimpse into the diverse field of magnetism. Other classes of magnetism include helical or spiral structures and spin glasses [48]. It is this large spectrum of different possible structures and properties which makes magnetism so exciting, both from a theoretical and applied perspective.

2.2 Microscopic origin of magnetism

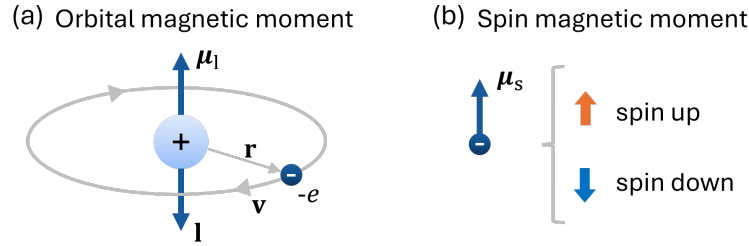


Figure 2.2: Illustration of the concept of magnetic moments of electrons. (a) Orbital magnetic moment μ_l which is proportional to the angular momentum $\mathbf{l}$ but with opposite sign. In a classical picture this can be understood by looking at an electron with the charge $-e$ circulating around its nucleus in a distance $\mathbf{r}$ with a velocity $\mathbf{v}$. (b) The spin magnetic moment μ_s is caused by the spin $\mathbf{s}$ of the electron and can take exactly two values, corresponding to spin up and spin down. Panel (a) adapted from [48].

To understand the origin of magnetism and its diverse facets, we have to delve into the microscopic world. The following description of the underlying physics follows references [47], [48] and [56].

The root of magnetism in solids lies in the properties of the electrons. Each electron has an intrinsic magnetic moment. It has two sources, the orbital and spin angular momentum of the electron (Fig. 2.2). The magnetic moment caused by the orbital angular momentum can be derived in the framework of the Bohr model (Fig. 2.2 a). Using the analogy of a conductor loop, the *orbital magnetic moment* μ_l caused by the current I around an area A can be determined as $\mu_l = IA$. The current I of an electron with charge $-e$ traveling with a speed v on an orbit with radius r is given as $I = -e/\tau$ with the period of rotation $\tau = 2\pi r/v$. For a circular orbit the area is given as $A = \pi r^2$. The direction of the orbital magnetic moment follows from Ampère's law, which, however, assumes positive charges [57]. Using this, the orbital magnetic moment is given as [48]:

$$\mu_l = -\frac{e}{2}\mathbf{r} \times \mathbf{v} \quad (2.1)$$

To understand where the velocity of the electron comes from, we have to look at quantum mechanics. According to quantum mechanics, electrons can be described as waves. For a circulating electron, its wave function Ψ has to fulfil the boundary condition $\Psi(\Phi + 2\pi) = \Psi(\Phi)$

at each angle Φ [56]. To better understand the magnetic moment, it is useful to express the velocity in terms of the orbital angular momentum $\mathbf{l} = m_e \mathbf{r} \times \mathbf{v}$. Summarizing all constant prefactors into the gyromagnetic ratio $\gamma = -e/2m_e$, we obtain for the orbital magnetic moment [48]:

$$\boldsymbol{\mu}_l = -\frac{e}{2m_e} \mathbf{l} = \gamma \mathbf{l} \quad (2.2)$$

According to quantum mechanics, the angular momentum is quantized. The component of angular momentum along a fixed direction is given as $l_z = m_l \hbar$ with orbital magnetic quantum number $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ and reduced Planck constant $\hbar$. Therefore, also the orbital magnetic moment is quantized. Along a fixed direction z it is given by Equation 2.3. Its natural unit turns out to be the Bohr magneton μ_B [48].

$$\mu_{l,z} = -\frac{e\hbar}{2m_e} m_l = -\mu_B m_l, \quad \text{with } m_l = 0, \pm 1, \pm 2, \dots \quad (2.3)$$

Additionally to the orbital angular momentum $\mathbf{l}$, each electron also has a spin angular momentum $\mathbf{s}$, causing a *spin magnetic moment* $\boldsymbol{\mu}_s$ (Fig. 2.2 b). It is an intrinsic property, associated with the spin of fermions. The corresponding spin magnetic quantum number m_s can take exactly two values $m_s = \pm 1/2$, referred to as “spin up” and “spin down”. In contrast to the orbital magnetic moment, the magnitude of the spin magnetic moment cannot be derived classically. Experimentally, the spin magnetic moment along a fixed direction $\mu_{s,z}$ turned out to be almost one μ_B . This is approximately twice as large as would be obtained classically from $-\mu_B m_s$. The additional factor is called *g-factor* $g_s \approx 2$. It implies that a given angular momentum leads to an almost twice as large magnetic moment in the case of the spin magnetic moment compared to the orbital magnetic moment. The corresponding equations are [47]:

$$\boldsymbol{\mu}_s = g_s \gamma \mathbf{s} \approx -\frac{e}{m_e} \mathbf{s} \quad (2.4)$$

$$\mu_{s,z} = -g_s \mu_B m_s, \quad \text{with } m_s = \pm 1/2 \quad (2.5)$$

2.2.1 Spin-orbit coupling

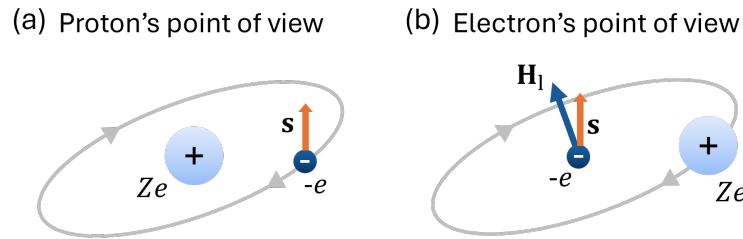


Figure 2.3: Illustration of the concept of spin-orbit coupling. (a) The electron circulating around the nucleus from a proton’s point of view. (b) Same situation from the electron’s point of view. The electron carries the spin $\mathbf{s}$ and the rotation of the nucleus around the electron causes a magnetic field $\mathbf{H}_l$ at the position of the electron which interacts with the spin. Figure adapted from [48].

The orbital and spin angular momentum interact via spin-orbit coupling (SOC). The concept can be visualized as depicted in Figure 2.3. Equivalently to looking at the orbital angular momentum of the electron, visualized in Figure 2.3 a as a circular orbit, we can also consider the situation from the electron’s point of view. From that perspective, the nucleus appears to move around the electron, causing a magnetic field $\mathbf{H}_l$ at the electron’s position. This magnetic field

is proportional to the orbital angular momentum $\mathbf{l}$ of the electron. For a hydrogen-like atom, the magnetic field can be simplified to [47]:

$$\mathbf{H}_l \propto -\frac{Ze}{m_e r^3} \mathbf{l} \quad (2.6)$$

where Ze is the charge of the nucleus, m_e the mass of the electron, r the distance between the electron and the nucleus and the minus is caused by the negative charge of the electron. This field interacts with the spin magnetic moment, resulting in an additional term in the Hamiltonian $\mathcal{H}_{\text{SOC}}$ [47]:

$$\mathcal{H}_{\text{SOC}} \propto -\boldsymbol{\mu}_s \cdot \mathbf{H}_l \quad (2.7)$$

$$\propto \frac{Ze^2}{m_e^2 r^3} \mathbf{s} \cdot \mathbf{l} \quad (2.8)$$

From this result for hydrogen-like atoms we learn that the SOC is particularly strong for heavy elements (high Ze) and for the electrons close to the nucleus (small r).

Now, we are ready to look at a multi-electron atom. The magnetization $\mathbf{M}$ of an atom is given by the total angular momentum $\mathbf{J}$ which is defined by the valence electrons. How the spin and orbital angular momenta couple to the total angular momentum $\mathbf{J}$ is determined by the strength of the SOC, compared to electrostatic interactions between the electrons. If the spin-orbit interaction is weak and can be treated as a perturbation, Hund's rules apply. In that case, first the orbital angular momenta $\mathbf{l}_i$ of all electrons couple to the total orbital angular momentum $\mathbf{L}$ and all spin angular momenta $\mathbf{s}_i$ couple to the total spin angular momentum $\mathbf{S}$ in the way determined by Hund's rules. Afterward, $\mathbf{L}$ and $\mathbf{S}$ couple to the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$. This is called *L-S coupling*. However, for heavy elements with high atomic number Z , the spin-orbit interaction can be so strong, that the spin and orbital angular momenta of each electron first couple together to $\mathbf{j}_i = \mathbf{l}_i + \mathbf{s}_i$ and then the total angular momentum is given as $\mathbf{J} = \sum_i \mathbf{j}_i$. This type of coupling is called *j-j coupling* [47].

This demonstrates the fundamental role of SOC in magnetism. Additionally to its influence on the coupling of the magnetic moments of the electrons, the SOC is also the basis for many macroscopic magnetic phenomena like the crystalline anisotropy, as we will see later in this chapter.

2.3 Long-range magnetic order

Next we will look at the coupling between different atoms, more precisely the *exchange interaction*. The observation of collective, long-range magnetic order like in FMs and AFMs is actually a quite surprising observation and cannot be explained classically. It is caused by the Pauli exclusion principle, a purely quantum mechanical effect [47].

2.3.1 Heisenberg exchange interaction

To understand the effect, we will first look at the electrons on two neighboring atoms. According to the Pauli exclusion principle, two electrons can never have the same quantum mechanical state. We can now consider an electron which wants to reduce its energy by increasing its spacial expansion. As soon as this leads to an overlap with the wave function of another electron, the two electrons need to have opposite spin to ensure a difference in their quantum numbers. In this case, flipping the spin to the parallel direction is directly related with an energy cost (Fig. 2.4 a). This can cause long-range AFM ordering [47, 48]. However, this is only one possible scenario. Which magnetic state minimizes the energy depends a lot on the type of atoms and

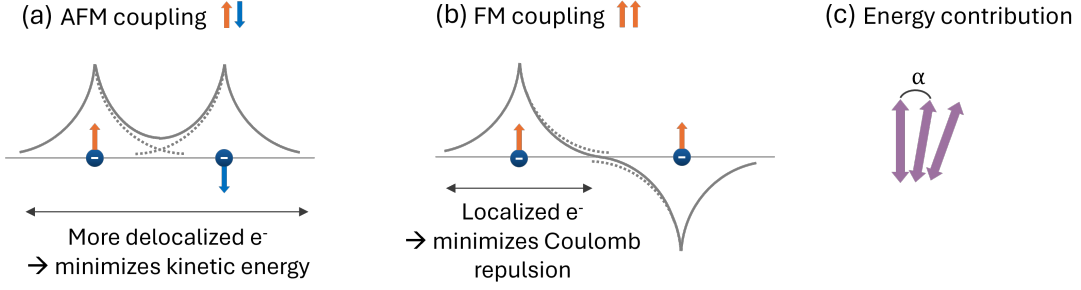


Figure 2.4: Illustration of the quantum mechanical origin of the exchange interaction. (a) Symmetric and (b) antisymmetric wave function of an H_2 molecule, demonstrating that the symmetric wave function minimizes the kinetic energy of the electrons while the antisymmetric wave function minimizes the Coulomb repulsion. (c) Energy cost due to exchange coupling. The energy is proportional to the angle α , favoring collinear alignment of all spins. Panels (a) and (b) are adapted from [48].

their arrangement. It should also be noted, that inside a single atom, the exchange interaction between two electrons usually leads to FM coupling. In this case, the dominant energy is the Coulomb repulsion which can be minimized for orthogonal orbitals with zero overlap, which we can ensure by having identical spins (Fig. 2.4 b). This is the basis for Hund's first rule [47].

To get a more thorough understanding, we will now look at the underlying equations, starting with a simple system of only two electrons. For this we will follow reference [47]. According to quantum mechanics, for fermions the overall wave function must be antisymmetric. Furthermore, we know that for electrons we have a spacial ψ and spin χ part of the wave function. Therefore, one of the two has to be symmetric and the other one antisymmetric. For the spin wave function of a two-electron system, the antisymmetric state (spin quantum number $S = 0$) is called the *singlet* χ_S and the symmetric state ($S = 1$) is called the *triplet* χ_T . They correspond to the following eigenstates [47]:

$$\chi_S = \frac{|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle}{\sqrt{2}} \quad (2.9)$$

$$\chi_T = |\uparrow\uparrow\rangle; |\downarrow\downarrow\rangle; \frac{|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle}{\sqrt{2}} \quad (2.10)$$

If we call the spacial wave functions of the two electrons ψ_a and ψ_b and the locations of the electrons $\mathbf{r}_1$ and $\mathbf{r}_2$, we can write down the full wave function Ψ of the two-electron system for the spin singlet and triplet case [47]:

$$\Psi_S = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) + \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \chi_S \quad (2.11)$$

$$\Psi_T = \frac{1}{\sqrt{2}} [\psi_a(\mathbf{r}_1)\psi_b(\mathbf{r}_2) - \psi_a(\mathbf{r}_2)\psi_b(\mathbf{r}_1)] \chi_T \quad (2.12)$$

To determine how difficult it is to switch between these two states, we have to calculate their energy difference. The energies of the two states are defined as [47]:

$$E_S = \int \Psi_S^* \hat{\mathcal{H}} \Psi_S \, d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.13)$$

$$E_T = \int \Psi_T^* \hat{\mathcal{H}} \Psi_T \, d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.14)$$

The difference between the two energies is defined as twice the *exchange constant*, also called *exchange integral*, J . For normalized χ_S and χ_T it is given as [47]:

$$J = \frac{E_S - E_T}{2} = \int \psi_a^*(\mathbf{r}_1) \psi_b^*(\mathbf{r}_2) \hat{\mathcal{H}} \psi_a(\mathbf{r}_2) \psi_b(\mathbf{r}_1) \, d\mathbf{r}_1 d\mathbf{r}_2 \quad (2.15)$$

With this, the spin-dependent term in the effective Hamiltonian is given as [47]:

$$\hat{\mathcal{H}}^{\text{spin}} = -2J \mathbf{s}_1 \cdot \mathbf{s}_2 \quad (2.16)$$

Heisenberg generalized this to systems with many electrons. The exchange interaction is then defined between each pair of spins i and j as J_{ij} , such that we get for the Heisenberg Hamiltonian [47]:

$$\hat{\mathcal{H}} = - \sum_{ij} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j \quad (2.17)$$

For positive exchange constant $J > 0$, $E_S > E_T$, so the triplet state is favored. This corresponds to *ferromagnetic coupling*. For $J < 0$, $E_S < E_T$, so the singlet state is favored, corresponding to *antiferromagnetic coupling*. In general, the exchange interaction favors the alignment of all spins and therefore enables long-range magnetic order and large magnetic domains (Fig. 2.4 c). Furthermore, the magnitude of the exchange interaction determines at which temperature the material loses its permanent magnetic properties. Above this temperature, the thermal energy becomes larger than the exchange coupling such that the material loses its magnetic order and becomes paramagnetic. For AFMs this temperature is called *Néel temperature* T_N , for FMs it's called *Curie temperature* T_C . The corresponding energy, $k_B T_C$ for a FM, with the Boltzmann constant k_B , is proportional to the exchange constant J . To get a feeling for the corresponding internal energy, it can be expressed via an internal molecular field B_{mf} , which is the field created at the i^{th} site by all other electrons according to the Weiss model of a FM [47].

$$k_B T_C \propto J \propto \mu_B B_{\text{mf}} \quad (2.18)$$

For FMs with a Curie temperature around 1000 K, like for Fe and Co [48], this yields an internal molecular field in the order of 1000 T [47]. Such high internal fields cannot be explained via dipolar interactions between the electrons, confirming the fundamental importance of the exchange interaction for magnetism.

To understand the overall magnetic state of a material, we now have to consider the atomic arrangement. If the exchange interaction is present between electrons from two neighboring magnetic atoms, it is called *direct exchange*. However, in many materials, the magnetic atoms are too far apart such that the overlap between their electronic wave functions is very small. For example in rare earth elements, the valence electrons belong to the 4f-shells and are very localized [47]. In other cases, nonmagnetic atoms lie in between the magnetic atoms, for example in oxides

like CoO. In these cases, indirect exchange can play a significant role. For indirect exchange, many options exist, such as *superexchange* (important e.g. in magnetic oxides), *double exchange* (important e.g. for magnetic ions with mixed valency), the anisotropic exchange interaction, also known as *DMI*, important when spin-orbit coupling becomes large, as well as the mediation via *itinerant electrons*. In the next chapter, we will discuss the mechanism of exchange coupling via the itinerant electrons in more detail, as this is the basis for magnetism in metals. Detailed descriptions on the other types of indirect exchange interaction can be found e.g. in references [47] and [48].

2.3.2 Magnetism of itinerant electrons

The Heisenberg Hamiltonian, discussed in the previous section, assumed that electrons are localized on their atoms. In metals, this assumption does not hold. Therefore, the Heisenberg Hamiltonian can only be applied, if the net magnetic moment is associated with electrons which remain localized. Often, however, the magnetic moment is associated with the valence electrons which can wander freely and are therefore also called *itinerant electrons*. This becomes clear when looking e.g. at the magnetic moment of iron which is about $2.2 \mu_B$ per atom [47]. This cannot be explained with localized electrons.

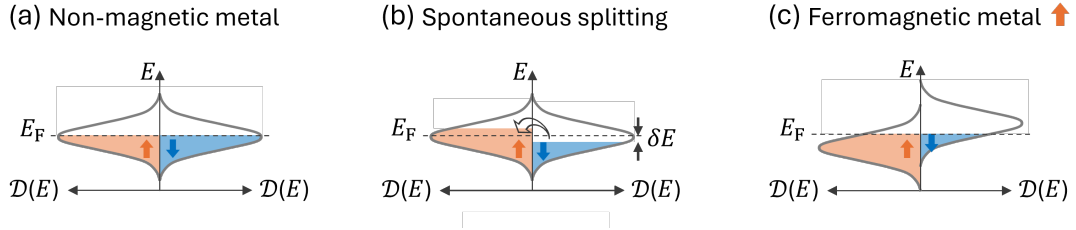


Figure 2.5: Illustration of the process of the spontaneous magnetization in FMs. (a) Density of states $\mathcal{D}(E)$ for a d -band of a non-magnetic metal. The spin-up and spin-down subband are equally populated. (b) Redistribution of spins which can cause a spontaneous splitting of the energy bands. This happens spontaneously and in the absence of any external magnetic field. (c) Band structure of a FM metal, showing the spin-split d -band. Panels (a) and (c) are adapted from [48].

The concept of itinerant magnetism is illustrated in Figure 2.5. In metals the electrons fill up the bands until the Fermi energy E_F . Each state in k -space can be occupied with two electrons with opposite spin. In a nonmagnetic metal, the two spin subbands are equally populated (Fig. 2.5 a). However, the two electrons which occupy the same state in k -space experience a Coulomb repulsion. To reduce this repulsion, we could consider moving some of the electrons from one spin subband (e.g. the ones in the energy range $E_F - \delta E$ to E_F) to the other spin subband (so into the energy range E_F to $E_F + \delta E$) (Fig. 2.5 b). The number of spin-flipped electrons is then $\delta n = \mathcal{D}(E_F)\delta E$, with the density of states (DOS) at the Fermi level $\mathcal{D}(E_F)$ and the number n of electrons in each subband before flipping the spins. To estimate the reduction of the Coulomb repulsion, we consider the simple case of only on-site Coulomb repulsion of energy U . Then, the Coulomb energy is given as $E_{\text{pot}} = U n_{\uparrow} n_{\downarrow}$. With this, the reduction of the Coulomb energy is given as [47]:

$$\Delta E_C = U(n + \delta n)(n - \delta n) - U n^2 \quad (2.19)$$

$$= -U(\delta n)^2 \quad (2.20)$$

$$= -U(\mathcal{D}(E_F)\delta E)^2 \quad (2.21)$$

Moving spins to the other spin subband, however, also costs kinetic energy. This energy cost is given as the number of moved electrons $\delta n = \mathcal{D}(\mathcal{E}_F)\delta\mathcal{E}$ times their energy increase δE . Therefore, the increase in kinetic energy is given as [47]:

$$\Delta E_{\text{kin}} = \mathcal{D}(E_F)(\delta E)^2 \quad (2.22)$$

Overall, this is energetically favorable, if the decrease in Coulomb energy is larger than the increase in kinetic energy, $\Delta E \leq 0$, with [47]:

$$\Delta E = \Delta E_{\text{kin}} + \Delta E_C \quad (2.23)$$

$$= \mathcal{D}(E_F)(\delta E)^2(1 - U\mathcal{D}(E_F)) \quad (2.24)$$

This yields the *Stoner criterion* [47]:

$$U\mathcal{D}(E_F) \geq 1 \quad (2.25)$$

Therefore, spontaneous ferromagnetism is possible, if the Coulomb repulsion and the DOS at the Fermi energy are large. This is very logical considering that the cost of kinetic energy when flipping spins becomes smaller, the larger the DOS at the Fermi energy is. This explains the large difference in the results when considering localized or itinerant electrons.

When the Stoner criterion is fulfilled and spontaneous magnetization occurs, the bands split. This is illustrated in Figure 2.5 c. The Stoner criterion is fulfilled for Fe, Co and Ni, which have very narrow 3d-bands and a large DOS at the Fermi energy [48].

2.4 Thermodynamical description of magnetism

To understand the magnetic structure in samples with a defined shape and size, it is convenient to switch to a thermodynamic description of magnetism based on the *micromagnetic approximation*. The fundamental assumption is that the exchange coupling is strong enough to keep the magnetization aligned over an area significantly larger than individual atoms. In this case, a continuum approximation is justified and we can define a continuous magnetization vector field instead of looking at individual magnetic moments. The magnetization vector $\mathbf{M}(\mathbf{r})$ is defined as:

$$\mathbf{M}(\mathbf{r}) = M_S \mathbf{m}(\mathbf{r}) \quad (2.26)$$

with the saturation magnetization M_S and the normalized magnetization $\mathbf{m}(\mathbf{r})$. The normalized magnetization is a unit vector which points in the same direction as the total magnetic moment at position $\mathbf{r}$. The micromagnetic approximation thereby allows to treat magnetism in a semi-classical framework which, however, incorporates quantum mechanical phenomena, such as the exchange coupling.

To determine the ground state of the magnetization, the micromagnetic free energy E_{total} has to be minimized. The adjective *free* thereby points out the temperature dependence of the energy contributions. It is given as [56]:

$$E_{\text{total}} = \int_V [\mathcal{E}_{\text{ex}}(\mathbf{r}) + \mathcal{E}_Z(\mathbf{r}) + \mathcal{E}_{\text{demag}}(\mathbf{r}) + \mathcal{E}_{\text{anis}}(\mathbf{r}) + \mathcal{E}_{\text{EB}}(\mathbf{r}) + \dots] d^3r \quad (2.27)$$

where the energy contributions per volume $\mathcal{E}_{\text{ex}}(\mathbf{r})$ is the exchange energy (Fig. 2.6 a), $\mathcal{E}_Z(\mathbf{r})$ the Zeeman energy (Fig. 2.6 b), $\mathcal{E}_{\text{demag}}(\mathbf{r})$ the demagnetization energy (Fig. 2.6 c), $\mathcal{E}_{\text{anis}}(\mathbf{r})$ the anisotropy energy (Fig. 2.6 d) and $\mathcal{E}_{\text{EB}}(\mathbf{r})$ the exchange bias energy, which is a unidirectional

anisotropy energy. These are the main contributions which determine the magnetic state in the samples investigated in this thesis. The individual energy contributions will be described in more detail in the following sections.

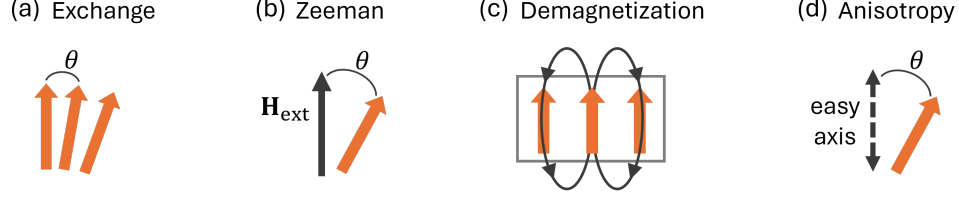


Figure 2.6: Energies involved in the ground state of a magnetic system. (a) Exchange energy, favoring collinear alignment of all spins. (b) Zeeman energy, favoring the alignment of the magnetization to an externally applied magnetic field $\mathbf{H}_{\text{ext}}$. (c) Demagnetization energy, favoring minimal stray fields because of the energy cost of spins unaligned to the stray field (indicated by the black elliptical arrows). (d) Anisotropy energy, occurring in all materials which have an energetically preferred magnetization direction, called *easy axis*, or magnetization plane, called *easy plane*.

2.4.1 Exchange energy

The exchange energy (Fig. 2.6 a), corresponding to the Heisenberg Hamiltonian, is responsible for the long-range magnetic order. As discussed above, it determines whether a material is a FM or AFM and it favors the collinear alignment of all spins (Fig. 2.4 c). In the micromagnetic approximation, it is therefore expressed in terms of the gradient of the normalized magnetization $\mathbf{m} = (m_x, m_y, m_z)$. As it does not depend on the direction of the gradient but only the absolute value, the gradients contribute quadratically [47]:

$$E_{\text{ex}} = \int_V \mathcal{E}_{\text{ex}}(\mathbf{r}) d^3r = A_{\text{ex}} \int_V [(\nabla m_x)^2 + (\nabla m_y)^2 + (\nabla m_z)^2] d^3r \quad (2.28)$$

where A_{ex} is the *exchange stiffness* and defined as $A_{\text{ex}} = 2JS^2z/a$. Hereby, J is the exchange constant, which is assumed to be constant between nearest neighbors and zero otherwise, S is the magnitude of the spin per atom, z is the number of sites in the unit cell and a is the nearest neighbor distance [47].

2.4.2 Zeeman energy

The Zeeman energy (Fig. 2.6 b) describes the reaction of the magnetization to an external magnetic field $\mathbf{H}_{\text{ext}}(\mathbf{r})$. The energy is minimized if all magnetic moments are aligned to the external field. Therefore, the energy term is proportional to the scalar product of the magnetization $\mathbf{M}(\mathbf{r})$ and $\mathbf{H}_{\text{ext}}(\mathbf{r})$, with the vacuum magnetic permeability constant μ_0 [48]:

$$E_Z = \int_V \mathcal{E}_Z(\mathbf{r}) d^3r = -\mu_0 \int_V \mathbf{M}(\mathbf{r}) \cdot \mathbf{H}_{\text{ext}}(\mathbf{r}) d^3r \quad (2.29)$$

$$= -\mu_0 M_S H_{\text{ext}} \int_V \cos(\theta(\mathbf{r})) d^3r \quad (2.30)$$

2.4.3 Demagnetization energy

The demagnetization energy (Fig. 2.6 c) is caused by the dipolar interaction between the magnetic moments. Figure 2.6 c illustrates the basic concept. For a FM with fully aligned mag-

netization, this magnetization causes a magnetic field, the so-called *stray field*. The stray field penetrates back into the material and now opposes the magnetization direction. The resulting energy cost can be reduced by diminishing the total magnetization via the formation of *magnetic domains*, areas with different magnetization directions (see Chapter 2.4.6). Therefore, the stray field is also called *demagnetizing field* $\mathbf{H}_d(\mathbf{r})$. The corresponding energy term can be written as [56]:

$$E_{\text{demag}} = \int_V \mathcal{E}_{\text{demag}}(\mathbf{r}) d^3r = -\frac{\mu_0}{2} \int_V \mathbf{M}(\mathbf{r}) \cdot \mathbf{H}_d(\mathbf{r}) d^3r \quad (2.31)$$

The factor of 1/2 thereby accounts for double counting of the magnetization, as it is comprised in $\mathbf{M}(\mathbf{r})$ as well as in $\mathbf{H}_d(\mathbf{r})$ [48]. To calculate the demagnetizing field, we can express it in terms of a 3x3 matrix $\mathcal{N}$ which comprises the shape of the magnetic material [48]:

$$\mathbf{H}_d = -\mathcal{N}\mathbf{M} \quad (2.32)$$

The matrix $\mathcal{N}$ is called the *demagnetizing tensor*. For ellipsoids with homogeneous magnetization, it turns out that the demagnetizing field is collinear to the magnetization along all three principal axis. In this case, the demagnetizing tensor can be diagonalized, where the components on the diagonal are N_x , N_y and N_z and all off-diagonal components are zero. The diagonal components are called *demagnetizing factors* and they fulfill the relation $N_x + N_y + N_z = 1$.

2.4.3.1 Shape anisotropy

For some simple geometries, we can determine these demagnetizing factors (see e.g. reference [48]). In particular, for a thin film, $N = 0$, if the magnetization is lying inside the sample plane and $N = 1$, if the magnetization is orthogonal to the sample plane. This means, that due to the demagnetization energy, in-plane magnetization is always energetically favored in thin films. Equivalently, for long needles, $N = 0$, if the magnetization is lying along the axis and $N = 1/2$, if the magnetization is lying orthogonal to the axis. For a sphere, $N = 1/3$, for the magnetization in any direction. This causes the magnetization to align radially, following the shape of the sphere with a singularity at the center, to allow for flux closure. This phenomenon, that the magnetic structure is influenced by the shape of the material due to the demagnetizing field, is called *shape anisotropy*. The demagnetizing energy is therefore also called the *shape anisotropy energy*.

In this thesis, we will mostly look at thin films. For a thin film in the x-y plane, with completely aligned magnetization of magnitude M_S , the demagnetizing factors are $N_x = N_y = 0$ and $N_z = 1$. Therefore, the energy gain when the magnetization realigns from OOP magnetization to IP magnetization is:

$$E_{\text{film}} = \frac{\mu_0}{2} M_S^2 V \quad (2.33)$$

Additionally to causing the shape anisotropy, the demagnetizing energy is also responsible for the domain formation in FMs, as we will discuss in more detail at the end of this section.

2.4.4 Anisotropy energies

Anisotropy describes the phenomenon that the magnetization preferentially lies along a fixed axis or inside a fixed plane of a material (Fig. 2.6 d). In systems with uniaxial anisotropy, this direction, which is energetically most favorable is called *easy axis*. The most unfavorable direction is called *hard axis*. If a plane inside the material is energetically most favorable, this plane is called *easy plane*. For a uniaxial anisotropy, the anisotropy constant K can be defined, which is a measure for the energy gain when the magnetization aligns along the respective easy axis. For $K < 0$, the easy axis lies in the plane, for $K > 0$, OOP magnetization is favored.

The anisotropy can have different origins. It can be either a bulk effect, like for the shape anisotropy, the magnetocrystalline anisotropy and the magnetoelastic anisotropy, or an interfacial effect. Which term dominates, depends on the strength of the different anisotropies and on the film thickness. The thinner the film, the larger the influence of interfacial anisotropies. Considering all uniaxial bulk anisotropies (summed up in K_{bulk}), the shape anisotropy and all interfacial anisotropies (summed up in K_{int} , considering both interfaces), the effective anisotropy constant K_{eff} for a magnetic film with thickness t can be written as [47, 58]:

$$K_{\text{eff}} = (K_{\text{bulk}} - \frac{\mu_0}{2} M_S^2) + \frac{K_{\text{int}}}{t} \quad (2.34)$$

Tuning the thickness of a magnetic thin film, can therefore lead to a change of the effective easy axis and thereby a rotation of the magnetization. This is a common and well known way to tune the magnetization direction in thin films [58, 59] and will also be used in this thesis. In the following, we will discuss different possible origins of anisotropy.

2.4.4.1 Magnetocrystalline anisotropy

Magnetocrystalline anisotropy plays a significant role in all crystals and crystallites with large SOC. It is caused by the electrostatic interaction between the orbitals which carry the valence electrons, or, in other words, the interaction of an electron with the crystal field created by all the other electrons [48]. This causes an energy splitting, which makes certain orbitals more energetically favorable. In combination with the SOC, this leads to preferential spin orientations. For example Cobalt shows uniaxial anisotropy with easy axis along the “stacking direction of the hexagonally closed packed planes” [47].

For a system consisting of crystallites with easy axis along direction $\hat{\mathbf{e}}_k(\mathbf{r})$ and with a magnetization lying in an angle $\theta(\mathbf{r})$ toward this easy axis, the anisotropy energy can be expressed to first order as:

$$E_{\text{MagCr}} = K_{\text{MagCr}} \int_V 1 - (\mathbf{m}(\mathbf{r}) \cdot \hat{\mathbf{e}}_k(\mathbf{r}))^2 d^3r \quad (2.35)$$

$$= K_{\text{MagCr}} \int_V \sin^2(\theta(\mathbf{r})) d^3r \quad (2.36)$$

2.4.4.2 Magneto-elastic anisotropy

The magneto-elastic anisotropy takes account of the interaction between the magnetization and lattice distortions. It describes the effect, that materials experience a spontaneous deformation due to their magnetic ordering. This can be observed e.g. in FM crystals, which can never be perfectly cubic [48]. The origin of the magneto-elastic anisotropy are SOC and the exchange interaction. Their dependence on the inter-atomic distance defines the strength of the magneto-elastic coupling [60, 61, 62].

The magnitude of the response of the magnetization to mechanical strain, or equivalently, the magnitude of the response of the lattice to an externally applied magnetic field, is expressed in the *magneto-elastic constant* λ . For $\lambda > 0$, a uniaxial FM would exhibit an elongation in the direction of the externally applied field, for $\lambda < 0$, it would show a contraction [48]. The strain inside the material can be expressed as a 3x3 matrix $\mathcal{U}$ called *strain tensor*. The diagonal elements u_{xx} , u_{yy} and u_{zz} represent the normal strains in the respective directions. The off-diagonal elements $u_{ij, i \neq j}$ represent the shear strains.

The magneto-elastic anisotropy energy is especially important for the formation of AFM domains (see Chapter 2.4.6.1). Therefore, we will give the energy term for AFM materials. The magnetization direction in AFMs is represented by the Néel vector $\mathbf{n}$. The coupling between the strain tensor $\mathcal{U}$ and the Néel vector $\mathbf{n}$ is described by the magneto-elastic constant λ . In the case

of a collinear AFM, it can be expressed as a 4-dimensional tensor λ_{ijkl} . The magneto-elastic energy for small deformations is then given as [63]:

$$E_{\text{MagEl}} = \sum_{ijkl} \lambda_{ijkl} u_{ij} n_k n_l \quad (2.37)$$

2.4.4.3 Interfacial perpendicular magnetic anisotropy

Anisotropies can not only be induced in the bulk of a crystal, but they can also stem from the interface. This is the case for interfacial PMA. It was found to be remarkably strong at interfaces between magnetic metals and heavy metals, as well as between magnetic metals and oxides, even in systems with weak SOC [58]. The origin of this anisotropy is the hybridization of the orbitals at the interface. For interfaces between Co and oxides, as will be discussed in this thesis, the hybridization takes place between the Co-3d and the O-2p orbitals [64].

The energy contribution of the interfacial anisotropy can be expressed as a surface integral, with the unit vector $\hat{\mathbf{e}}_n(\mathbf{r})$ standing orthogonal on the surface and the magnetization lying in an angle $\theta(\mathbf{r})$ to the surface normal [48]:

$$E_{\text{int}} = K_{\text{int}} \int_A 1 - (\mathbf{m}(\mathbf{r}) \cdot \hat{\mathbf{e}}_n(\mathbf{r}))^2 d^2r \quad (2.38)$$

$$= K_{\text{int}} \int_A \sin^2(\theta(\mathbf{r})) d^2r \quad (2.39)$$

2.4.5 Exchange bias

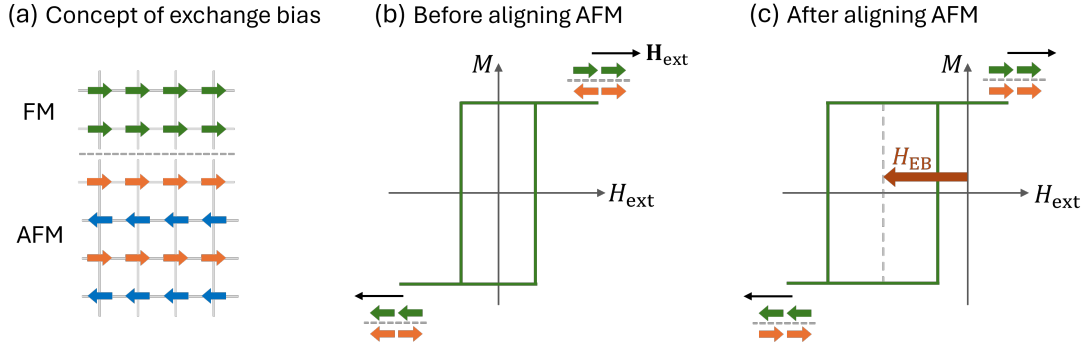


Figure 2.7: Illustration of the exchange bias (EB) between a FM and an AFM. (a) The EB is induced by the coupling of aligned AFM interfacial spins to adjacent FM spins. (b) If the interfacial spins in the AFM are not aligned (e.g. the Néel vector of different AFM grains points in different directions, indicated by the orange arrows), the magnetization loop of the FM material remains centered around zero. (c) After aligning the AFM spins by annealing in an external magnetic field, the magnetization loop shifts by H_{EB} and the width of the loop, namely the coercivity, increases.

Similar to the interfacial anisotropy, also the exchange bias (EB) is an interfacial effect. It describes the coupling between the magnetic moments of a FM and an adjacent AFM, which can lead to a shift of the magnetization loop of the FM along the magnetic field direction (Fig. 2.7) [47, 65]. To observe the shift, the interfacial magnetic moments of the AFM have to be aligned such that they cause a net magnetic field which is acting on the FM moments. This alignment can be induced by heating the magnetic stack to a temperature above the Néel

temperature of the AFM but below the Curie temperature of the FM. When the system is cooled back down inside a magnetic field which is strong enough to align the magnetic moments of the FM, these moments exert a strong field on the adjacent disordered magnetic moments of the AFM. This causes a preferential direction of the interfacial magnetic moments in the AFM during the magnetic ordering. This process is called *annealing in a magnetic field* or *field cooling* (see Chapter 3.1.2) [65]. The magnetization loop of the FM then shifts by H_{EB} in the direction opposite to the net magnetic field caused by the AFM (Fig. 2.7 c). This reflects that the additional field $|H_{\text{EB}}|$ has to be overcome to align the magnetization of the FM in the opposite direction as favored by the AFM.

For some materials, the Néel temperature is, however, so high that it cannot be reached without getting significant intermixing between the elements in the different material layers [66]. For example PtMn has a bulk Néel temperature of 975 K [67]. Although heating above this Néel temperature is not possible, PtMn is commonly used for EB applications in industry. The reason is that the high Néel temperature leads to very good robustness of the magnetic order against thermal fluctuations for room-temperature applications [68]. To understand how the EB can be set for polycrystalline AFMs like PtMn, we have to consider the origin of the EB in these systems. Unlike in perfect crystals or 2D-materials, where a perfect interface with single termination is possible to establish the EB (Fig. 2.7 a, extended identically to the whole lattice), this is never the case in polycrystalline systems. In contrast, in these systems the interfacial grains of the AFM set the EB [65]. The size of the EB is therefore given by the competition between thermal fluctuation and the anisotropy of the AFM grains which contribute to the EB. The temperature required to set the EB in these polycrystalline systems is called *blocking temperature*. It is defined as the temperature at which the EB shift H_{EB} gets lost when heating the sample up [65].

Additionally to the EB shift, often an increased width of the magnetization loop, called *coercivity*, is observed in systems with EB. This means that the energy barrier to reverse the magnetization got larger, so a higher magnetic field is required. The reason can be increased interfacial roughness due to the annealing [69], as well as the exchange coupling itself, likely due to interfacial spin clusters [65].

The anisotropy term for the exchange bias can be expressed by Equation 2.40, with the exchange anisotropy constant K_{EB} and the angle θ between the direction of the magnetization and the anisotropy [48]. Notably, the anisotropy is unidirectional in this case.

$$E_{\text{EB}} = \int_A \mathcal{E}_{\text{EB}}(\mathbf{r}) d^3r = - \int_A K_{\text{EB}} \cos \theta d^2r \quad (2.40)$$

2.4.6 Magnetic domains

To understand the magnetic configuration of a system, the total micromagnetic free energy E_{total} (Eq. 2.27) has to be minimized. In many cases, this results in the formation of *magnetic domains*, regions with uniform magnetization inside but a different magnetization compared to outside [47, 48]. The interfaces between the domains, in which the spins realign, are called *domain walls* [47, 48].

Figure 2.8 shows the domain formation inside a thin rectangular FM. If the shape anisotropy dominates the other anisotropy terms, the magnetic moments orient along the longest axis of the film. The exchange energy favors the alignment of all magnetic moments. However, if they are all aligned, this leads to large stray fields (Fig. 2.8 a). A splitting into two magnetic domains with opposite magnetization reduces the stray fields significantly (Fig. 2.8 b). A further reduction of the stray fields can be achieved by forming closure domains at the top and bottom of the film (Fig. 2.8 c). Depending on the system, the magnetization can also break into even smaller domains (Fig. 2.8 d). How they look exactly, however, strongly depends on the strength of the different energy scales, in this case the shape anisotropy energy compared to the

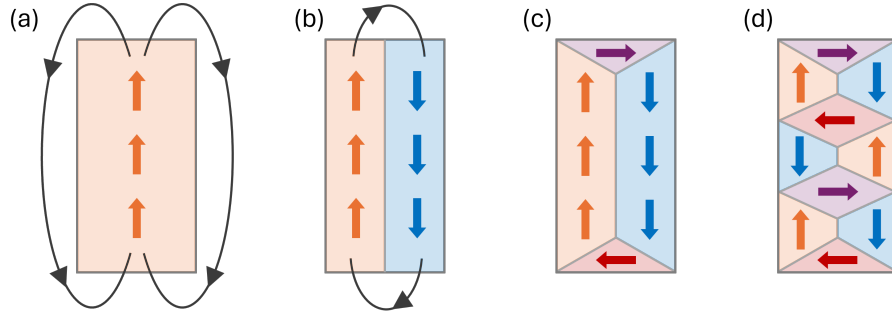


Figure 2.8: Formation of magnetic domains in a FM. (a) Full alignment of all spins leads to large stray fields. (b)–(d) Breaking into domains can reduce the stray fields significantly. Panel (d) is adapted from [48].

demagnetization energy. Additionally, because of the exchange energy which favors fully aligned spins, every domain wall has a cost. This limits the maximum number of domains. In magnetic systems with other shapes or other dominating anisotropy terms, the resulting magnetization can look very different. Some examples with a detailed discussion can be found in reference [70].

2.4.6.1 Antiferromagnetic domains

AFM materials have no net magnetic moment, so stray fields play no role in the domain formation. Still, magnetic domains were observed in different AFM materials [71, 72, 73]. One option to induce domains in an AFM is the coupling to a FM [74]. Domains were also observed to correlate with changes in the crystallographic orientation or defects [73, 75]. However, AFM domains were also observed in single crystals without any adjacent FM [71]. This demonstrates that defects or interactions with FMs cannot be the only origin of the AFM domain structure.

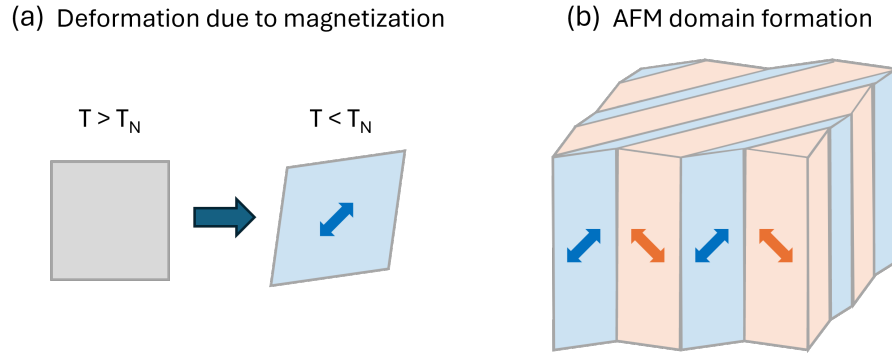


Figure 2.9: Formation of magnetic domains in an AFM. (a) Illustration of the deformation of a square piece of an AFM material when cooling through the Néel temperature from the paramagnetic to the AFM state. (b) Formation of AFM twin domains in a crystal to compensate for the lattice distortion. Panel (b) is adapted from [76].

Figure 2.9a illustrates the effect of magnetostriction for an AFM material cooled through the Néel temperature. Due to the magneto-elastic coupling, the ordering of the AFM's magnetic moments causes a deformation of the material. This deformation can cause significant internal strains. These strains can be reduced by forming domains with opposite deformation, e.g. twin

domains as proposed by Slack [76] (Fig. 2.9 b). The drive to create different domains to relax the strains can be expressed as a *destressing field*. It was theoretically predicted and demonstrated experimentally, that destressing fields in AFMs are the analog to the demagnetizing fields in FMs [77, 78, 79]. The resulting domain structure depends on the size, shape and interfaces of the material, which define the strain profile. It can be obtained by minimizing the micromagnetic free energy E_{total} together with the destressing energy.

2.4.7 Stoner-Wohlfarth model

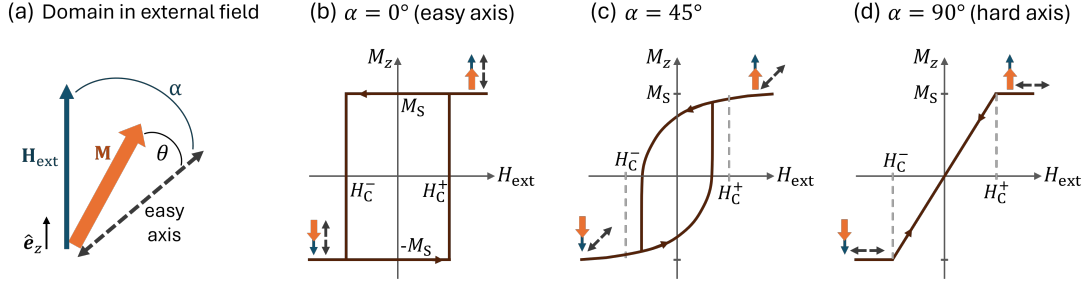


Figure 2.10: Response of a domain with fully aligned magnetization $\mathbf{M}$ and uniaxial easy axis in an external magnetic field $\mathbf{H}_{\text{ext}}$. (a) The easy axis is lying in an angle α toward the external magnetic field and the direction of the magnetization is defined by the angle θ toward the easy axis. The coordinate system is chosen such that $\mathbf{H}_{\text{ext}}$ is pointing along the z -direction. (b)–(d) Magnetization loops for $\alpha = 0^\circ$, 45° and 90° . M_S gives the saturation magnetization, H_C^- and H_C^+ are the coercive fields. The arrows at the saturated ends of the magnetization loop represent the directions of $\mathbf{M}$, $\mathbf{H}_{\text{ext}}$ and the easy axis at the respective position of the loop. Panels (b)–(d) are adapted from Figure 7.11 of [48].

To understand the response of a magnetic material to an external magnetic field, we can consider the *Stoner-Wohlfarth model* [47, 48]. In this model we consider a single-domain FM particle with fully aligned magnetization along its easy axis. Inside an external magnetic field, the magnetic moment of the particle rotates coherently to align with the magnetic field. This model is of course a significant simplification. Most magnetic materials consist of many domains, and domain wall propagation plays a significant role in the magnetization reversal inside an external magnetic field. Still, the Stoner-Wohlfarth model can give very helpful insights into the response of magnetic materials to an external magnetic field.

Figure 2.10 shows the magnetization loops of the magnetic particle along different field directions compared to its easy axis. Figure 2.10 b shows the loop along the easy axis of the magnetization (denoted as *easy axis loop*). It shows a square shape. The magnetization direction inverts at the coercive fields H_C^- and H_C^+ , where it flips between the two directions along the easy axis. The width of the hysteresis loop is defined as the coercivity $H_C = H_C^+ - H_C^-$.

When rotating the easy axis away from the magnetic field direction, the magnetization only remains aligned with $\mathbf{H}_{\text{ext}}$ for fields larger than the coercive field. At smaller fields, the magnetization direction rotates toward the easy axis direction. At zero applied field, the magnetization is aligned with the easy axis. If the easy axis spans an angle smaller 90° with the external field direction (Fig. 2.10 c), the loop shows a hysteresis with finite remanence (so $M_z(H_{\text{ext}}=0) \neq 0$). If the magnetization is measured along the hard axis (denoted as *hard axis loop*, Fig. 2.10 d), the magnetization gets pulled away from the easy axis direction toward the magnetic field direction continuously, resulting in a straight line with zero remanence. It saturates at the coercive fields, where the magnetization is fully aligned with the external magnetic field ($M_z = M_S$).

These different shapes of the magnetization loop, depending on the relative orientation of the easy axis and the magnetic field, can be used to determine the direction(s) of the easy axis. For all magnetic materials with a single easy axis, the total anisotropy energy can be determined by calculating the area between the easy axis and hard axis loop. Also the saturation magnetization and the coercivity can be determined from the easy axis and hard axis loops. However, it should be noted, that for magnetic materials with other magnetization reversal mechanisms than a coherent rotation, as assumed for the Stoner-Wohlfarth model, the coercivity can be significantly smaller [48]. Also the shape of the hysteresis loop can differ, depending on the domain structure and interactions between the different grains or adjacent layers.

Experimental techniques

In this chapter, the experimental techniques used in this thesis will be explained, starting from sample growth, the structural, chemical and magnetic characterization as well as ionic liquid gating which was used to manipulate the magnetic state of the samples. To perform the ionic liquid gating experiments in Mainz, a setup was built as part of this thesis. This setup will be presented and explained in section 3.7.

3.1 Sample fabrication

All samples discussed in this thesis were grown using *magnetron sputtering*. In some cases they were *annealed* in an external magnetic field afterward to set a specific magnetic state. These two techniques will be explained hereafter.

3.1.1 Magnetron sputtering

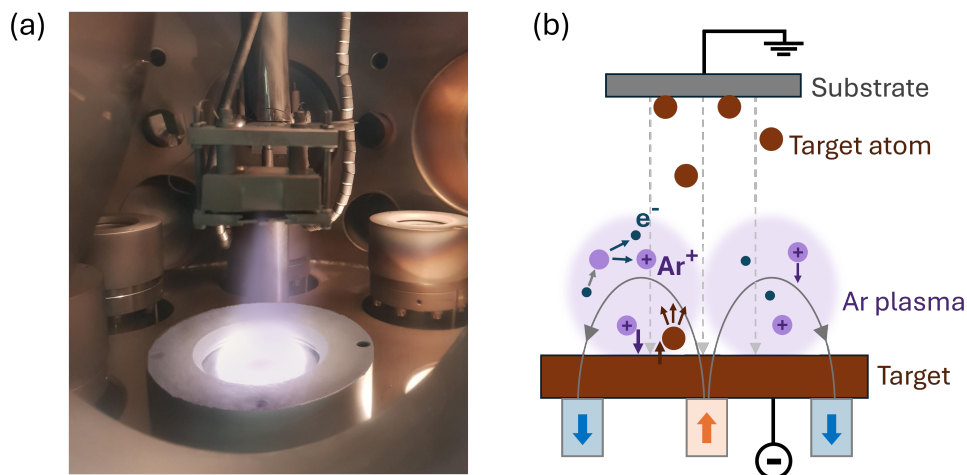


Figure 3.1: (a) Photograph of the sputtering process in a magnetron sputtering chamber from the Kläui lab. (b) Schematic of the process of magnetron sputtering.

Sputtering is one of the physical vapor deposition techniques, in which elements get sublimated from a target material and deposited on a substrate. In the case of sputtering, the elements of the target get ejected by ion bombardment using an inert ion species as sputtering gas, typically Argon (Ar). Figure 3.1 illustrates the sputtering process, including a photograph and a schematic. To create sufficient ions in the sputtering gas, a plasma is ignited (purple in Fig. 3.1) by applying a large voltage between the substrate and the target. Thereby, the free electrons get accelerated toward the substrate through the sputtering gas. Inelastic collisions with the atoms of the sputtering gas lead to an ionization, resulting in a positively charged ion and a secondary electron, which in turn ionizes further atoms of the sputtering gas. To make this process even more efficient, a magnetic field can be applied. Its component perpendicular to the electric field causes a Lorentz force which acts on the charged particles. Therefore, the electrons move in a spiral trajectory, which increases the number of inelastic collisions with the sputtering gas. This setup is called *magnetron sputtering*.

In the photograph of the sputtering process in Figure 3.1 a, the target material is at the bottom and the substrate at the top facing downward. The chamber is filled with an Ar sputtering gas, which causes the light purple plasma above the target. Figure 3.1 b depicts the identical geometry. The substrate is grounded while a negative direct current (DC) voltage of a few hundred volts is applied to the target. The plasma is strongest where the magnetic field lines are horizontal and therefore the Lorentz force on the electrons is largest. This causes a donut shaped plasma. The electric field accelerates the positively charged Ar ions from the plasma toward the target. By transmitting their kinetic energy to the atoms inside the target, these target atoms get ejected and move toward the substrate where they deposit. In this way, a thin film of target atoms forms on the substrate. More details on sputtering can be found in reference [80].

In this thesis, metals were deposited using a DC electric field, while a radio frequency (RF) field was used for oxides to avoid charging of the target. The Ar pressure was usually kept in the range of $5 \cdot 10^{-3}$ to $5 \cdot 10^{-2}$ mbar to minimize the scattering events between the target material and the Ar gas. All samples were sputtered at room temperature.

3.1.2 Annealing

Annealing describes the process of heating up a sample in vacuum and cooling it back down. It can be used to modify the crystalline or the magnetic structure of a material. In this thesis, we use annealing to set an EB between an antiferromagnet and an adjacent ferromagnet (see Chapter 2.4.5). For that purpose, the samples were heated up to 300 °C and an external magnetic field of several hundred mT (usually 800 mT) was applied during the annealing process. This temperature is below the Curie temperature of Co ($T_C(\text{Co}) = 1394 \text{ K}$) [47], as required, and the magnetic field is high enough to align the magnetization of the Co. In this way, the magnetization of the Co can exert a large magnetic field onto the adjacent AFM. Ideally, the annealing temperature should additionally be above the Néel temperature of the AFM, so that, upon cooling through the ordering transition, the uncompensated magnetic moments of the AFM align with the direction of the externally applied magnetic field. However, in this thesis I used PtMn as the AFM which has a bulk Néel temperature of around 700 °C [67]. At such high temperature, interdiffusion of the atoms of the different layers increases significantly, modifying the interfaces and material properties. In EB systems with PtMn and Co, the annealing temperature should therefore not exceed approximately 300 °C. Instead of the Néel temperature, the blocking temperature of the AFM is considered as the minimum temperature required to set the EB (see Chapter 2.4.5). More details and a good explanation on how to determine the blocking temperature and anisotropy constant of the AFM, including a measurement protocol for reproducibly setting the EB, can be found in the paper “A new paradigm for exchange bias in polycrystalline thin films” by K. O’Grady et al. [65].

3.2 X-ray diffraction and X-ray reflectivity

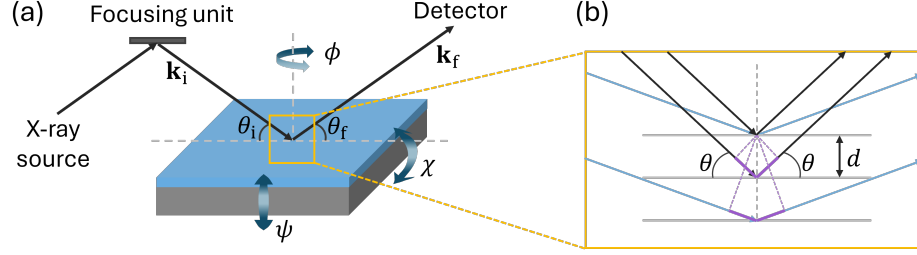


Figure 3.2: (a) Scattering setup used to measure X-ray diffraction and X-ray reflectivity. To obtain a focused, monochromatic beam, the X-rays first pass a focusing unit consisting of a Göbel mirror, a slit and a monochromator. The reflected beam is measured at the detector. To allow for a precise alignment and extensive characterization of the sample, the sample can be rotated around all three axes. (b) The scattering of the X-rays takes place at planes inside the sample. Two exemplary incoming angles are shown in black and blue, each for X-rays scattered at two different planes inside the same material. The distance marked in purple has an identical length in both cases. It depicts the extra distance traveled by the wave scattered at a lower plane.

X-ray diffraction (XRD) and X-ray reflectivity (XRR) were used to characterize the crystal structure and layer thicknesses of the sputtered thin films, respectively. Figure 3.2 shows the general principle of both methods. A monochromatic X-ray beam is focused onto the sample surface. The incoming beam has a wave vector $\mathbf{k}_i$ and hits the surface at an angle θ_i toward the sample plane. The reflected beam has a wave vector $\mathbf{k}_f$ and is measured at an angle θ_f between the sample plane and the detector. When hitting the sample, the X-rays get scattered at the crystal lattice planes (for XRD) or at the interfaces between the material layers with different electron density (for XRR). Constructive interference happens when the spacing between the layers, at which the X-rays get scattered, fulfills the Bragg condition (Fig. 3.2 b). For scattering inside a single material layer the Bragg condition is [81]:

$$m\lambda = 2d\sin(\theta) \quad (3.1)$$

Thereby, λ is the wavelength of the X-rays, m is a positive integer and $2d\sin(\theta)$ is the additional distance traveled by the wave scattered elastically at a plane at distance d (purple path in Fig. 3.2 b) in a specular geometry, so $\theta_i = \theta_f = \theta$. Therefore, the lattice spacing to which the techniques is sensitive, depends on the wavelength λ and the angle θ . The smaller θ , the larger the minimum distance d which can be detected, as depicted by the black and blue X-rays in Figure 3.2 b. This causes the difference between XRD and XRR: XRD is measured at large angles larger than 15° which allows a characterization of the crystal lattice. In contrast, XRR is measured at very shallow angles, between 0.3° and 10° , at which the method is sensitive only to the much larger spacing between the interfaces of the different materials. Therefore, with XRR the film thickness and roughness of the interfaces can be characterized.

More details on both techniques can be found in the following sections.

In this thesis, a Bruker D8 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$) was used. The sample can be rotated around all three axis, as shown in Figure 3.2 a, allowing to characterize the crystal lattice not only in the z-direction but also tilted planes, the mosaicity and the in-plane ordering of the sample.

3.2.1 X-ray diffraction

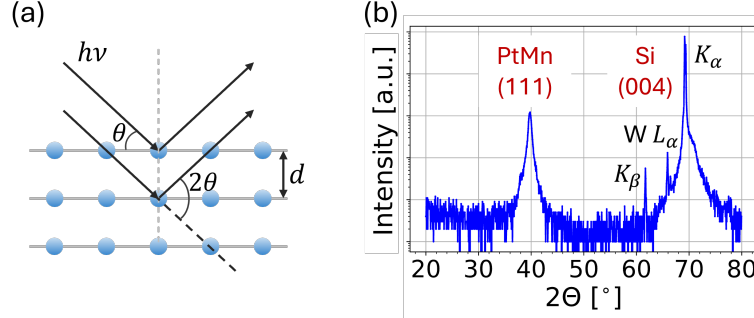


Figure 3.3: (a) Scattering on lattice planes, as performed for XRD. (b) Result of a θ - 2θ scan for 20 nm platinum manganese (PtMn) grown on a silicon (Si) substrate (full stack: Si/SiO₂ (100 nm)/ Ta (5 nm)/ Pt (3 nm)/ PtMn (20 nm)/ Co (0.9 nm)/ HfO₂ (3 nm)). The intensity is scaled logarithmically. The Si peak displays two artifact peaks at its left shoulder, stemming from the Cu K_β and W L_α line of the X-ray source. They are present additionally to the main Cu K_α peak when performing the measurement without a monochromator to enhance the total intensity. The data shown in panel (b) was published in reference [82] and is replotted here.

For XRD, scattering of the X-rays happens at the crystal lattice planes. Therefore, it allows for a versatile characterization of the crystal lattice including lattice constants, crystal orientations, mosaicity and lattice strain, as well as the coherent domain size perpendicular to the lattice planes [83].

Figure 3.3 a shows the geometry of a standard θ - 2θ scan. Thereby, the angle of the reflected beam is identical to the angle of the incoming beam $\theta_i = \theta_f = \theta$. This scattering geometry is usually referred to as θ - 2θ scan because the sample is tilted by θ and the detector by 2θ . In this geometry, the lattice spacing orthogonal to the sample plane is probed.

Figure 3.3 b shows the resulting diffraction pattern for a PtMn sample grown on a thermally oxidized Si substrate. The intensity is plotted on a logarithmic scale to increase the visibility of smaller peaks. The diffraction pattern shows two very pronounced peaks, one at 40°, corresponding to PtMn (111) and one at 69°, corresponding to the Si (004) peak of the substrate. Additionally, two small, sharp peaks are visible at the left shoulder of the Si peak. They are present because the measurement was performed without a monochromator, to increase the total intensity of the X-rays. Therefore, the incoming X-rays do not only have the energy of the main K_α transition of Cu but the K_β transition of Cu and the L_α transition of the W atoms evaporated from the filament to the copper cathode are also present.

In this thesis, XRD is mainly used to analyze crystal orientations, the degree of crystallinity as well as internal strains. The crystallinity can be estimated from the size and width of the respective peak. The larger the intensity of a peak, the higher the crystalline volume which contributed to the scattering. Additionally, the width of the peak is a measure for microstrains as well as the coherent domain size perpendicular to the lattice planes. Larger strains, which can e.g. result from lattice mismatch between neighboring layers, reveal themselves via a shift in the peak positions. Depending on the type of strain, so whether the lattice is compressed or elongated in the direction orthogonal to the lattice planes, the lattice spacing changes and the peak moves slightly. Especially for thin layers the shift of the peak position can be well visible. More information and details on XRD analysis can be found in reference [83].

3.2.2 X-ray reflectivity

XRR is measured at very shallow angles where the scattering takes place at layer boundaries. Thereby, film thicknesses, densities and interfacial roughness can be determined. To obtain these quantities, typically a model-dependent analysis is performed. Thereby, the material layers, and, if known, their constraints in thickness, density and roughness are predefined. For this so-called slab model, the corresponding XRR profile is calculated. The ideal values for the thickness, density and roughness are then determined by fitting the model to the measurement data. Obviously, the quality of the result depends heavily on the correctness of the underlying model. Therefore, it is very important to choose the model carefully and consider all prior knowledge.

Figure 3.4a and c depict typical slab models as used in this PhD thesis. Figure 3.4b and d show the corresponding XRR measurement data. From Bragg's law we find that the period of the oscillations $\Delta\theta$ is related to the corresponding layer thickness d and the wavelength λ of the X-rays by:

$$\Delta\theta = \lambda/2d \quad (3.2)$$

In XRR, the intensity is usually plotted against 2θ . The period of the oscillations is then also doubled. It should be noted, that for dimensionality reasons the angle has to be inserted in radiant into the equation. Using this equation, the layer thicknesses can be estimated right from the XRR measurement when the period of the oscillations is clearly visible as in Figure 3.4b. Typical for all XRR measurements is also, that the intensity initially increases at very shallow angles around $2\theta = 0.3^\circ$. The reason is the divergence of the X-ray beam, which hits the sample edge at these angles. With increasing angle, the illumination of the sample surface and therefore also the XRR intensity increases until the whole X-ray beam hits the sample surface.

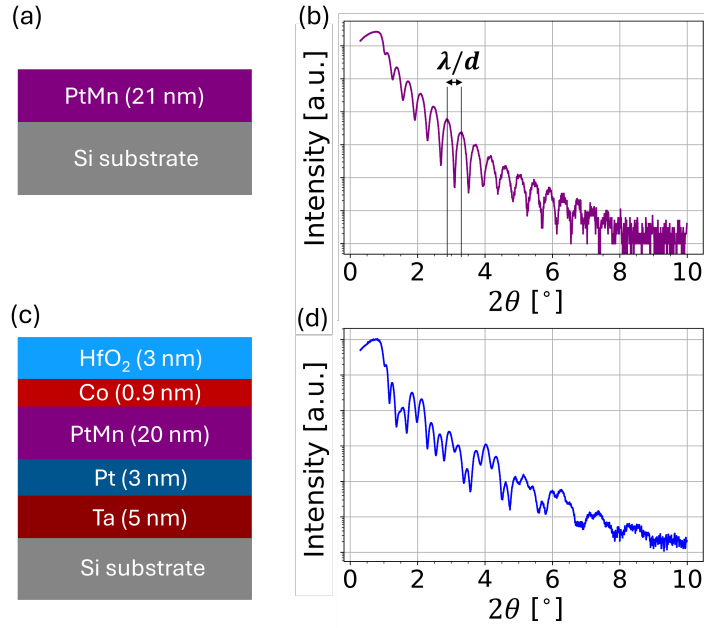


Figure 3.4: XRR slab models and the corresponding θ - 2θ scans (a)–(b) for a sample with a single PtMn layer on top of a Si substrate and (c)–(d) for a multilayer sample.

To get more insight into the way how the data can be fitted, the theory behind specular reflectometry will be discussed in the following sections. We will first look at the underlying

physics behind the interaction of the X-rays with the material and then introduce Snell's law and the Fresnel equations for reflectivity and transmittivity at an interface. Afterward, we will consider multilayer stacks and Parratt's algorithm to determine the reflectivity from the full stack. Finally, we will introduce roughness and discuss the differences between different types of roughness.

For more details on XRR analysis, the online tutorial “A Guide to Reflectometry” [84] as well as the additional material on the website of the Open Reflectometry Standards Organisation (ORSO) [85] give a very instructive introduction into XRR fitting. Additionally, the book “Elements of modern X-ray physics” by Jens Als-Nielsen and Des McMorrow provides more details and discussions on the underlying equations [81]. This material forms the basis of the following description of the reflectivity theory.

3.2.2.1 Scattering at a single interface

XRR makes use of the scattering of X-rays. X-rays are transverse electromagnetic waves with wavelength λ and wave number $k = 2\pi/\lambda$. The electric and magnetic components of the fields point orthogonal to each other and to the direction of propagation of the wave. They interact with the electrons in the material via the electron's charge, spin and orbital magnetic moment. In this thesis, we will use X-ray scattering only to investigate the layer thickness, roughness and density, not the magnetic structure of the material. Therefore, in the following we will focus on the interaction of the electric field of the X-rays with the charge of the electrons. The electric field component of a linearly polarized electromagnetic wave can be expressed as follows [81]:

$$\mathbf{E}(\mathbf{r}, t) = E_0 \hat{e} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} \quad (3.3)$$

with the unit vector $\hat{e}$ pointing in the direction of polarization, the wave vector $\mathbf{k}$ pointing along the direction of propagation, the position vector $\mathbf{r}$, the angular frequency ω and the time t .

To understand the behavior of X-rays at interfaces, we first consider a single layer with a sharp, flat surface. We assume that the layer has a uniform distribution of atoms and a refractive index n . For vacuum, the refractive index is $n_{\text{vacuum}} = 1$ by definition. While the refractive index can deviate significantly from this value in the case of visible light (e.g. 1.5 to 1.8 in glass), the deviation is very small in the case of X-rays (in the order of 10^{-5}) [81]. In general, the refractive index for X-rays can be written in the following form [81]:

$$n = 1 - \delta + i\beta \quad (3.4)$$

with

$$\delta = \frac{2\pi\rho_e r_e}{k^2} \quad (3.5)$$

$$\beta = \frac{\mu}{2k} \quad (3.6)$$

Thereby, δ accounts for the dispersion and depends on the number density of the electrons ρ_e , the scattering length of the electrons r_e and the wave number $k = |\mathbf{k}|$. The factor $\rho_e r_e$ is called the scattering length density (SLD). In XRR, which makes use of monochromatic, focused X-rays, the SLD is a measure of the material-dependent part of the reflection. Therefore, it is commonly used to describe the scattering properties of the different materials, instead of using the refractive index (Fig. 3.5 c). The number density of the electrons ρ_e can be determined from the density of atoms ρ_{at} and the atomic scattering factor $f(\mathbf{Q})$ via $\rho_e = \rho_{\text{at}} f(\mathbf{Q})$. Thereby, $\mathbf{Q} = \mathbf{k}_I - \mathbf{k}_R$ is the *wave vector transfer* or *scattering vector*, defined as the difference between the incoming and reflected wave vectors $\mathbf{k}_I$ and $\mathbf{k}_R$ (Fig. 3.5 b). The resulting SLDs for different materials as a function of the X-ray energy, material density and magnetization can be obtained from the ORSO SLD database [86].

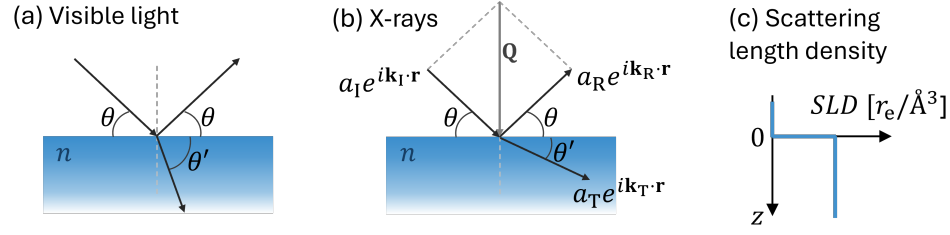


Figure 3.5: Refraction and reflection at a single interface between vacuum and a material with refractive index n for (a) visible light and (b) X-rays. This scenario corresponds to an infinitely thick layer. The scattering vector $\mathbf{Q}$ gives the wave vector transfer, defined as the difference between the wave vector of the incoming wave $\mathbf{k}_I$ and the reflected wave $\mathbf{k}_R$. a_I and a_R denote the respective amplitudes. Correspondingly, $\mathbf{k}_T$ and a_T are the wave vector and amplitude of the transmitted wave. (c) The scattering length density (SLD) is defined as the number density of electrons ρ_e times the scattering length of electrons r_e . Panels (a)–(b) are adapted from [81].

The imaginary term $i\beta$ of the refractive index describes the effect of absorption inside the material. It is determined by the attenuation of the intensity $1/\mu$. It becomes clear why the imaginary term accounts for absorption when inserting n into the equation of the electromagnetic wave. When a wave with wave number $k = |\mathbf{k}|$ enters into a material, the absolute value of the transmitted wave vector is nk . Therefore, the electric field component of the wavefunction inside the material, propagating in the direction z , becomes $E(z) \propto e^{inkz} = e^{i(1-\delta)kz} e^{-\beta kz}$. The term $e^{-\beta kz} = e^{-\frac{\mu}{2}z}$ describes the attenuation inside the material.

In contrast to visible light, the refractive index for X-rays is smaller than one (Fig. 3.5 a and b). This is due to the dependence of the refractive index on the frequency ω of the beam. When increasing the frequency, every time a resonance frequency of an electronic transition is passed, the refractive index is reduced. For X-rays, most resonances are passed and the refractive index turns out smaller than one. Figure 3.5 shows the resulting refraction and reflection of X-rays in comparison to visible light at the interface between vacuum and a material with refractive index n . The angle θ' of the refracted beam can be obtained using *Snell's law*:

$$\cos(\theta) = n \cos(\theta') \quad (3.7)$$

The negative refractive index for X-rays also implies that there is a critical angle θ_c below which total reflection occurs. It can be calculated by Equation 3.7 when setting $\theta = \theta_c$ and $\theta' = 0$ and Taylor expanding the cos to second order around $\theta = 0$. After neglecting β because $\beta \ll \delta$ we obtain:

$$\theta_c = \sqrt{2\delta} \quad (3.8)$$

From Snell's law and the boundary condition that the wave function as well as its derivative have to be continuous at the interface, the *Fresnel equations* for the reflectivity r and transmittivity t at the interface can be derived. With the amplitudes of the initial wave a_I , of the reflected wave a_R , and of the transmitted wave a_T , they are given as [81]:

$$r := \frac{a_R}{a_I} = \frac{\theta - \theta'}{\theta + \theta'} \quad (3.9)$$

$$t := \frac{a_T}{a_I} = \frac{2\theta}{\theta + \theta'} \quad (3.10)$$

To obtain the corresponding reflectivity R and transmittivity T of the intensity, the absolute square of r and t has to be calculated, respectively.

3.2.2.2 Multiple interfaces

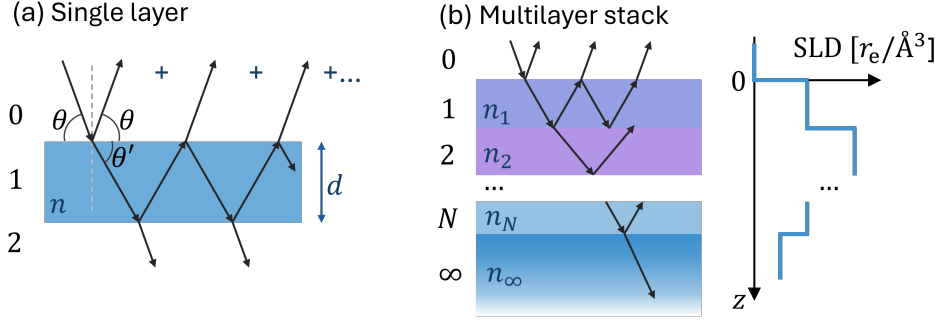


Figure 3.6: Refraction and reflection for (a) a single layer with finite thickness d and (b) a multilayer stack. The total reflected wave is given as the sum over all waves leaving the upper interface. For the multilayer stack, the corresponding SLD profile as a function of sample depth is given on the right. The substrate is assumed to be infinitely thick and therefore denoted as ∞ .

Next, we will consider a single layer with finite thickness. In this case, the transmitted X-rays scatter at the bottom interface and get partly reflected and partly transmitted (Fig. 3.6 a). The resulting consecutive reflections inside the layer at the bottom and top interface lead to interference of the reflected X-rays. This is the origin of the so-called *Kiessig fringes*, the oscillations visible in the measured XRR spectrum.

To obtain the total reflected wave, the amplitudes of all X-rays leaving the upper interface have to be summed. Thereby, it has to be considered that the waves gain a phase factor $p = e^{iQd/2}$ when crossing the layer once. Therefore, the wave reflected immediately at the interface 0 to 1 has an amplitude reflectivity r_{01} . The wave transmitted through interface 0 to 1, then reflected at interface 1 to 2 and finally transmitted through interface 1 to 0 has an amplitude reflectivity $t_{01}r_{12}t_{10}p^2$ and so on. By summing all terms and simplifying the resulting expression using the Fresnel equations, one obtains the following expression for the total amplitude reflectivity of the layer [81]:

$$r_{\text{total}} = \frac{r_{01} + r_{12}p^2}{1 + r_{01}r_{12}p^2} \quad (3.11)$$

This can be generalized to any layer j lying between layers $j-1$ and $j+1$. The reflectivity is calculated at the upper interface of layer j , so between j and $j-1$. This leads to the expression:

$$r_{j-1,j} = \frac{r_{j-1,j} + r_{j,j+1}p_j^2}{1 + r_{j-1,j}r_{j,j+1}p_j^2} \quad (3.12)$$

Using this, we can now recursively calculate the reflectivity from a multilayer stack like the one in Figure 3.6 b. We assume the substrate to have infinity thickness. The first layer is labeled with number 1, the layer right above the substrate with number N . The refractive index of any layer j is called n_j and its thickness d_j . To get the total reflected amplitude at the top of the stack, we start by calculating the reflectivity between layer N and the substrate. Since the substrate is assumed to be infinitely thick, we can neglect its bottom interface and use the Fresnel Equation 3.9 to calculate the reflectivity. Using the result, we can calculate the reflectivity at the upper interface of layer N using Equation 3.12. This can be continued recursively until reaching the surface of the stack. This method is called *Parratt's method* and is the standard algorithm to calculate reflectivities from multilayer stacks [81, 87].

3.2.2.3 Including roughness

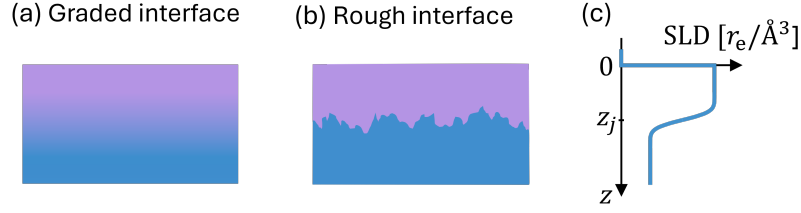


Figure 3.7: Interface roughness caused by (a) a graded interface and (b) topographical roughness. (c) shows the corresponding SLD which has a gradient instead of a step at the interface now. Panels (a) and (b) are adapted from [81].

So far we have discussed multilayers with perfectly smooth interfaces. However, in actual samples the interfaces always contain some amount of roughness. Roughness can be present in two ways, as a grading between two layers caused by interdiffusion of the atoms (Fig. 3.7 a) or as topographical roughness expressed by height differences at the interface (Fig. 3.7 b). Of course, also mixtures between the two can exist in samples. To take account of grading and topographical roughness, the gradient in the electron density ρ_e at the interface has to be considered. Most commonly, the atomic distribution around the interface is assumed to be Gaussian. For the electron density, this leads to an error function around the interface position z_j [81]. Consequently, also the SLD displays this gradient (Fig. 3.7 c). The SLD_j for a layer j with a graded or rough interface at position z_j is then given as:

$$\text{SLD}_j(z) = r_e \rho_e \frac{1}{2} \left(1 - \text{erf} \left(\frac{z - z_j}{\sqrt{2}\sigma} \right) \right) \quad (3.13)$$

The shape of the gradients for graded interfaces and interfaces with topographical roughness are assumed to be the same. This is justified because for specular measurements it is impossible or at least very difficult to distinguish between the two. For interfaces with a topographical roughness with completely uncorrelated height distributions, it can even be shown in the kinematic approximation that the resulting reflectivity signal is exactly the same as for the graded interface [81]. In both cases, the intensity reflectivity $R(\mathbf{Q})$ of a layer with topographical roughness or grading at its upper surface is found to be [81]:

$$R(\mathbf{Q}) = R_F(Q_z) e^{-Q_z^2 \sigma^2} \quad (3.14)$$

Thereby, R_F is the Fresnel reflectivity of the intensity, Q_z is the specular component of the scattering vector $\mathbf{Q}$ and σ is a measure of the width of the grading or, for topographical roughness, the root mean square roughness. From Equation 3.14 we learn that an increasing topographical roughness or grading reduces the reflectivity of the layer. This effect increases with increasing wave vector transfer in z -direction Q_z .

The confinement of the scattering to the z -direction, as found in Equation 3.14, only holds for graded but otherwise perfectly flat interfaces and fully uncorrelated interfaces (which is physically not plausible for very short distances on the surface). For topographically rough interfaces with correlated height variations, the reflectivity shows a component of diffuse (off-specular) scattering additional to the specular component [81]. This component can, however, not be measured in specular experiments.

It is important to note, that the roughness of an interface should ideally be not much more than 20 % of the thickness of the thinnest adjacent layer. Otherwise, artifacts can occur, because

the tail of the Gaussian at the rough interface extends beyond the thickness of the adjacent layer and therefore also influences the next interface. A more detailed discussion on this effect and the resulting limitation in accuracy when analyzing very rough interfaces with this method can be found in reference [84].

3.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a tool to characterize the chemical composition of the surface of organic and inorganic compounds. By shining an X-ray beam onto the surface, electrons from the core levels get excited, travel to the surface and escape into the vacuum. The kinetic energy of the ejected electron, the photoelectron, is then measured by a hemispherical electron energy analyzer. Using the kinetic energy E_k , the fixed photon energy $h\nu$ with which the electron got excited and the work function Φ of the spectrometer, the corresponding electron binding energy E_b can be calculated using Equation 3.15. The binding energy is a fingerprint of the orbital from which the electron got excited.

$$E_b = h\nu - E_k - \Phi \quad (3.15)$$

The binding energy is, however, only obtained relative to the sample Fermi level E_F if the sample and spectrometer are in electrical equilibrium and therefore have the same Fermi level. Otherwise, if there is a relative charge, the resulting electric field will accelerate or slow down the photoelectrons and shift the XPS spectrum. This shift can be corrected by measuring the valence band position [88]. Alternatively, it can be determined if a material is present in the sample from which the exact peak position is known. Traditionally, the adventitious carbon atoms adsorbed on the sample surface during the exposure to atmosphere were used for this purpose. However, in our experiments we found that platinum (Pt) is the more reliable reference layer in our samples, where available, since it is unaffected by oxidation.

After the photoionization, two possibilities for the relaxation exist. In both cases the core-hole is filled by an electron from a higher state. The energy released by this process can either be emitted as a photon in a fluorescence process or via the emission of a secondary electron, the Auger electron. In the latter case, the atom is left behind with two holes.

The elemental composition of a sample can be determined by comparing the binding energies found from the XPS measurement to literature values. Shifts of individual peak positions indicate differences in chemical environment such as changed oxidation states. The fraction of an element in the sample can be determined from the corresponding peak intensities, including the sensitivity factors. However, several things have to be considered when analyzing the data.

Background

XPS is a surface sensitive technique, because only the electrons excited from atoms close to the surface can escape without experiencing inelastic scattering events. The deeper down in the material a photoelectron is excited compared to the inelastic mean free path, the more kinetic energy it will likely lose by inelastic scattering events before leaving the sample. These electrons contribute to the background signal, with stepwise increasing counts toward lower kinetic energies (so higher binding energies, see Fig. 3.8a and b). Additionally, the inelastic scattering can lead to secondary electrons which also contribute to the background.

The most precise but also most effortful way to subtract the background is by measuring an electron energy loss spectrum (EELS) which can be fitted by a Tougaard background. Since this would require an additional complex measurement, usually the background is approximated by fitting the Tougaard background to the data by eye or by approximating it with a Shirley background [89, 90].

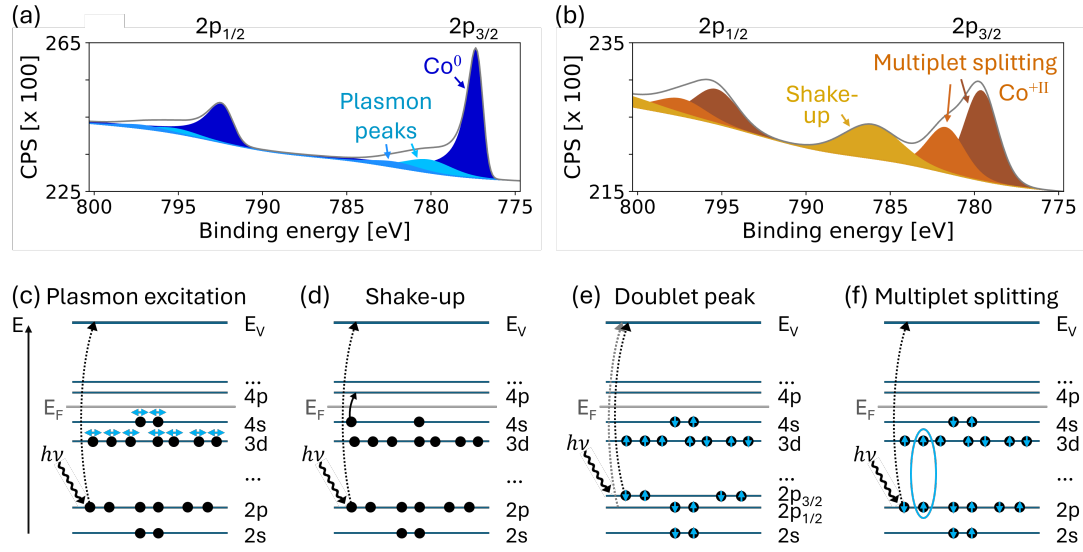


Figure 3.8: (a) Exemplary XPS spectrum of metallic Co, showing the asymmetric Co^0 -peak, its two plasmon peaks and the doublet splitting into the $2p_{1/2}$ and $2p_{3/2}$ peaks. (b) Exemplary XPS spectrum of CoO, showing the multiplet splitting of Co^{+II} and its characteristic shake-up peak. The gray envelope shows the sum of the peaks. (c)–(f) Schemes of the processes during the photoemission which can cause satellite peaks (c and d) or splitting of peaks (e and f).

Satellite peaks

If photoelectrons interact with the valence electrons while leaving the material, it can happen that the photoelectrons loose a discrete amount of energy. In this case, a satellite peak shows up at the lower kinetic energy side (so higher binding energy side) of the core peak. Two main mechanisms exist for this:

- **A Plasmon loss peak** appears if the photoelectron excites a collective oscillation of the conduction electrons in a metal (Fig. 3.8 c). These oscillations have a characteristic frequency and therefore the photoelectron looses a discrete amount of energy quanta when exciting the oscillation. The excitation can take place in the bulk (bulk plasmon) or at the surface (surface plasmon), with a smaller required energy for a surface plasmon.
- **A shake-up peak** is observed when a valence electron is excited into a higher unfilled shell as a result of the interaction with the photoelectron (Fig. 3.8 d). The energy for this transition is taken from the photoelectron. According to [89] such shake-up peaks can be especially well visible for atoms with unpaired valence electrons in the 3d or 4f shell. If the valence electron is excited to an unbound state, the process is called “shake-off” and contributes to the background, as the required energy is not quantized. Also in metals, the shake-up process does not lead to a satellite peak but to a low energy-tail of the core peak, because a band of unfilled states are available (see paragraph on peak forms below).

Peak forms

The peak form and splitting of peaks depend on the interactions inside the material:

- **The width** of the peak is a convolution of the natural width of the core level (Lorentzian) with the width of the X-ray source and the analyzer resolution (Gaussian). The natural width of the core level is set by the core-hole lifetime.

- **Metals** show an asymmetric peak form because of energy losses of photoelectrons to the valence electrons (Fig. 3.8 a). In a “shake-up”-like process, an interaction with a photoelectron can lead to an excitation of a valence electron into higher states. For metals, there is, however, a continuous distribution of states above the Fermi level, leading to a continuous tail of the core peak instead of a discrete shift.
- **Doublet peaks** arise for all orbitals higher than the s-orbital, so with orbital angular momentum quantum number $l > 0$. In this case, the spin-orbit coupling leads to a splitting of the core energy levels with $j = l \pm s$, where j is the total angular momentum quantum number and $s = 1/2$ the spin quantum number (Fig. 3.8 e). The ratio of the areas of the two belonging peaks depends on the number of electrons in each of the two core levels, so on their respective degeneracy. For the whole atom it is given as $2J + 1$. Therefore, for example for the 2p orbital, the $2p_{3/2}$ state is occupied by $2J + 1 = 4$ electrons, the $2p_{1/2}$ state by $2J + 1 = 2$ electrons. Therefore, the integral of the $2p_{3/2}$ peak has to be twice as large as for the $2p_{1/2}$ peak.
- **Multiplet splitting** describes the splitting of the photoelectron peak when different final states are possible after the photoionization (see Fig. 3.8b and f). This is the case for atoms with unpaired valence electrons. In that case, the unpaired electron in the core, which remains after the photoionization process, couples to the unpaired valence electrons. Because of the exchange interaction between the spins, as well as spin-orbit coupling, the different possible spin orientations of the final state lead to an energy splitting.

For the most pronounced and most commonly analyzed XPS peak of an element, typical peak models including the approximate peak splitting distances for doublets and, if present, multiplet peak splitting, as well as the positions of satellite peaks, can often be found from literature. Sources used in this thesis are e.g. the ThermoFisher XPS database [91] and the paper by Biesinger et al. [92], which provides an overview over peak fitting models for the 2p-peak regions of Cr, Mn, Fe, Co and Ni. Comparing the measured XPS spectra to the ones from literature can be very helpful to distinguish oxidation states and interpret the data. However, for many peak regions analyzed in this thesis, no reference data was available from literature. In these cases, peak models were developed based on the known constraints.

3.3.1 Determining layer thicknesses

To determine not only the chemical composition but also the thickness profile, angle-resolved X-ray photoelectron spectroscopy (ARXPS) can be used. In this case, XPS spectra at different takeoff angles θ are measured (Fig. 3.9). For angles near grazing incidence, only the photoelectrons very close to the surface reach the surface without inelastic collisions. At angles near normal incidence the probing depth is much deeper. This is depicted in Figure 3.9 b, where λ is the inelastic mean free path (IMFP), which is a measure of the distance which the electrons can travel on average without inelastic collisions. To determine the thickness profile of different layers, e.g. the thickness of an oxidized layer at the surface of a material, we need to know which photoelectron intensity we expect from which layer. For this we first consider a single layer and determine the intensity of emitted photoelectrons generated in a slice with thickness dz at a depth z below the sample surface (Fig. 3.9 a). The intensity dI_0 of photoelectrons generated in the layer is proportional to the layer thickness with the proportionality constant C [93, 94]:

$$dI_0 = Cdz \quad (3.16)$$

The fraction of electrons which reach the sample surface without inelastic scattering, so without losing energy, depends on the IMFP λ inside the respective material. According to

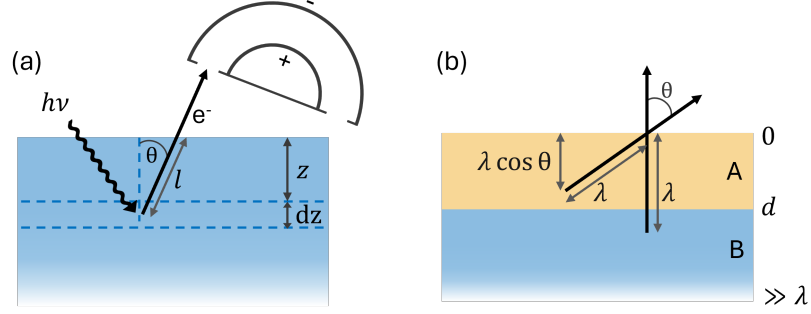


Figure 3.9: (a) Photoelectrons generated in a layer with thickness dz at a thickness z below the surface. The hemispherical electron energy analyzer is positioned such that the electrons emitted at a takeoff angle θ from the surface normal are analyzed. (b) Dependence of the photoelectron intensity at the sample surface on the depth in which the photoelectrons got excited, the takeoff angle θ and the inelastic mean free path λ of the material. Figures adapted from [93].

the Beer-Lambert law, it can be expressed as a function of the distance l which the electrons travel through the material [93]:

$$dI = dI_0 e^{-l/\lambda} \quad (3.17)$$

When neglecting the elastic scattering, which is increasing the distance traveled by an electron, we can write $l = z/\cos(\theta)$ and get:

$$dI = dI_0 e^{-z/\lambda \cos(\theta)} \quad (3.18)$$

$$= C dz e^{-z/\lambda \cos(\theta)} \quad (3.19)$$

For a material with two layers, as depicted in Figure 3.9 b, the total intensity for each layer can be obtained by integrating over the respective thickness. We assume a homogeneous material in each layer with an IMFP λ which only depends on the material and the photoelectron's energy. For electrons emitted from an element a in layer A we call the corresponding IMFP $\lambda_{a,A}$ and for electrons from an element b in layer B $\lambda_{b,B}$. Then, the total signal from layer A is given as [93]:

$$I_A = \int_0^{I_A} dI'_A \quad (3.20)$$

$$= \int_0^d C_{a,A} e^{-z/\lambda_{a,A} \cos(\theta)} dz \quad (3.21)$$

$$= C_{a,A} \lambda_{a,A} \cos(\theta) \left(1 - e^{-d/\lambda_{a,A} \cos(\theta)}\right) \quad (3.22)$$

For the signal from layer B, we can first calculate the total signal reaching the interface between the two layers. We assume, that layer B is much thicker than the IMFP, such that we use an infinite thickness for the calculation. With this we get:

$$I_{B, \text{interface}} = \int_0^\infty C_{b,B} e^{-z/\lambda_{b,B} \cos(\theta)} dz \quad (3.23)$$

$$= C_{b,B} \lambda_{b,B} \cos(\theta) \quad (3.24)$$

$$:= I_B^\infty \cos(\theta) \quad (3.25)$$

Thereby, we define the result as I_B^∞ because of the assumption of infinite thickness. When comparing with Equation 3.22 we find the same prefactor which we can equivalently label $I_A^\infty = C_{a,A} \lambda_{a,A}$. This signal is then passing through layer A. According to the Beer-Lambert law, the attenuated signal reaching the surface is given as [93]:

$$I_B = I_B^\infty \cos(\theta) e^{-d/\lambda_{b,A} \cos(\theta)} \quad (3.26)$$

The thickness d of layer A can be found as the ratio between the signals from the two layers. If we estimate $\lambda_{a,A} = \lambda_{b,A} = \lambda_A$, which can be assumed if the electrons from layers A and B have a similar energy, the result simplifies to [94]:

$$\frac{I_A}{I_B} = \frac{I_A^\infty (1 - e^{-d/\lambda_A \cos(\theta)})}{I_B^\infty e^{-d/\lambda_A \cos(\theta)}} \quad (3.27)$$

$$= \frac{I_A^\infty}{I_B^\infty} (e^{d/\lambda_A \cos(\theta)} - 1) \quad (3.28)$$

After some rearrangement we obtain:

$$d = \lambda_A \cos(\theta) \ln \left(1 + \frac{I_A/I_B}{I_A^\infty/I_B^\infty} \right) \quad (3.29)$$

with $I_i^\infty = C_i \lambda_i$. This equation will be referred to as the *single energy model* [95].

The ratio I_A^∞/I_B^∞ can be obtained from measuring thick samples of the respective materials under identical conditions [93, 94]. In the case of analyzing an element and its oxide layer on top, the ratio I_A^∞/I_B^∞ can be simplified. The metallic peak of the element and the peak of the corresponding cation in the oxidized layer are then only shifted by a few eV compared to each other. In this case, “(1) the instrument response function, (2) the attenuation due to inelastic scattering in any surface contaminant layer, and (3) the differential photoelectric cross section” can be assumed to change only negligibly between the metal and oxide layer, as explained by Hill et al. in reference [96]. The constant C_i then simplifies to the number density N_i , which is the density of metal atoms in the metal and oxide, respectively [96]. Therefore, the ratio between the intensities at infinite thickness can be simplified to:

$$\frac{I_A^\infty}{I_B^\infty} = \frac{N_A \lambda_A}{N_B \lambda_B} \quad (3.30)$$

3.3.2 Angle- and energy-resolved XPS

The single energy model is the basis for angle-resolved XPS, where θ is varied to determine d . However, it can also be used to estimate d from a single emission peak and angle θ . This is a common approach to obtain a rough estimate, but because of uncertainties in the fitting, this is very prone to errors. Therefore, it is very advisable to vary either the emission angle (ARXPS) or analyze different emission peaks which correspond to different energies and therefore different values for the IMFP (energy-resolved XPS) [95]. The latter has the advantage, that this is possible with every XPS setup, also with those setups which do not allow for angular scans. However, in literature, information on fit models is often only available for the most pronounced emission peak. Therefore, new fit models might need to be developed when using energy-resolved XPS. Helpful in this respect is that the intensity ratios $\frac{I_A}{I_B}$ of different emission peaks are interdependent for a fixed oxide thickness d .

The lowest uncertainty on the oxide thickness d can be obtained by combining angle- and energy-resolved XPS. This was done in this thesis whenever oxide thicknesses were calculated from XPS data.

3.3.3 Including roughness

The above derivations assumed perfectly smooth interfaces. In real samples, this is often not a valid assumption. Therefore, we will now include roughness at the interface. Equivalently to XRR, we will assume an error function of width σ at the interface. This error function will be multiplied with the number densities N_i of the two layers to define a smooth transition. When considering an element covered by its own oxide, such that $C_i \approx N_i$, as well as $\lambda_{a,A} = \lambda_{b,A} = \lambda_A$ and $\lambda_{b,B} = \lambda_B$, the total signal from layers A and B is given as:

$$I_A = \int_0^\infty \frac{N_A}{2} \operatorname{erfc}\left(\frac{z-d}{\sqrt{2}\sigma}\right) e^{-z/\lambda_A \cos(\theta)} dz \quad (3.31)$$

$$I_B = \int_0^\infty \frac{N_B}{2} \operatorname{erfc}\left(\frac{d-z}{\sqrt{2}\sigma}\right) e^{-(z-d)/\lambda_B \cos(\theta)} e^{-d/\lambda_A \cos(\theta)} dz \quad (3.32)$$

with the complementary error function $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$. The resulting intensity ratio is, according to [97]:

$$\begin{aligned} \frac{I_A}{I_B} = & \frac{N_A \lambda_A}{N_B \lambda_B} \exp\left(\frac{d}{\lambda_A \cos \theta} - \frac{d}{\lambda_B \cos \theta}\right) \\ & \cdot \frac{\operatorname{erfc}\left(-\frac{d}{\sqrt{2}\sigma}\right) - \operatorname{erfc}\left(\frac{\sigma}{\sqrt{2}\lambda_A \cos \theta} - \frac{d}{\sqrt{2}\sigma}\right) \exp\left(\frac{\sigma^2}{2(\lambda_A \cos \theta)^2} - \frac{d}{\lambda_A \cos \theta}\right)}{\operatorname{erfc}\left(\frac{d}{\sqrt{2}\sigma}\right) + \operatorname{erfc}\left(\frac{\sigma}{\sqrt{2}\lambda_B \cos \theta} - \frac{d}{\sqrt{2}\sigma}\right) \exp\left(\frac{\sigma^2}{2(\lambda_B \cos \theta)^2} - \frac{d}{\lambda_B \cos \theta}\right)} \end{aligned} \quad (3.33)$$

This intensity ratio has two variables now, the oxide thickness d and the interface roughness σ . Therefore, to solve it, intensity ratios of different emission peaks or different emission angles have to be measured (angle- or energy-resolved XPS). The different intensity ratios can then be fitted and d and σ obtained as fit parameters.

To obtain the values for d and σ , the values for λ_A and λ_B are required. According to the derivation above, they denote the inelastic mean free path. However, as part of this thesis, I contributed to improving Equation 3.33, among others, by substituting the inelastic mean free path λ_i by the effective attenuation length L_i , which additionally considers elastic scattering of the photoelectrons [98]. More details on the calculation of the effective attenuation length, the developed methodology to obtain d and σ and my contributions to this can be found in Chapter 6.2.

3.4 Anomalous Hall effect

The Hall effect was first discovered in 1879 by Edwin Hall [99]. He observed a voltage across a thin strip of gold when both an electric current and an external magnetic field were applied. This voltage appeared perpendicular to both the current and the magnetic field. Figure 3.10a depicts this so-called *ordinary Hall effect (OHE)*. The force acting on the charge carriers, which causes the Hall voltage, is called the Lorentz force $\mathbf{F}_L$. For a charge carrier with charge q and velocity $\mathbf{v}$ moving through an external magnetic field $\mathbf{H}_{\text{ext}}$ it is given by the following equation [47]:

$$\mathbf{F}_L = q\mathbf{v} \times \mathbf{B} \quad (3.34)$$

where $\mathbf{B}$ is the magnetic flux density inside the metal, caused by the external magnetic field $\mathbf{H}_{\text{ext}}$ and $\times$ denotes the cross product. If an electric field $\mathbf{E}$ is applied, it leads to an additional term $q\mathbf{E}$ in the Lorentz force: $\mathbf{F}_L = q\mathbf{E} + q\mathbf{v} \times \mathbf{B}$.

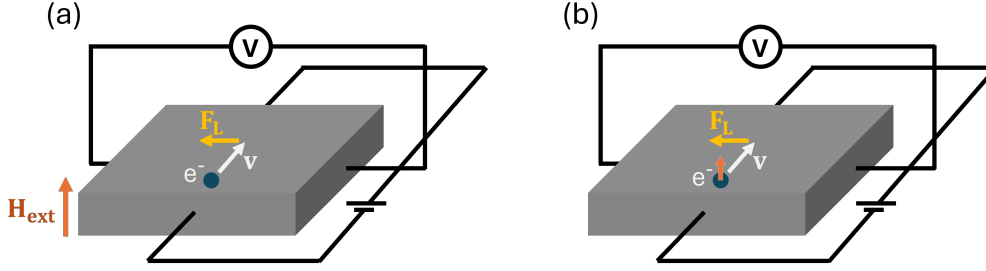


Figure 3.10: Hall setup for (a) the ordinary Hall effect and (b) the anomalous Hall effect. Thereby, $\mathbf{v}$ denotes the velocity of the electrons caused by the applied electric field, $\mathbf{H}_{\text{ext}}$ an externally applied magnetic field and $\mathbf{F}_L$ the Lorentz force.

Shortly after, Hall discovered that the Hall voltage was much larger in ferromagnetic than in nonmagnetic metals [100]. This formed the basis of the discovery of the *anomalous Hall effect* (AHE) (Fig. 3.10 b). The AHE is present for all metals with broken time-reversal symmetry, which include ferromagnets, but also e.g. altermagnets, and is caused by spin-orbit coupling [101]. It can be used to detect the magnetization direction by varying the direction of the current and observing the effect on the Hall voltage. When current and magnetization are parallel, the Hall voltage disappears, when they are orthogonal the Hall voltage is maximum.

For many materials, the dependence of the Hall resistivity $\rho_{x,y}$ on the external magnetic field $\mathbf{H}_{\text{ext}}$ and the magnetization $\mathbf{M}$ was empirically shown to be [101, 102]

$$\rho_{xy} = R_0 H_z + R_s M_z \quad (3.35)$$

where H_z is the z-component of $\mathbf{H}_{\text{ext}}$, orthogonal to applied current and measured voltage which are defined to be along x and y , M_z the z-component of $\mathbf{M}$ and R_0 and R_s are the Hall coefficients of the ordinary and anomalous Hall effect, respectively. While R_0 was shown to depend mainly on the density of carriers [101], the origin of R_s was under debate for many years. By now, it is understood, that three main mechanisms contribute to the AHE: an intrinsic deflection, related to the Berry-phase curvature, and two scattering effects, namely side jump and skew scattering. Which one of them dominates depends on material and measurement regime. Details on the three mechanisms and the regimes in which they dominate can be found in the review by Nagaosa et al. [101].

Further closely related effects were discovered over the years, like the spin Hall effect in metals without net magnetization but with strong spin-orbit coupling, and the quantum Hall effect. More details can be found in the following reviews [103, 104].

3.5 Superconducting quantum interference device

A superconducting quantum interference device (SQUID) is an extremely sensitive tool to measure magnetic flux and, consequently, for determining the amplitude and direction of the magnetic moment of a material [105]. For this, it makes use of quantum interference of supercurrents in a superconducting loop containing one or two Josephson junctions for an RF or DC SQUID, respectively.

A Josephson junction is based on a thin nonsuperconducting barrier sandwiched between two superconductors on either side (Fig. 3.11 a). The barrier can be a normal metal, as drawn in Figure 3.11 a, but can also be e.g. an insulator, superconductor with smaller critical temperature or geometrical constriction [106]. The Cooper pairs can be transmitted across the barrier,

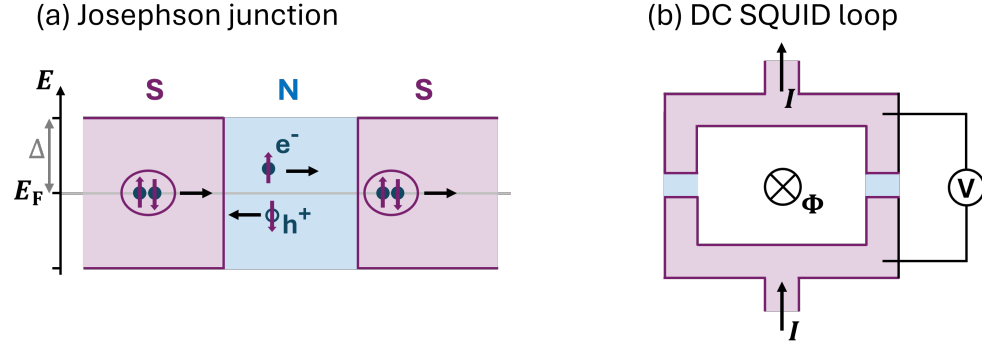


Figure 3.11: (a) Josephson junction, consisting of a nonsuperconducting barrier (here a normal metal N) sandwiched between two superconductors (S). Inside each superconductor, the electrons form Cooper pairs (here singlets with opposite spin) all of which condensate into a single quantum state with energy E_F . Therefore, a gap of width Δ opens around the Fermi energy E_F . The Cooper pairs can be transferred across the barrier via Andreev reflections mediated by an electron-hole-pair. Figure adapted from [106]. (b) DC SQUID loop, consisting of two superconducting arms, each with a Josephson junction, enclosing the magnetic flux Φ . A current I is applied across the loop and the voltage V is measured across the Josephson junctions. Figure adapted and slightly simplified from [105].

leading to a supercurrent. The total supercurrent which flows depends on the phase difference $\delta\varphi$ between the two superconductors [106]. It is given as $I_S(\delta\varphi) = I_0 \sin(\delta\varphi)$ with the critical current I_0 [106]. This is known as the DC Josephson effect. The equation holds as long as the applied current is smaller than the critical current I_0 . In this regime, a pure supercurrent is flowing and no voltage drops across the junction. For currents above I_0 , a voltage builds up across the junction which modulates the phase difference [105].

Figure 3.11 b depicts the design of a DC SQUID loop. It consists of a superconducting loop with two arms, each with a Josephson junction. A supercurrent enters on one side of the loop, splits between the two arms and leaves on the opposite side. When no magnetic flux is applied, the supercurrents in both arms are in phase and interfere constructively. When applying a magnetic flux Φ through the loop, this leads to a global phase shift which results in a phase difference across the two junctions. This causes the SQUID's total critical current I_c to vary periodically with the applied flux such that I_c becomes maximum for magnetic flux values Φ which are multiples of the magnetic flux quantum $\Phi_0 = h/2e$ and approaches zero for half-integer multiples (in a perfectly symmetric system with negligible self-field) [105]. This periodic modulation of I_c can be detected via the voltage across the barrier, which shows the same periodicity. Therefore, the magnetic flux can be measured very precisely with a sensitivity better than a single flux quantum.

To measure the magnetization of a sample, the magnetic flux generated by its magnetic moment gets coupled into the SQUID loop. It should be noted that the total flux of all layers of the sample is measured. Also dia- or paramagnetic layers, like the substrate or other intermediate layers, contribute to the signal. However, the contribution of dia- and paramagnetic signals depends linearly on the externally applied magnetic field. Therefore, it can be subtracted as a straight line when performing field dependent measurements. To obtain the magnetization of a sample, the magnetic moment obtained from the voltage output of the SQUID is divided by the respective magnetic volume. In this thesis, the MPMS XL SQUID magnetometer from the company Quantum Design was used.

3.6 Ionic liquids

ILs are molten salts and therefore consist of only ions [35]. In case of the so-called *room-temperature ILs*, the poor coordination of the ions allows for an increased flexibility, resulting in a liquid state at room temperature [35]. ILs have spread rapidly in the beginning of the 2000s because of their large potential to substitute conventional solvents in synthesis and catalysis. Especially their high chemical and physical tunability as well as nonvolatility makes them less hazardous and more environmentally friendly compared to many of the traditional, often volatile, organic solvents [107]. By now, ILs are used in many research fields, such as energy technologies, including batteries, fuel cells and water splitting, in bioscience, pharmaceuticals as well as in spintronics [36, 108, 109]. Responsible for this versatility of applications are their unique properties, which include, next to the ones mentioned above, also their large electrochemical capacitance over a broad voltage window, low toxicity and large thermal stability range.

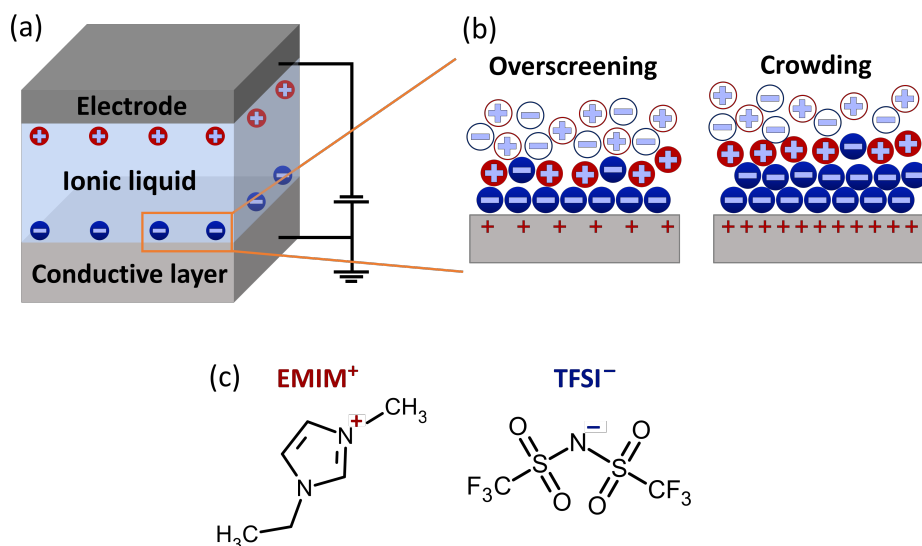


Figure 3.12: (a) Ionic liquid gating setup, as used in this thesis, with negative voltage applied to the top electrode. (b) Zoom into the EDL for the case of overscreening (typical at low voltages) and crowding (typical at high voltages). The ions represented by filled circles are the ones contributing to the EDL. Above, the charge is screened and the ions represented by unfilled circles are distributed similarly as in an ungated state. This figure was adapted from [110]. (c) Structural formula of the IL 1-ethyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl)-imide ([EMIM]⁺ [TFSI]⁻) used in this thesis.

In this thesis, ILs are used for electrical gating, which is particularly efficient when using ILs due to their high capacitance. This high capacitance is caused by an accumulation of ions of opposite polarity at the two interfaces when a voltage is applied, forming an electric double layer (EDL) (Figure 3.12 a). Figure 3.12 b shows a zoom into such an EDL for two cases: At low voltages, ions with charge opposing the applied voltage (here anions, depicted in blue) start accumulating along the interface. This causes the formation of a further layer, in this case with net positive charge, which screens the layer below. The applied voltage gets increasingly screened with every layer, such that the ions do not feel any significant attraction by the applied voltage anymore in the bulk of the IL (depicted by unfilled circles). At low voltages, the resulting arrangement of the ions in the EDL can be described as *overscreening*. At higher voltages, several layers of – in this case negatively charged – ions form at the interface, leading to an arrangement described as *crowding* [110]. Due to the screening, the voltage applied to the IL

mainly drops over the thin width of the EDL, which is typically of the order of 1 nm in the case of IL gating setups as depicted in Figure 3.12 a [36]. The resulting electric fields can be as high as 10 – 100 MV/cm [36].

3.6.1 EMIM TFSI

The IL used in this thesis is 1-ethyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl)-imide ($[\text{EMIM}]^+ [\text{TFSI}]^-$). Its structural formula is shown in Figure 3.12 c. It was chosen because of its large electrochemical window of more than 4 V [111, 112] and the short side chains of EMIM^+ , which allow for increased flexibility and consequently fast reaction to applied voltages. At room temperature and atmospheric pressure, it is a transparent liquid with a density of 1.53 g/cm^3 [113]. It has a melting point of -15°C [111] and a decomposition temperature of above 200°C for long term and around 400°C for short term exposure to high temperatures [114]. It is a hydrophobic IL with less than 0.5 % water, as specified by Sigma-Aldrich, where it was purchased (CAS number: 174899-82-2).

Further information on this and other ILs can be found in the NIST IL database. [115, 116] A comparison to other ILs can be found in the paper by Singh et al., which provides an overview over the most common classes of ILs, including their advantages and some typical applications [117].

3.7 IL gating setup built in Mainz

To perform the IL gating experiments, I built a setup in Mainz, inspired by the IL gating setup of the group of Liza Herrera Diez in Paris Saclay. The setup in Mainz allows to perform IL gating as well as AHE measurements for the magnetic characterization iteratively, or, if required, in parallel. In the following, I will first explain the process of IL gating. Afterward, the full setup, including the IL gating and AHE measurements, will be presented and further experimental details on the AHE measurements given.

3.7.1 Preparing the samples for IL gating

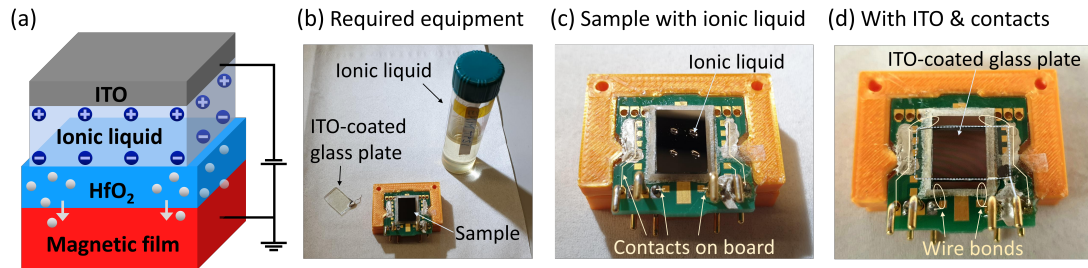


Figure 3.13: (a) Illustration of the process of IL gating. When a gate voltage is applied, the ionic liquid gets polarized and transmits the voltage to the sample. There, it acts on the oxygen ions (white spheres) which can thereby be moved inside or out of the magnetic film. (b)–(d) Preparation of the sample for the IL gating.

In this thesis, IL gating was performed on samples consisting of a metallic, usually magnetic, layer capped with a dielectric, which both protects the magnetic film from oxidation in ambient conditions and exhibits high oxygen-ion conductivity under applied electric fields (Fig. 3.13 a). For all investigated sample, HfO_2 was chosen as the capping layer because of its large ion mobility together with being a high- κ dielectric [118]. The IL was placed on top of the HfO_2 and the

gate voltage was applied across the IL and HfO_2 . The metallic layer below the HfO_2 , in which the gating effects were investigated, thereby also serves as the bottom contact of the gate. By applying a gate voltage, oxygen ions (white spheres in Fig. 3.13 a) can be moved down toward the metallic layer or retracted back upward.

Figure 3.13 b–d illustrate the process of preparing the samples for the IL gating. First, four drops of the IL (here $[\text{EMIM}]^+ [\text{TFSI}]^-$) have to be placed on the sample (Fig. 3.13 b). A glass plate coated with indium tin oxide (ITO) is placed on top of the IL as a top contact such that it is floating on the IL (Fig. 3.13 d). To contact it and at the same time stabilize its position, it is connected via a conductive wire to one of the contacts of the sample holder, to which it is glued with silver paste (in Fig. 3.13 d the bottom right corner of the glass plate to the board contact on the very right). Finally, the four edges of the sample are contacted by wire bonds to the contacts of the holder. One of these contacts will be used as the bottom contact of the gate. However, all four contacts are required to measure the AHE to characterize the magnetic state of the sample. To measure the AHE during IL gating, an additional contact has to be wirebonded to serve as the bottom contact of the gate.

3.7.2 Iterative IL gating and magnetic characterization

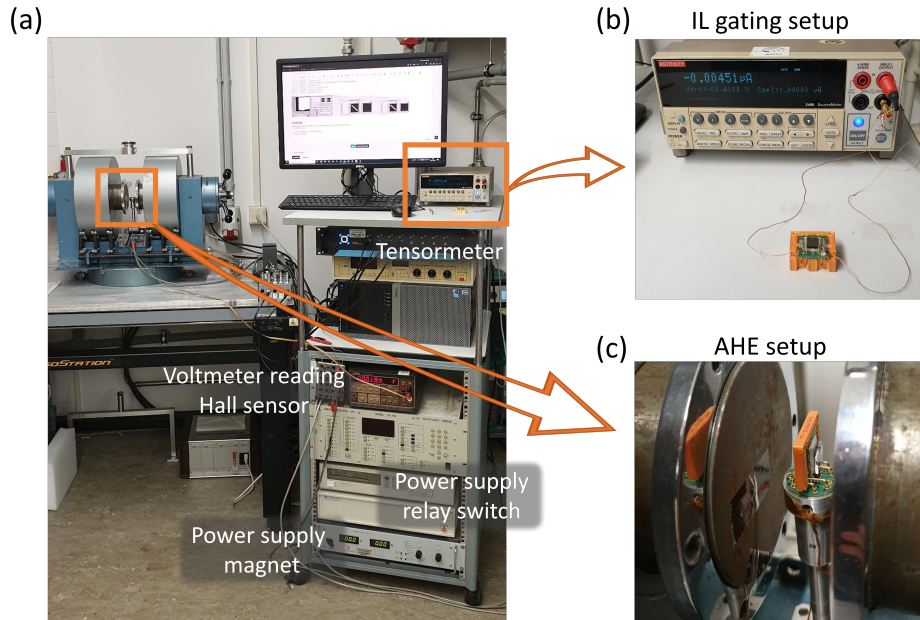


Figure 3.14: Setup for IL gating and AHE measurements. (a) Whole setup with all required instruments. (b) IL gating setup with the mounted sample and the voltage source. (c) Magnets of the AHE setup with the sample mounted inside. For both the IL gating and the AHE measurements, the sample remains on the same orange sample holder.

The core piece of the IL gating setup is the sample holder, which can be used for both the gating and AHE measurements. This has two advantages: First of all, the time between gating and AHE measurements can be minimized. Additionally, since the IL and glass plate do not have to be removed, also the wirebonds remain. Therefore, the Hall resistance, which is an extensive property and depends on the position of the wirebonds, can be compared more easily between measurements after different applied gate voltages.

Figure 3.14 a shows the complete measurement setup, comprising the IL gating setup (Fig. 3.14 b)

and the AHE setup (Fig. 3.14 c). The IL gate voltages were applied using a Keithley 2400, which allows to set a compliance for the current and observe the leakage current during the measurements. This is important to prevent short circuits which can occur if the ITO glass plate loses its balance and touches the sample with one corner. This happens with high chance when the leakage current starts to increase significantly. To allow for stable gating, the gating was performed progressively, starting with small gate voltages and then increasing the gate voltage up to voltages of -3 or $+4$ V, respectively. At larger voltages the gating becomes unstable because the voltage is approaching the limit of the electrochemical window (see Chapter 3.6.1). For all applied gate voltages, the sample was grounded via the bottom contact of the gate and a positive or negative voltage was applied to the top contact (ITO).

To characterize the change in magnetization during gating, the AHE was measured after every desired gate voltage. For that purpose, the gate voltage was set to zero, the sample unmounted from the gating setup and mounted into the electromagnet of the AHE setup (Fig. 3.14 c for OOP measurements). All AHE curves were measured at room temperature. To eliminate parasitic effects due to asymmetries of the contacts, the Hall voltages were measured across all diagonals of the sample using the tensormeter RTM2-501 from the HZDR Innovation GmbH and applying the lock-in technique at 625 Hz. To get the correct field values without hysteretic effects of the magnet's core, the field was measured using a Hall sensor.

3.7.3 Analyzing the AHE data

In the following section, all text, figures and equations marked with a line at their left are reprinted from [82]:

B. Bednarz et al.

“Stabilizing perpendicular magnetic anisotropy with strong exchange bias in PtMn/Co by magneto-ionics”

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As the magnetic field strength, which can be reached with the electromagnet, is not large enough to saturate all AHE magnetization curves, the ordinary Hall component was estimated from AHE measurements using a superconducting magnet (Fig. 3.15). The resulting ordinary Hall component was subtracted from all [unsaturated AHE curves] obtained with the electromagnet.

To estimate the ordinary Hall effect (OHE), magnetization curves were obtained by measuring the transverse resistivity with an applied current of 1 mA in a superconducting magnet cryostat at $T = 290$ K and up to magnetic field values of 8 T. The samples were connected by wire bonding the corners of the unpatterned samples (size of $5 \text{ mm} \times 10 \text{ mm}$). 2 ms long pulses of +1 mA and -1 mA were applied with a Keithley 6221 current source along the sample diagonal. The transverse Hall voltage was measured with a Keithley 2182A nanovoltmeter in Delta mode and was averaged out for 100 data points to remove noise due to temperature fluctuation and thermoelectric contributions. For every magnetic field value this procedure was repeated, and the Hall voltage measured for currents applied along both diagonals of the sample ($R_{\text{Hall,dir1}}$ and $R_{\text{Hall,dir2}}$). The van der Pauw-method was used to eliminate the longitudinal component in the Hall signal. For that purpose, the following formula was used at every field step:

$$R_{\text{Hall,corr}} = \frac{R_{\text{Hall,dir1}} + R_{\text{Hall,dir2}}}{2} \quad (3.36)$$

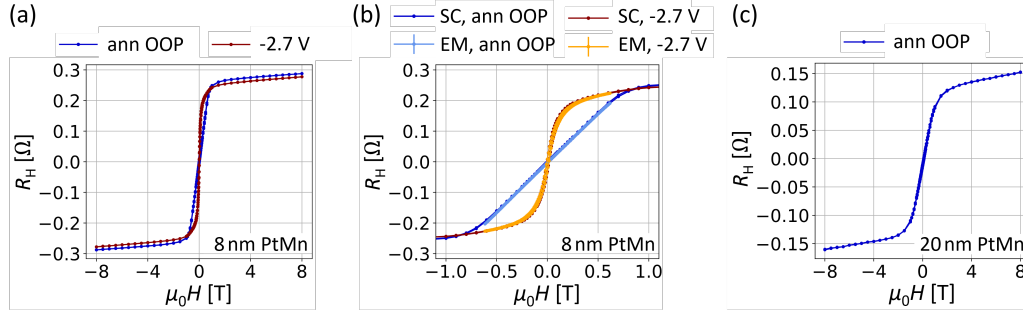


Figure 3.15: Hall measurements in a superconducting magnet cryostat, measured to determine the ordinary Hall effect (OHE) from the high field slope. From (a) a slope of $m = (3.3 \pm 0.3) \cdot 10^{-3} \Omega/\text{T}$ was obtained for the sample [Ta (5 nm)/Pt (3 nm)/PtMn (8 nm)/Co (0.9 nm)/HfO₂ (3 nm)] after saturation. From (c) a slope of $m = (3.9 \pm 0.3) \cdot 10^{-3} \Omega/\text{T}$ was obtained for the sample with 20 nm PtMn. (b) To confirm, that the magnetization curve measured in the superconducting magnet cryostat (SC) is identical to the one from the electromagnet (EM), the loops were plotted on top of each other.

The resulting magnetization curves are plotted in Figure 3.15. The slope was determined by fitting the data between 8 T and 4.5 T, as well as between -8 T and -4.5 T.

Figure 3.15a shows that the slopes obtained for the sample with 8 nm PtMn, in the annealed state and after applying -2.7 V, are very similar, so assuming a constant OHE for all gating steps seems reasonable. Additionally, Figure 3.15b shows that the same Hall resistances were obtained with the superconducting magnet cryostat (SC) and the electromagnet (EM). Therefore, the slopes obtained from the SC measurements at high fields were subtracted from all measurements performed with the EM. For time and capacity reasons, it was not possible to perform all measurements in the superconducting magnet cryostat.

3.7.4 Determining coercivity, shift and slope of the AHE loops

In the following section, all text, figures and equations marked with a line at their left are reprinted from [82]:

B. Bednarz et al.

“Stabilizing perpendicular magnetic anisotropy with strong exchange bias in

PtMn/Co by magneto-ionics”

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To characterize the magnetic state using the AHE loops, the coercivity, shift and slope were used. Thereby, the shift of the magnetization loop is a measure of the exchange bias. The slope, determined at zero remanent magnetization, was used to characterize the degree to which the magnetization loop is dominated by IP or OOP magnetization, respectively [58].

The data analysis was done using Python. The magnetization curves were first interpolated with a step size of 1 mT. For both the upward as well as the downward half of the interpolated loops the coercive field was determined as the datapoint closest to zero resistance on the positive resistance side (C_1 and C_2 in Fig. 3.16). The shift and coercivity were calculated as

the sum and difference of the two coercive fields, respectively.

The systematical error on the shift and coercivity was estimated to be 2.38 mT by investigating the shift of samples in the as deposited state. In that state, no exchange bias was set yet, so no shift should be present. Additionally, the error caused by the drift of the magnetization back toward the OOP state was added. The affected datapoints are the last two datapoints for the samples MASA697 D and E, after the application of 3.3 V and 3.5 V. The error was estimated as 4 mT and 5 mT, respectively, for the coercivity, and 1 mT for the shift.

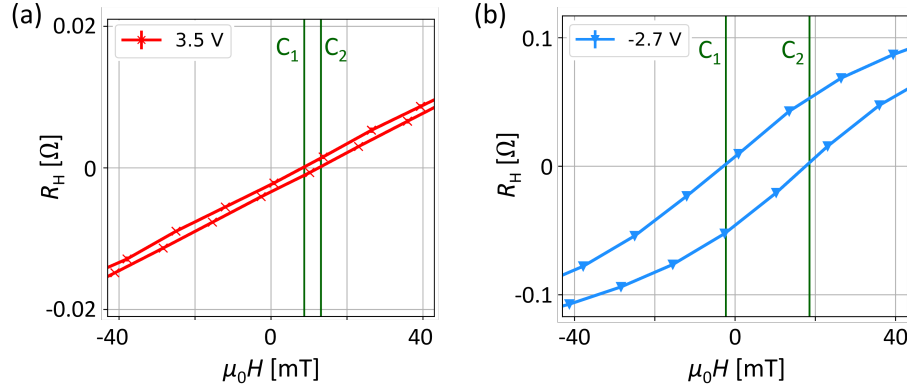


Figure 3.16: Determined coercive fields C_1 and C_2 displayed for two exemplary AHE curves of the sample with 8 nm PtMn (a) after the first application of 3.5 V and (b) after the application of -2.7 V gate voltage.

The slope at zero remanence magnetization was determined as the average between the slope at the first and second zero-magnetization-crossing of the magnetization curve. The difference between the two values is given as the error bar. It is a measure for the asymmetry of the magnetization curve.

Stabilizing PMA with strong EB

In the following section, all text, figures and equations marked with a line at their left are reprinted from [82]:

B. Bednarz et al.
 “Stabilizing perpendicular magnetic anisotropy with strong exchange bias in PtMn/Co by magneto-ionics”
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This work resulted from my secondments in Paris in the group of Liza Herrera Diez. For the results shown here, I performed all IL gating experiments myself and also built the IL gating setup in Mainz which I used for the gating. Also the XRD, SQUID, AHE and longitudinal resistance measurements for the sample characterization were done by me. Only the XPS data was not measured by me but by Leon Prädel from the Max Planck Institute of Polymer Research and the samples were grown by Maria-Andromachi Syskaki and Fabian Kammerbauer. All data analysis, including the XPS data, was performed by me. I also wrote the first version of the manuscript and incorporated all feedback from the co-authors and reviewers.

4.1 Introduction

In view of the climate crisis and the rapidly growing power consumption of information and communication technology, more energy-efficient data storage and processing is needed [119, 120]. In that respect, voltage control of magnetic properties is one of the central approaches with high potential for ultralow-power data storage as well as energy-efficient hardware for dissipative and neuromorphic computing [21, 32, 33, 34, 121, 122]. Particularly large magneto-electric effects of over 7000 fJ/Vm, calculated as the change in magnetic anisotropy divided by the applied electric field, can be obtained with magneto-ionics using the electric field induced motion of mobile ions [38]. Magneto-ionics was shown to allow for low-power switching of magnetization [123], manipulation of the exchange bias (EB) [40, 124] and the Dzyaloshinskii–Moriya interaction [125] as well as the control of domain wall nucleation and motion [126, 127].

The EB is fundamental to many technological applications. It describes the pinning of the magnetization of a ferromagnetic (FM) material by the uncompensated magnetic moments of an adjacent antiferromagnet (AFM), causing a shift of the magnetization curve along the magnetic field direction. Its applications range from pinning the reference layer in spin valves for magnetic memories, sensors, and spintronic devices [128], to replacing the auxiliary magnetic field and allowing for field-free switching of magnetization [129], to imprinting domain patterns for magnetophoretic applications [130]. So far, research on the control of the EB focused on the manipulation of the EB in samples with a fixed magnetization direction [33, 39, 40, 124, 131]. This was achieved by transfer of different ions, e.g. O [43], H [40], Li [132], as well as N [133]. Different material systems were shown to allow for the manipulation of the EB ranging from systems with the AFM on top [39] or below [124] the FM and with insulating [124] as well as metallic AFMs [39]. However, so far, a demonstration of the possibility to rotate the magnetization from an in-plane (IP) to an out-of-plane (OOP) state while retaining a strong EB is still missing. This would be highly desirable e.g. to program 3D magnetization sensors for which one part of the sensor needs to have IP magnetization and another part OOP magnetization.

In this [work], we investigated the effect of magneto-ionic gating on the EB between platinum-manganese (PtMn) and cobalt (Co) thin films. We applied the ionic liquid gating technique, enabling large-area gating with simple sample fabrication and applicability to a wide range of materials. In the as-grown state the system exhibits IP magnetization. By gating, we demonstrate the rotation of the magnetization into a non-volatile state with OOP magnetization and OOP EB. Notably, this OOP state is the energetically favorable one once it is reached. To better understand the influence of the AFM layer thickness, we compare two stacks with different PtMn thicknesses. We show that there is a trade-off between the strength of the EB in the final state and the speed of the gating process within the accessible gate voltage window until substantial oxidation of the Co. In thinner (8 nm) samples the magnetization can be rotated faster while thicker (20 nm) samples show a stronger EB.

4.2 Investigated material system

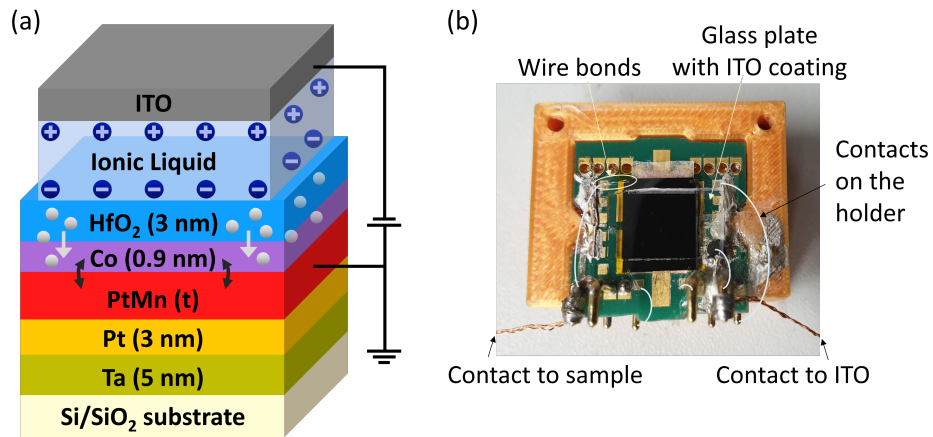


Figure 4.1: (a) Sample stack. The white spheres represent the oxygen ions which can be moved by applying a gate voltage across the HfO₂. The arrow between the Co and the PtMn represents the EB coupling between the two layers. (b) Picture of the mounted and contacted sample.

We have studied magnetic stacks with the composition Ta (5 nm)/Pt (3 nm)/PtMn (t)/Co (0.9 nm)/HfO₂ (3 nm) deposited on thermally oxidized Si/SiO₂ substrates, with two thicknesses of PtMn ($t = 8$ and 20 nm) (Fig. 4.1 a). Co was chosen as the FM material because it can have strong perpendicular magnetic anisotropy (PMA). PtMn, a metallic AFM, is commonly used in the industry because of its ability to provide a strong EB with high thermal stability [68, 66]. The seed layers Ta and Pt provide a smooth surface and matching lattice constant for an optimized growth of PtMn. Co was capped with HfO₂, which serves as a donor for mobile oxygen species. It is a high- κ dielectric with large technological relevance [134] and allows for high ion-mobility at low voltages. To ensure very high sample quality, the stacks were sputtered in an industrial Singulus Rotaris magnetron sputtering tool at room temperature. As an isolating layer, HfO₂ was sputtered using RF voltages. The further layers of the stack are metallic and sputtered by DC voltages. To move the mobile oxygen species inside the HfO₂, a droplet of the ionic liquid 1-ethyl-3-methylimidazolium-bis(trifluoromethylsulfonyl)imide ([EMIM]⁺ [TFSI]⁻) was added on the sample surface, and a glass plate coated with indium tin oxide (ITO) was placed on top. The gate voltage was then applied from the ITO electrode across the ionic liquid and HfO₂ to the metallic layers at the bottom of the material stack, which were contacted by wire bonding (Fig. 4.1). In this way, a sample area of approximately $5 \times 5 \text{ mm}^2$ was gated.

Superconducting quantum interference device (SQUID) measurements were performed using the Quantum Design MPMS-XL5 SQUID Magnetometer to analyze the initial magnetic state and the changes due to gating. [...] Before mounting the samples in the SQUID, the ITO-coated glass plate was removed, the ionic liquid washed off with acetone and the ungated areas of the sample were cut off. [...] For each magnetization curve, the data points with low fit quality < 0.7 were removed. The deviations from an ideal point dipole were corrected with a geometry factor, and a small offset in the magnetic field values caused by magnetic field lines trapped in the superconducting magnet was corrected. Then the diamagnetic contribution was subtracted from the data by subtracting the slope obtained from the first 3 data points.

In the as-deposited state, the samples show full IP magnetization for both 8 nm and 20 nm PtMn (Fig. 4.2 a and c). We aim to explore whether it is possible to reach OOP magnetization with OOP EB through ionic-liquid gating. Therefore, the samples were annealed in an OOP magnetic field of 800 mT at 300 °C for 2 h, to establish OOP EB. Annealing the samples leaves the magnetization IP, while the coercivity of the IP magnetization curve increases significantly (Fig. 4.2 b and d).

The structural characterization of the samples was done by XRD, measured in a Bruker D8 X-ray diffractometer (Fig. 4.3). All spectra show the PtMn(111) peak at 40.2° with a shoulder on its left, corresponding to the Pt(111) peak. Fig. 4.3 a shows that in both samples, with 8 nm as well as 20 nm PtMn, the PtMn grows in (111) orientation. The PtMn peak in the sample with 20 nm PtMn is larger and the center matches better with the theory position of the PtMn(111) peak, indicating less strain in the sample. Fig. 4.3 b shows that the annealing in an OOP magnetic field of 800 mT for 2 h at 300 °C, as well as gating at -2.7 V does not visibly influence the [vertical] crystal structure of the PtMn. The peak at 69.2° corresponds to the Si(004) substrate peak. The peaks at its left edge are the corresponding satellite peaks, observed because the beam monochromatization by the Goebel mirror is incomplete.

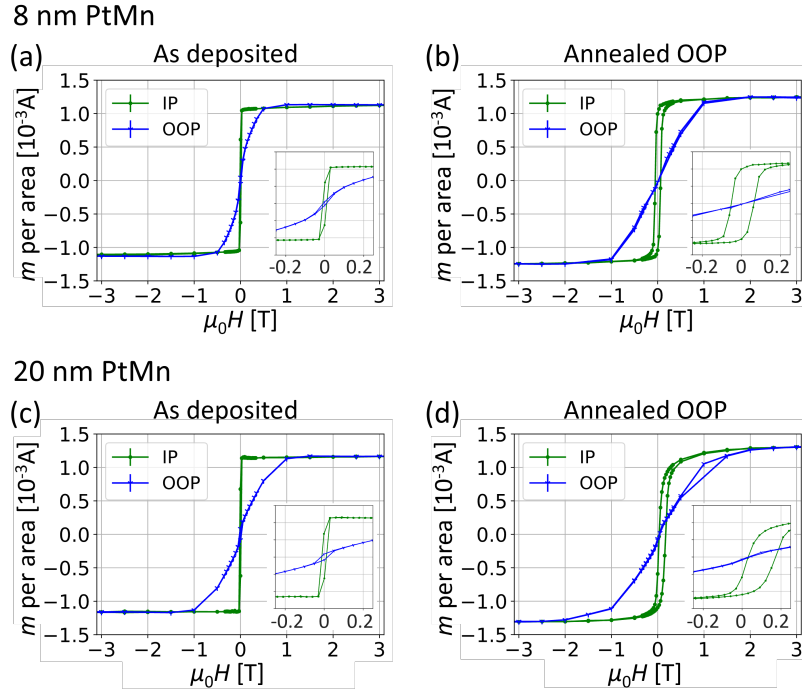


Figure 4.2: IP and OOP SQUID measurements of the samples Ta (5 nm)/Pt (3 nm)/PtMn (t)/Co (0.9 nm)/HfO₂ (3 nm), with 8 nm (a–b) and 20 nm PtMn (c–d), respectively. The measurements were done in the as-deposited state and after annealing in an OOP magnetic field of 800 mT for 2 h at 300 °C. The insets show the zoom into the center of the magnetization curves. All curves were measured up to magnetic fields of ± 4 T.

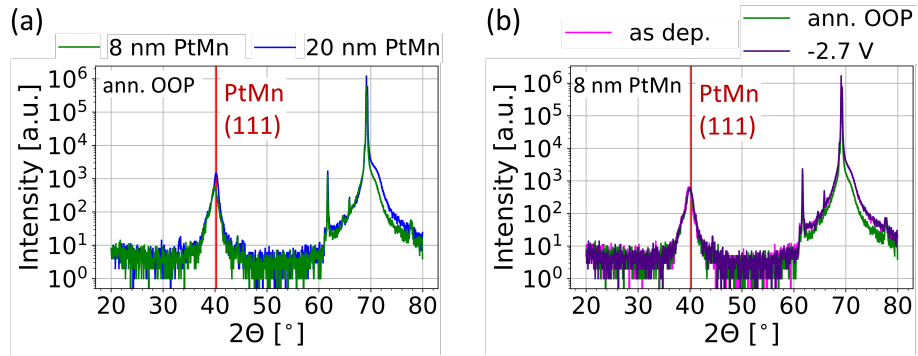


Figure 4.3: XRD patterns of the samples Ta (5 nm)/Pt (3 nm)/PtMn (t)/Co (0.9 nm)/HfO₂ (3 nm) (a) comparing samples with the thicknesses $t = 8$ nm and 20 nm PtMn after annealing in an out-of-plane (OOP) magnetic field of 800 mT for 2 h at 300 °C. (b) Influence of the annealing in the OOP magnetic field and subsequent gating with -2.7 V on the crystal structure for the sample with $t = 8$ nm PtMn. The red line in both figures shows the reference position of 40.2° for PtMn(111) [135]. The peak at 69.2° is the peak of the Si substrate. The sharp lines at 61.7° and 65.9° are resulting from the substrate and residual contributions of copper K_β and tungsten L_α radiation to the incoming beam.

4.3 Achieving stable OOP magnetization by IL gating

The gate voltages were applied using a Keithley 2400. For each gating step, the voltage was slowly increased to minimize instabilities until reaching the desired voltage. After waiting for the desired gating time, the gate voltage was turned off and the magnetization curve was measured via the anomalous Hall effect (AHE) at room temperature.

In this way, very short waiting times between gating and measurement of only a few minutes were achieved (see Chapter 3.7).

4.3.1 Stabilizing OOP magnetization

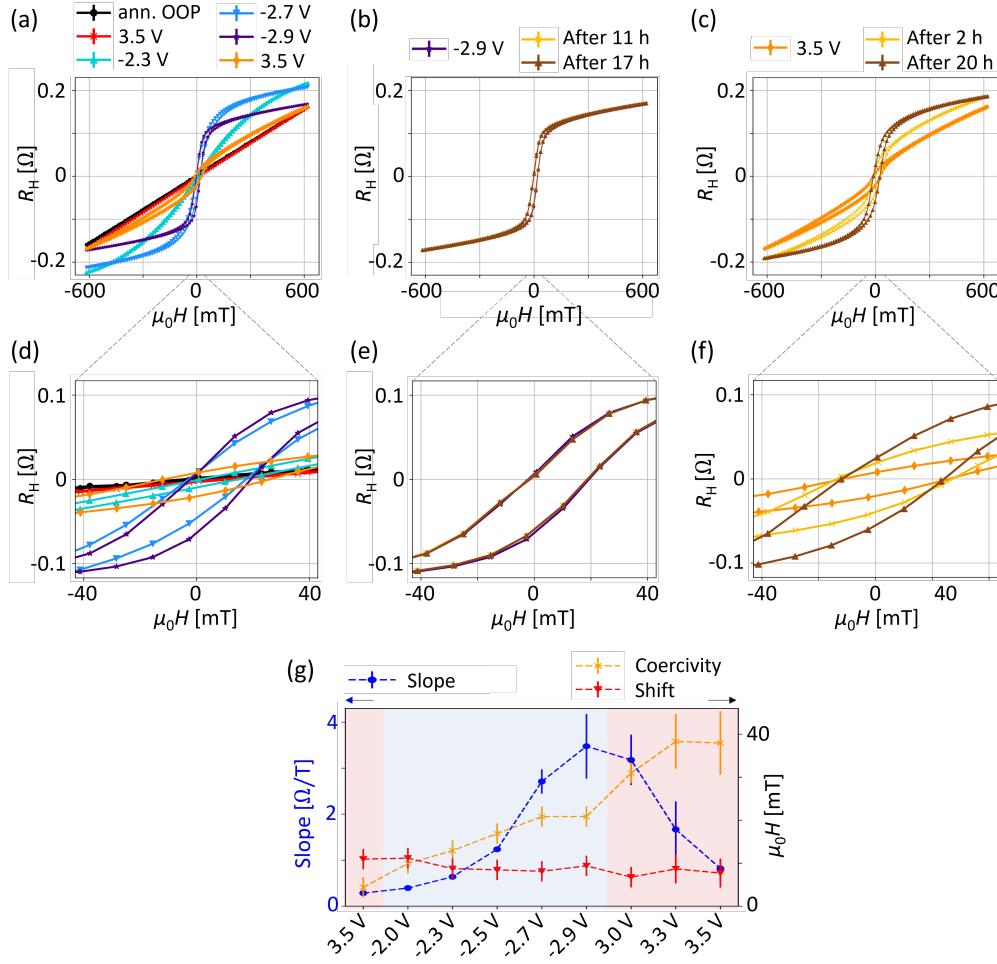


Figure 4.4: Evolution of magnetic properties by gating in the sample with 8 nm PtMn. (a) AHE curves from the first gating cycle. The initialization gate voltage of 3.5 V was applied for 5 min. All further gate voltages were applied for 2 min. (b) Stability check of the OOP state after the application of -2.9 V. (c) Time evolution of the AHE curve after the magnetization was brought back toward an IP state by applying a gate voltage of 3.5 V. (d)–(f) Zoom into subfigures (a)–(c). (g) Overview over slope, coercivity and EB shift of the AHE loops at zero remanent magnetization.

We will first discuss the samples with the thinner PtMn layer of 8 nm. To establish a defined initial state, first, a positive gate voltage of 3.5 V was applied. This positive voltage induces an upward drag on the oxygen species inside the HfO_2 layer. The Co is set to a state of minimum oxygen concentration. As shown in Fig. 4.4 a, the magnetization remains IP after this initialization step, with only minor changes in the magnetization curve. Subsequently, negative voltages were applied. In agreement with previous reports [37], we observe a progressive transformation toward a square-shaped magnetization loop. Since the AHE probes the OOP magnetization, this demonstrates that the magnetization rotates from the IP to the OOP direction. All AHE curves are shifted toward positive magnetic field values revealing the OOP EB (Fig. 4.4 d).

The OOP magnetization, which is reached by applying negative gate voltages, is very stable over time (Fig. 4.4 b). By applying positive gate voltages, the magnetization can be rotated back toward the IP direction. However, this IP state is no longer stable over time. Within a few hours, the sample evolves back to the OOP state (Fig. 4.4 c). Additionally, it is not possible in this material system to bring the sample to an IP state by overoxidation. Instead, at -2.9 V, we observe a decrease in the total Hall resistance, while the slope continues to increase. This demonstrates the stabilization of the OOP state with EB in an initially IP sample by ionic liquid gating.

Fig. 4.4 g shows the evolution of the EB shift and coercivity in comparison to the slope of the AHE loop during the different gating steps. The coercivity of the AHE loops increases when the magnetization rotates from IP toward OOP. When positive voltages are applied subsequently, the magnetization direction is no longer stable in time, and the AHE curve is drifting during the measurement. The resulting coercivities therefore have a large error. The EB shift initially decreases slightly when a negative voltage is applied. Then, it stabilizes and reaches a relatively constant value of 8.2 mT with a standard deviation of 0.8 mT and a systematical error, indicated by the error bars, of 2.4 mT (see Chapter 3.7).

4.3.2 Reproducibility of the results

To check the reproducibility of the results measured via the AHE in the electromagnet, the results on three nominally identical samples were compared. The samples show qualitatively the same behavior [(Fig. 4.5)].

In all samples, the slope shows a strong increase with negative gate voltages and a subsequent decrease with positive gate voltages. However, the samples show differences in the speed, in which they reach their maximum PMA state. For the green curve [(MASA697E), which was analyzed in Fig. 4.4], the slope still increases from -2.7 V to -2.9 V, although [its maximum Hall resistance decreases]. For the blue curve, the slope decreases at -2.9 V. [Also for this sample, the maximum Hall resistance decreased after the application of -2.9 V. This decrease in the maximum Hall resistance implies a decrease in the total magnetic moment. Since the slope is influenced both by a change in the total magnetic moment, as well as by a change in anisotropy, the change of the slope denotes which of the two happens faster. The difference between the two samples indicates that the speed in which the perpendicular magnetic anisotropy increases due to gating, compared to the change in total magnetic moment,] can slightly vary between the samples. The overall behavior, however, remains unchanged in all three samples.

The longitudinal resistance shows an increase with a negative gate voltage, as expected for oxidation. With positive gate voltage, the resistance decreases again.

The absolute longitudinal resistance depends on the wirebond positions and therefore differs between samples. For a given sample, however, the wirebonds remain unchanged during gating. Therefore, the qualitative results are unaffected. The sharp resistance drop at the last data point of sample MASA697D is most likely due to an instability in contact resistance.

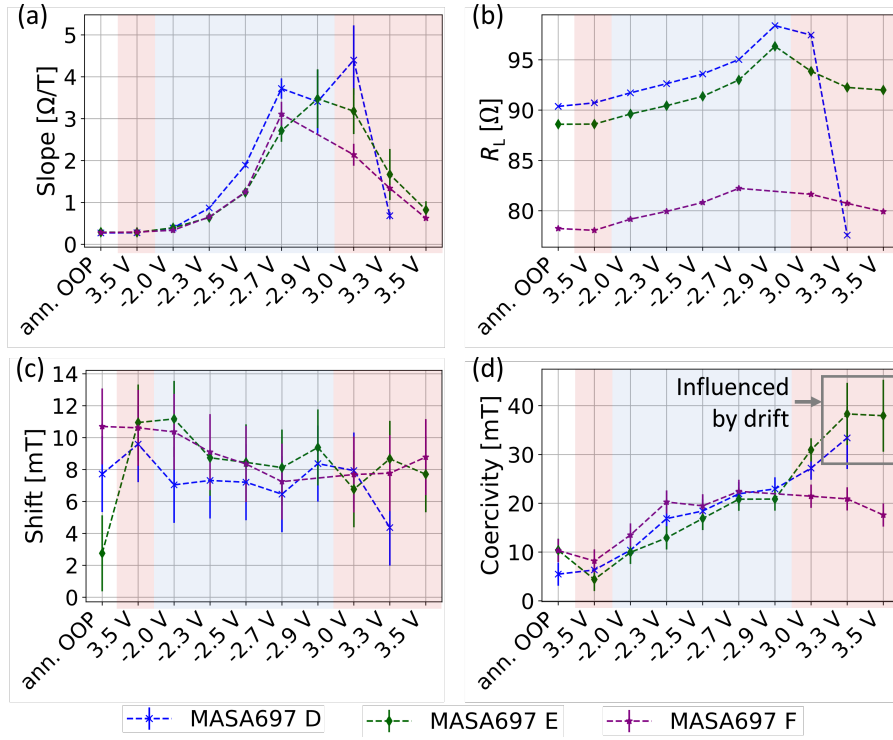


Figure 4.5: Overview over the slope, longitudinal resistance R_L , shift and coercivity, obtained from the AHE measurements of 3 nominally identical samples of Ta (5 nm)/Pt (3 nm)/PtMn (8 nm)/Co (0.9 nm)/HfO₂ (3 nm) with the labels MASA697 D, E and F. All samples were cut from the same wafer and annealed in the same run. The sample [analyzed in Fig. 4.4] is MASA697 E. The grey box in (d) marks the datapoints which showed a significant drift during the measurement because of the evolution of the magnetic state back towards the OOP direction. The sample MASA697 F was not significantly influenced by this drift because the measurement speed was largely increased for that sample. The voltages on the x-axis represent the successively applied gating voltages and lines only serve as a guide to the eye.

[The stabilization of the EB shift after successive negative gating can be seen in all samples, except for the outlier of the sample MASA697 D after the last positive gating step.] In the annealed state, the EB shift fluctuates. However, by performing the first gating cycle, it stabilizes for all nominally identical samples to an identical value within the error margin. This indicates a varying amount of oxygen ions at the PtMn/Co interface in the annealed state, which are removed by the positive gate voltage.

The coercivities of the three samples show the same trend for the first gating cycle. When positive gate voltages are applied to bring the magnetization back to the IP state, the drift of the magnetization, however, had a significant effect on the measured magnetization loops for the samples MASA697 D and E.

Before measuring the sample MASA697 F, the measurement program was updated, and the measurement speed significantly increased from 42 min to 11 min per measurement. Therefore, the data of MASA697 F was not significantly influenced by the slow drift anymore.

It shows a slow decrease of the coercivity for the last positive gate voltages.

4.3.3 Calculating the anisotropies from SQUID measurements

To better understand the underlying magnetic changes in this system, we performed magnetization measurements in a superconducting quantum interference device (SQUID) (Fig. 4.6 a–e).

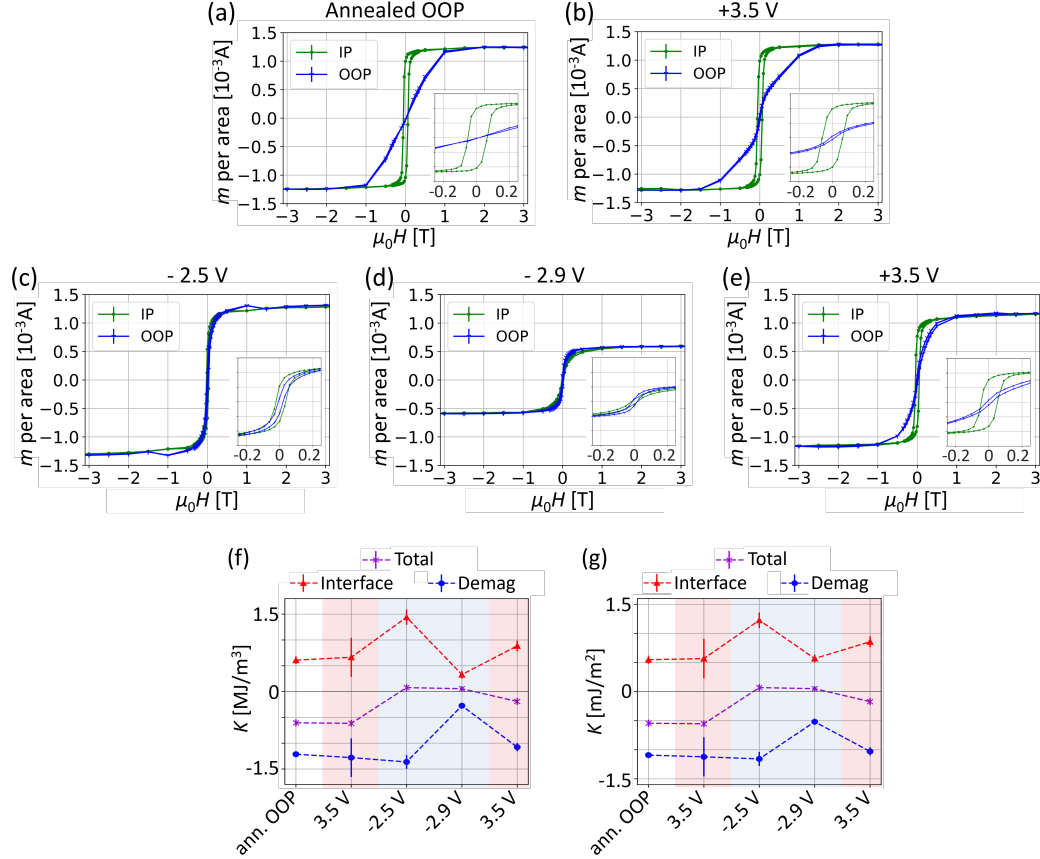


Figure 4.6: (a)–(e) IP and OOP SQUID measurements of the samples Ta (5 nm)/Pt (3 nm)/PtMn (8 nm)/Co (0.9 nm)/HfO₂ (3 nm). The measurements were done after annealing in an OOP magnetic field of 800 mT for 2 h at 300 °C and different subsequent gating steps. The first positive initialization voltage was applied for 10 min, all other voltages for 5 min each. The insets show the zoom into the center of the magnetization curves. All curves were measured up to magnetic fields of ± 4 T. (f)–(g) Evolution of the total anisotropy, demagnetization, and interfacial energy per volume, obtained from SQUID measurements at 300 K, calculated using (f) the assumption of constant Co thickness and changing magnetization, and (g) constant magnetization and changing Co thickness.

Initially, before applying negative gate voltages, [the] samples show an in-plane (IP) magnetization (Fig. 4.6 a). The small jump at the center of the OOP magnetization loop [...] after the application of 3.5 V indicates a small canting in the magnetization (Fig. 4.6 b). After negative gating of -2.5 V, a remanent moment is observed in both IP as well as OOP direction (Fig. 4.6 c). When applying the -2.9 V, the magnetic moment per area decreases (Fig. 4.6 d), as was also observed in the AHE loop. The OOP magnetization loop remains a magnetic easy axis loop, while the IP magnetization loop changes slightly towards a magnetic hard

axis loop. Subsequent gating with a positive voltage of 3.5 V brings the magnetization back towards the IP direction (Fig. 4.6 e).

From the IP and OOP SQUID loops, we obtained the magnetic anisotropy energies per volume after the different gating steps (Fig. 4.6 f and g). In this material system, we consider the demagnetization energy, which favors IP magnetization, and the interfacial anisotropy energy, which favor OOP magnetization, as the most important energy contributions. The total anisotropy energy was obtained from the area between the OOP and IP magnetization curves (Eq. 4.1). The demagnetization energy was calculated using its proportionality to the squared saturation magnetization M_S^2 (Eq. 4.2) [47]. The interfacial anisotropy energy, stemming from the two Co interfaces, can then be calculated using Eq. 4.3.

$$K_{\text{total}} = \frac{1}{\mu_0} \int_{\text{shift}}^{\mu_0 H_{\text{max}}} (\mu_0 M_{\text{OOP}} - \mu_0 M_{\text{IP}}) d(\mu_0 H) \quad (4.1)$$

$$K_{\text{demag}} = \frac{1}{2} \mu_0 M_S^2 \quad (4.2)$$

$$K_{\text{interface}} = K_{\text{total}} - K_{\text{demag}} \quad (4.3)$$

Equations 4.1–4.3 assume that the thickness of Co remains unchanged, such that the nominal thickness of Co can be used to determine the magnetization M from the total magnetic moment measured in SQUID. However, the oxidation might narrow the thickness of the magnetic Co layer. Therefore, as the second limiting case, a changing Co thickness but constant magnetization should be considered. In this case, the anisotropies have to be calculated per area instead of per volume. For this purpose, the magnetic moment m per area, so (Mt) is used for the total anisotropy energy. The demagnetization energy, can accordingly be calculated as $K_{\text{demag}} = \frac{1}{2} \mu_0 (M_{\text{St}}) M_{\text{S,annOOP}}$, where (M_{St}) is obtained from the SQUID measurement and $M_{\text{S,annOOP}}$ is using the assumption that the magnetization remains constant during gating. Figures 4.6 f and g show the results of the two limiting cases. Qualitatively, their behavior is the same.

In Fig. 4.6 f and g, the total anisotropy energy (purple) shows a clear trend of becoming more negative (toward IP magnetization) when applying positive voltages and becoming more positive (toward OOP magnetization) when applying negative voltages. This supports the presumed underlying mechanism of oxygen ion migration. The total anisotropy energy reaches its maximum positive value (maximum PMA) at -2.5 V. This is explained by the strong increase of the interfacial anisotropy (red), of a factor of 2.2 [(calculated for the anisotropy per volume)], after the application of -2.5 V. This, in turn, can be explained by the additional oxygen at the Co interfaces, especially the Co/HfO₂ one. It allows for a stronger hybridization between the Co-3d and the O-2p orbitals, which is known to cause interfacial PMA [64]. Notably, the demagnetization energy (blue) remains quite constant and even slightly increases up to -2.5 V, in accordance with the observations from the AHE effect measurements. This [suggests] that the rotation of the magnetization is caused by the increasing interfacial PMA and not by a reduction of the demagnetization energy.

After the application of -2.9 V, both the demagnetization and the interfacial anisotropy energy drop significantly. For the demagnetization energy, this is clearly related to the reduction of the total magnetic moment caused by the overoxidation of Co.

For the interfacial anisotropy energy, its reduction due to overoxidation suggests that the oxygen content at the Co/HfO₂ interface has gone past the optimum oxidation point which corresponds to maximum PMA or that the PMA at the PtMn/Co interface got diminished. This interfacial PMA cannot be fully recovered by applying a positive voltage of 3.5 V. From the results on the AHE measurements, we can, however, assume that over time the oxygen ions will diffuse back to the positions which lead to the maximum PMA.

4.3.4 Contribution of reduced demagnetization energy

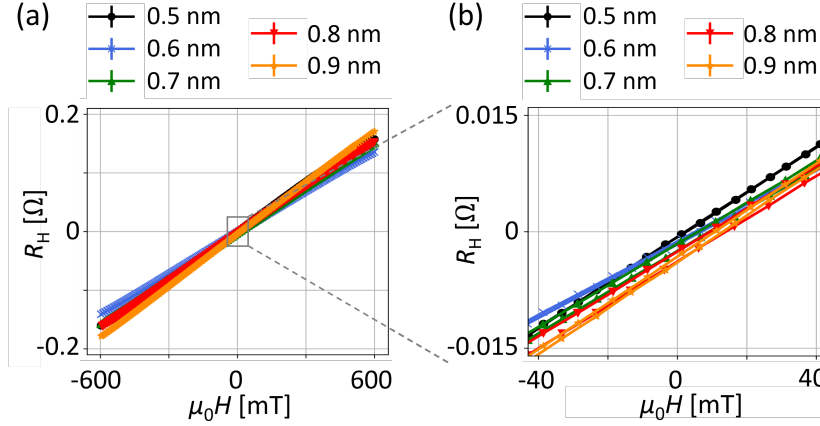


Figure 4.7: Influence of the Co thickness on the AHE curves, analyzed for the sample Ta (5 nm)/Pt (3 nm)/PtMn (8 nm)/Co (t_{Co})/HfO₂ (3 nm) after annealing in an OOP field of 800 mT at 300 °C for 2 h. (a) AHE curves as a function of the Co film thickness. (b) Zoom into the center of the AHE curves. To correct for the OHE, a slope of $3.3 \cdot 10^{-3} \Omega/T$ was subtracted, as described in Chapter 3.7.3.

The change of the magnetization direction from IP to OOP during oxidation can be induced by two factors, the increasing interfacial PMA due to hybridization with the oxygen ions or a decrease in Co film thickness, expressed as a reduction of demagnetization energy. The nearly constant demagnetization energy up to -2.5 V in Figures 4.6 f and g suggested that, in these samples, the rotation of the magnetization direction is purely due to an increasing interfacial PMA.

To disentangle the two effects and check how much a reduction of the Co film thickness could support a further rotation of the magnetization toward the OOP direction, I analyzed a set of samples with decreasing Co thickness. Samples with the composition Ta (5 nm)/Pt (3 nm)/PtMn (8 nm)/Co (t_{Co})/HfO₂ (3 nm) were deposited on thermally oxidized Si/SiO₂ substrates by Fabian Kammerbauer, with Co thicknesses of $t_{Co} = 0.5$ to 0.9 nm (Fig. 4.7). To establish the same conditions as for the gated samples, I performed the same annealing procedure, applying an OOP field of 800 mT at 300 °C for 2 h.

Figure 4.7 shows the dependence of the magnetization curves on the Co film thickness. No systematic increase in the slope with decreasing thickness can be observed. The nearly identical slopes of the 0.5 and 0.9 nm curves suggest that the observed variations between samples are primarily due to variations in the distances between the wirebonds. Therefore, in the annealed state, the interfacial PMA of this material system is too small such that even for Co thicknesses as low as 0.5 nm the reduction in demagnetization energy does not significantly influence the magnetization direction. Reducing the Co thickness even more would reduce the demagnetization energy further. However, already at 0.5 nm Co it gets difficult to achieve a full-film, ferromagnetic Co layer which still allows for exchange bias. This can be seen in the evolution of the exchange bias shift with decreasing Co thickness, portrayed in Fig. 4.7 b. For the sample with 0.5 nm Co, the magnetization curve has reached almost zero exchange bias shift. Therefore, to achieve a rotation of the magnetization into the OOP direction and retain the exchange bias, as demonstrated by ionic-liquid gating, an increase of the interfacial anisotropy energy is required in this material system.

4.4 Influence of PtMn thickness

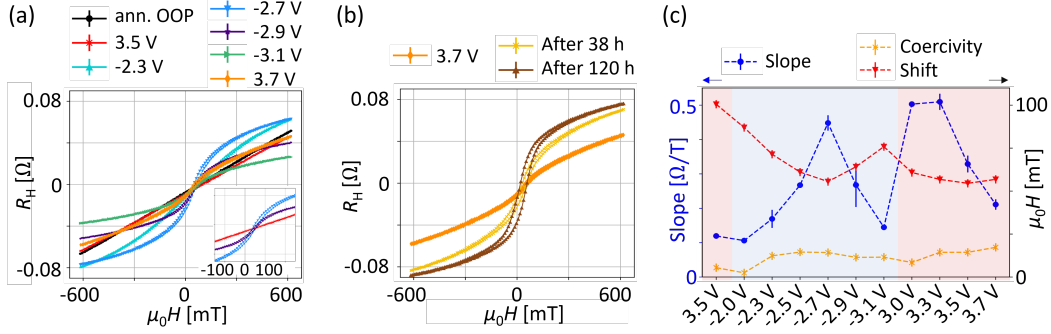


Figure 4.8: Evolution of magnetic properties by gating in the sample with 20 nm PtMn. (a) AHE curves from the first gating cycle. All gate voltages were applied for 2 min. (b) Time evolution of the AHE loop after the magnetization was brought back toward an IP state by applying 3.7 V. (c) Overview over slope, coercivity and EB shift of the AHE loops.

So far, we have shown that we can establish a stable OOP magnetization with OOP EB in a sample with initial IP magnetization by ionic-liquid gating. However, for applications, a much larger EB is required. Therefore, we also investigated a sample with thicker PtMn of 20 nm (Fig. 4.8). Equivalently to the stack with 8 nm PtMn, the magnetization of the sample is initially IP and stays IP after applying +3.5 V (Fig. 4.8 a). As expected, the AHE loop evolves toward a square-shaped magnetization loop by negative gating. Like in the sample with thinner PtMn, applying -2.9 V or larger negative voltages leads to overoxidation of the Co, expressed by a decrease in the total Hall resistance. However, the coercivity and the slope remain low for the applied gate voltages in the sample with thicker PtMn (Fig. 4.8 c). This changes only after performing the full first gating cycle and then waiting five days (Fig. 4.8 b). Most likely, this gives the oxygen ions time to diffuse into the energetically favored lattice positions where they can hybridize with the Co atoms, resulting in increased interfacial PMA. Presumably, this slower reorientation of the magnetization towards the OOP state, both after applying the accessible negative voltages as well as by waiting after overoxidation, is caused by a higher degree of crystallinity of Co. The Co is grown on thicker and therefore more crystalline PtMn and a higher degree of crystallinity is known to slow down oxygen diffusion [136]. This highlights the importance of the underlayer on the gating dynamics.

Just like in the thinner sample, the OOP state becomes energetically favorable as soon as it is reached once. A positive voltage initially brings the magnetization from the OOP state back toward an IP state, which, however, evolves back toward the OOP direction over time (Fig. 4.8 b). Notably, the EB shift stabilizes to a value above 50 mT in this sample, which is more than 5 times greater than in the thinner sample.

4.5 Analysis of induced oxidation

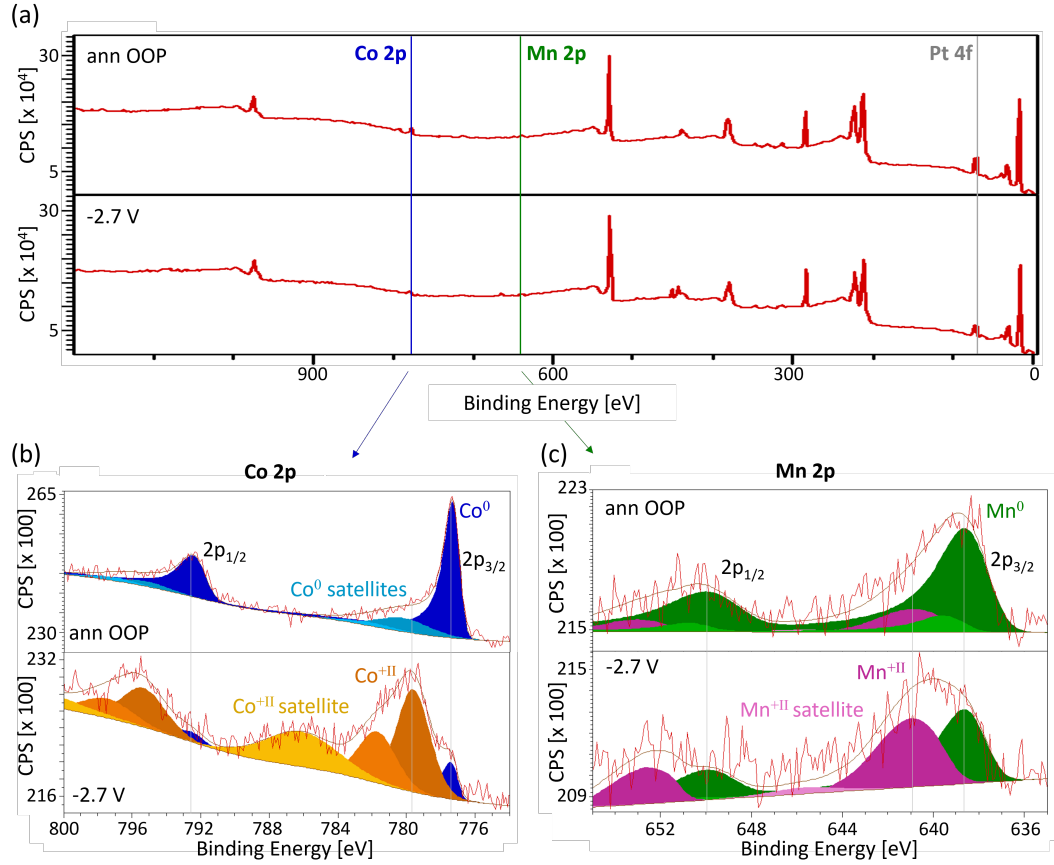


Figure 4.9: XPS spectra of the sample with 8nm PtMn, showing (a) the survey spectra encompassing the complete measured energy range, (b) the Co 2p-edge and (c) the Mn 2p-edge in the states after the annealing in an OOP magnetic field and after applying -2.7 V for 5 min, respectively. The Co^{+II} and Mn⁰ peaks show a multiplet splitting. The Pt 4f peak was used for the charge compensation.

To verify whether the magnetic changes are caused by an oxidation of Co, we performed X-ray photoelectron spectroscopy (XPS) measurements. Fig. 4.9 b shows the XPS spectra at the Co 2p-edge in the annealed state (top) and after applying a gate voltage of -2.7 V (bottom). The annealed state shows pure metallic Co⁰ (blue peaks). By gating, a clear Co^{+II} signal arises (orange peaks), confirming the partial oxidation of the Co. From SQUID measurements we know that for the oxidized sample, around half of the magnetization is lost in the oxidized state. The strong reduction of the Co⁰ peak intensity in the oxidized sample is most likely due to the surface sensitivity of XPS, indicating a stronger oxidation in the upper layers of the Co compared to the lower ones.

Understanding the oxidation of the interface between Co and PtMn is very important to retain a strong EB. Therefore, its oxidation was probed by measuring XPS at the Mn 2p-edge (Fig. 4.9 c). Overall, the signal-to-noise ratio is worse, since the Mn atoms are lying further down below the sample surface. In the annealed state, the sample consists mainly of metallic Mn⁰ (green peaks). However, after applying the negative gate voltage, also the Mn shows a clear signal of oxidation (magenta peaks). Some oxygen therefore reached the

PtMn/Co interface. This is likely the reason why the EB initially drops with negative gating. However, the AHE data revealed that the EB stabilizes at a value larger than zero. This indicates that the interface does not fully get oxidized or that this oxidation does not break the exchange coupling completely. Additionally, the thinning of the Co layer by oxidation reduces the Zeeman energy and consequently leads to a relative increase in the exchange bias field. Overall, this allows for the retention of a significant EB.

4.6 Conclusion

In summary, we achieved the stabilization of a magnetic state with OOP magnetization and OOP EB in a sample with initial IP magnetization by ionic liquid gating. In the stack Ta (5 nm)/Pt (3 nm)/PtMn (8 nm)/Co (0.9 nm)/HfO₂ (3 nm), we showed that by applying a gate voltage of -2.7 V the magnetization could be reoriented to OOP, with an exchange bias shift of (8.2 ± 2.4) mT. SQUID and XPS measurements confirmed that the changes are due to oxygen migration in the sample. As the oxygen ions reach the Co/HfO₂ interface, the interfacial anisotropy increases, causing the reorientation of the magnetization toward the OOP direction. [This reorientation cannot be achieved purely by reducing the demagnetization energy.] At large negative voltages of more than -2.7 V both the demagnetization energy and the interfacial anisotropy energy decrease due to overoxidation of the Co. Subsequent positive voltages lead to a reorientation of the magnetization back toward the initial IP state. However, this state is volatile and evolves back toward the OOP state over time, demonstrating that the OOP state becomes the energetically favorable state once it is reached. Some of the oxygen ions also reach the bottom interface of the Co after negative gating, visible in a partial oxidation of the Mn atoms in PtMn. Notably, this oxidation does not lead to a loss of EB, just to an initial reduction of EB which then saturates.

The sample with the thicker PtMn film of 20 nm exhibits a slower gating dynamics in the accessible voltage window, highlighting the importance of the PtMn/Co interface on the gating process. Notably, in the final state, we found fully shifted magnetization loops with a strong EB of more than 50 mT.

These results contribute to the advancement of easier and better device fabrication for energy-efficient data storage and processing as well as sensor applications.

Controlling the EB with fixed PMA

5.1 Introduction

In the previous chapter, I demonstrated that the magnetic anisotropy can be manipulated by IL gating while maintaining the EB. For other applications it would be desirable to manipulate the EB while maintaining the PMA.

A successful control of the magnitude of the EB was already demonstrated in different FM metals in contact with an AFM. Zehner et al. demonstrated in Fe/IrMn that the manipulation of the thickness of the FM by partial oxidation allows for a control of the EB [43]. Several groups worked on the control of EB in NiCo systems. Gilbert et al. as well as Murray et al. showed that the reduction of AFM $\text{Ni}_{1-x}\text{Co}_x\text{O}$ to ferromagnetic NiCo induced the formation of EB after field cooling [137, 138]. Zhou et al. presented the inverse direction by oxidizing Ni/Co and demonstrating the appearance of tunable EB below 200 K [139].

Additionally to these effects based on the control of oxide layer formation or reduction, it was shown that the EB can be manipulated by intercalation of ions into the AFM and accumulation at the FM/AFM interface. Using lithium ions, Mustafa et al. presented the control of EB in Co/Co₃O₄ by inducing a reversible spin disorder in the AFM Co₃O₄ [132]. For oxygen ions, it was demonstrated by Wang et al. in IrMn/Pt/Co that the oxygen ions can be moved through the IrMn toward the Co interface for IrMn layers with a thickness of up to 5 nm. Thereby, the effects are significantly smaller at 5 compared to 3 nm IrMn. Due to the small thickness of the IrMn layer, the EB could, however, only be established at temperatures significantly below room temperature [39].

Here, I aimed to control the EB in Co/PtMn at room temperature using oxygen ions. To apply the electric fields, I used IL gating. In contrast to solid state gating, e.g. in the case of lithium ions, only an oxygen conducting capping layer is required to use my setup. For gating with lithium ions, the lithium donor layer is typically grown below the functional magnetic layers to allow for high quality growth of the lithium donor layer [38, 132]. This can, however, pose challenges for a high quality growth of the functional magnetic layers on top. Therefore, it can be advantageous to use IL gating for the control of EB at room temperature, as done here.

The samples for this chapter were grown by Maria-Andromachi Syskaki in an industrial Singulus Rotaris magnetron sputtering chamber at room temperature. All experiments, including the annealing, IL gating and AHE measurements, were performed and analyzed by myself. I also wrote all text and made all figures.

5.2 Investigated material system

As in the previous chapter, I used a bilayer of Co and PtMn. To manipulate the EB instead of the anisotropy, it is now required that the EB is set at the upper interface of the Co and the PMA at its bottom interface. Therefore, the Co was grown on top of Pt, which allows for a strong PMA. The PtMn, setting the EB, was grown on top of the Co and the stack was capped again with HfO_2 (Fig. 5.1 a). For the first sample, identical film thicknesses were used as for the samples from the previous chapter with 8 nm PtMn (Fig. 5.1 a). The first measurements, however, showed that it is very difficult to move enough oxygen through the PtMn layer. Therefore, thinner PtMn films were grown with PtMn thicknesses of $t = 2, 4$ and 6 nm (Fig. 5.1 b). For these samples, the HfO_2 film thickness was reduced to 2 nm to allow for larger electric fields at the same applied voltages. Additionally, the Pt thickness was reduced to 2 nm to allow for a smoother growth of the Co.

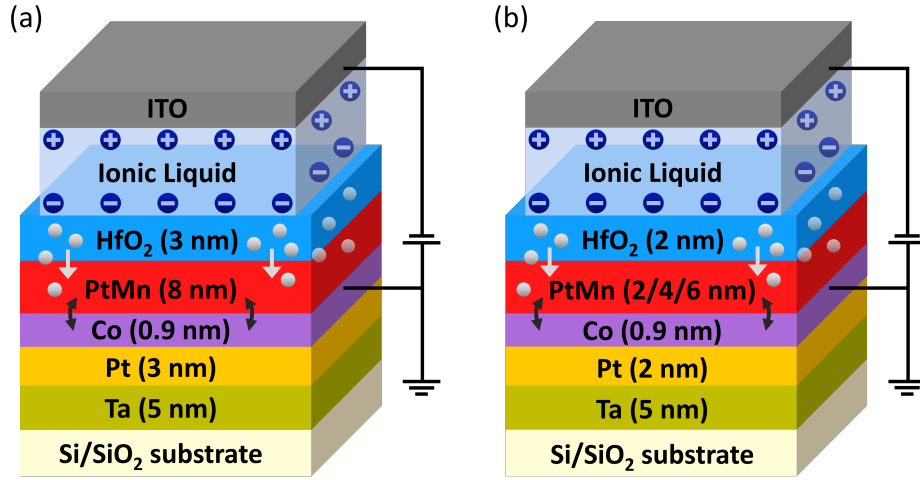


Figure 5.1: Sample stack with PtMn grown on top of Co for the samples with (a) 8 nm PtMn and (b) 2 to 6 nm PtMn. The white spheres represent the oxygen ion species which can be moved by applying a gate voltage across the HfO_2 . The arrow between the Co and the PtMn represents the EB coupling between the two layers.

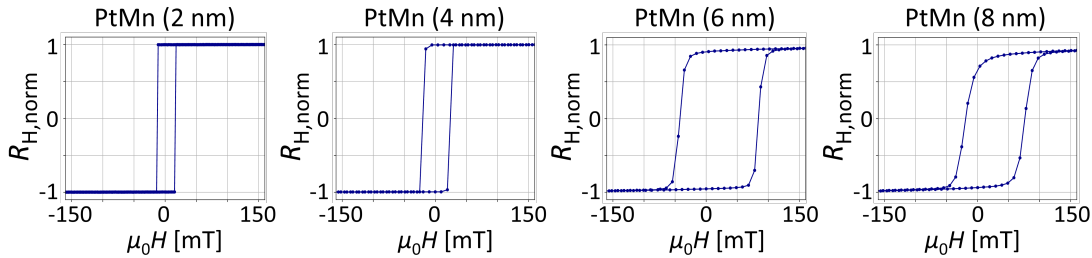


Figure 5.2: Magnetization loops showing the evolution of the EB as a function of the PtMn thickness. All samples were annealed in an OOP magnetic field of 800 mT at 300 °C for 2 h. The loops were measured via the AHE and then normalized.

To establish the EB, I annealed the samples in an OOP magnetic field of 800 mT at 300 °C for 2 h. The resulting magnetization loops are shown in Figure 5.2. All samples show a square-shaped magnetization loop demonstrating strong PMA. The samples with 2 and 4 nm PtMn show no clear EB. However, the sample with 6 nm PtMn shows an EB of 21 ± 2 mT. The sample with 8 nm PtMn even exhibits an EB of 29 ± 2 mT. Therefore, out of these samples, the one with 6 nm PtMn is the sample with the thinnest PtMn layer which still has a significant EB. To maximize the amount of oxygen which reaches the Co/PtMn interface at a given voltage, I therefore performed the IL gating experiments on this sample.

5.3 Controlling the EB

The sample with 6 nm PtMn was gated with increasingly negative gate voltages. Each gate voltage was applied for 2 minutes. The magnetization loops were measured via the AHE up to magnetic fields of 250 mT. At each magnetic field, approximately 7 data points were measured and averaged. The error bars show the standard deviation of the data. To obtain the data without the linear contribution caused by the OHE, the corresponding slope was subtracted by fitting a straight line through the data in the range between 150 and 250 mT. Figure 5.3 shows the results of the IL gating experiment. The magnetization loops stay clearly OOP during all gating steps (Fig. 5.3 a). The close-up views in Figures 5.3 b and d depict the changes due to the gating.

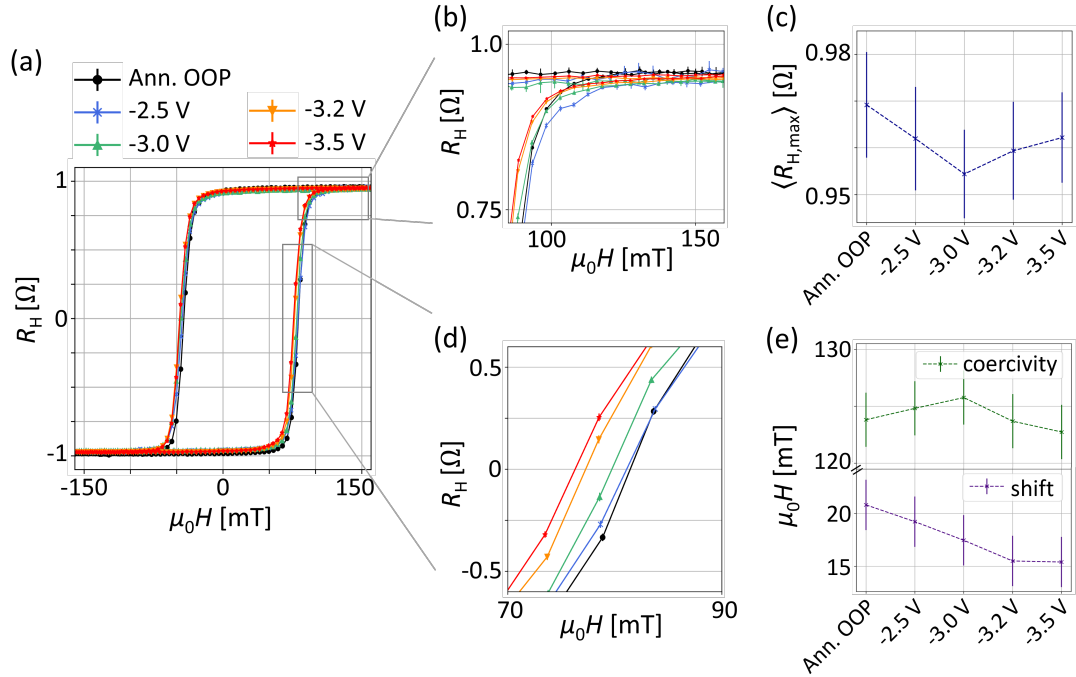


Figure 5.3: Influence of the IL gating on the magnetic properties of the sample with 6 nm PtMn. (a) Magnetization loops as a function of the applied gate voltage. (b) Zoom into the magnetization loops at maximum Hall resistances. (c) Change in the average maximum Hall resistance as a function of the applied gate voltage. (d) Zoom into the magnetization loops in the switching regime at positive magnetic fields. (e) Change of coercivity and shift as a function of the applied gate voltage.

The average maximum Hall resistance $\langle R_{H,\max} \rangle$, plotted in Figure 5.3 c, is a measure of the saturation magnetization. It was determined from the magnetization loops by calculating the weighted average of all Hall resistance values measured between 150 and 250 mT, as well as between -150 and -250 mT. The error bars show the standard deviation. During negative gating, $\langle R_{H,\max} \rangle$ seems to first decrease and then increase slightly. However, inside the error bar $\langle R_{H,\max} \rangle$ remains constant throughout the gating. Thus, only a negligible fraction of the Co got oxidized.

For the coercivity and shift, plotted in Figure 5.3 e, the error bars give the systematic error on the magnetic field which was estimated to be 2.4 mT (see Chapter 3.7.4). The coercivities show a similar trend as the average maximum Hall resistance. Also here, the relative change is only small, in this case 2 % of the coercivity. In contrast, the EB shift decreases steadily from 21 ± 2 mT to 15 ± 2 mT, by 29 %, with increasingly negative gate voltage (Fig. 5.3 c). Since the error bars denote systematical errors, this decrease in EB is not due to fluctuations but reveals a significant change. Time evolution experiments showed that the EB shift does not recover over time but remains in the diminished state. This demonstrates that oxygen ions reach the Co/PtMn interface and affect the exchange coupling.

5.4 Influence of post-annealing

Figure 5.4 reveals the effect of post-annealing the gated sample. Figure 5.4 a shows the magnetization loop after the post-annealing (blue) in comparison to two previous loops: the initial loop before the IL gating (black), for which the sample was annealed at the same conditions as during the post-annealing, as well as the loop in the state right before the post-annealing (after -3.5 V gate voltage for 10 min, red). The magnetization loop after the post-annealing still shows the square shape corresponding to OOP magnetization. However, the coercivity is significantly increased. Interestingly, the magnetization loop has a kink around -45 mT, indicating that it is the superposition of two loops. The hypothesis was, that the two loops correspond to the gated and ungated region of the sample (Fig. 5.4 b). Both regions contribute to the signal, as the wirebonds must be placed outside of the IL during gating experiments and were positioned at the same locations after post-annealing. In my gating experiments, I consistently placed the wirebonds close to the ITO to minimize the area of the ungated region. Consequently, the ungated region contributes less magnetic material, resulting in a magnetization loop with a smaller amplitude. This leads to the assignment of the loops as indicated by the orange (ungated region) and pink (gated region) dotted circles in Figure 5.4 a. Similar effects were observed previously in other magnetic systems [39, 140].

To verify that the same effect is observed here, I repeated the measurement of the sample in the post-annealed state with wirebonds placed inside the gated region. In that way, the magnetization loop of only the gated region could be measured. Figure 5.4 c shows this magnetization loop (pink) in comparison to the magnetization loop of the full sample as plotted in (a). The magnetization loop of the gated region does not show the kink, confirming the hypothesis that the full loop is the superposition of the loops of the gated and ungated region. As proposed, the magnetization loop corresponding to the ungated region has the lower coercivity and therefore switches first at negative fields. The reason for the larger coercivity of the gated region could be the additional oxygen ions which form extra pinning sites.

Notably, at the positive magnetic field side of the magnetization loop, only a very small kink is visible. This indicates a larger EB of the ungated region after the second annealing compared to the gated region. In this case, the additional shift due to the larger EB in the ungated region could lead to a similar switching field compared to the gated region which has the larger coercivity. If the EB in the ungated region gets larger after the post-annealing compared to the gated region, this implies that likely part of the oxygen ions remained at the Co/PtMn interface.

It should be noted that the superposition of the magnetization loops inside and outside of

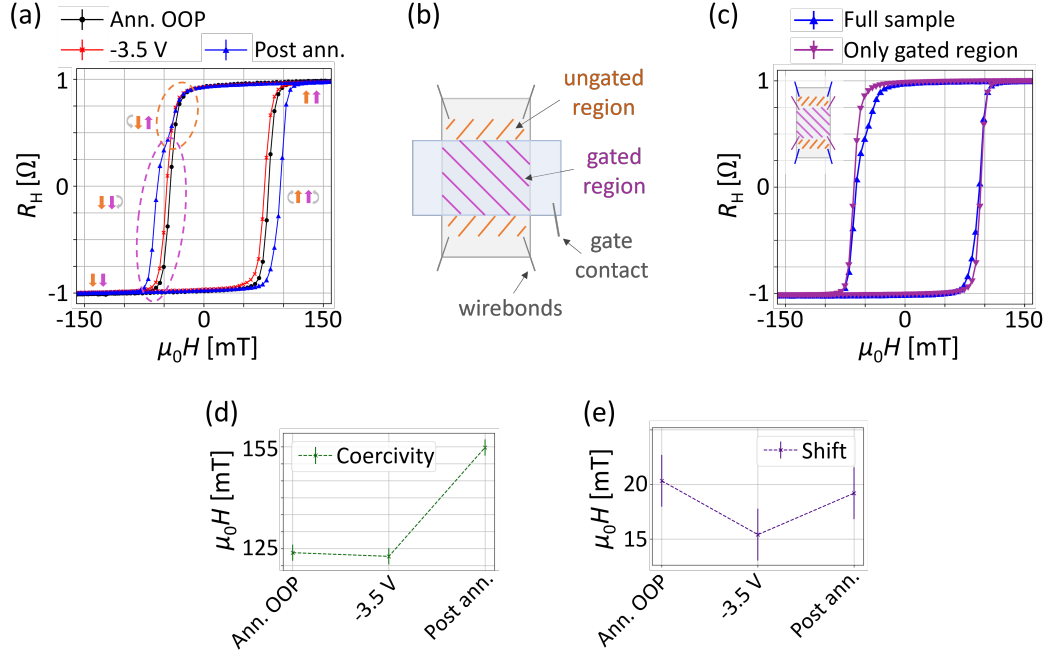


Figure 5.4: Influence of post-annealing the sample with 6 nm PtMn in an OOP magnetic field of 800 mT at 300 °C for 2 h after IL gating up to -3.5 V. (a) Magnetization loop after post-annealing in comparison to the gated state right before the post-annealing as well as to the initial state before the gating, which was annealed with the same settings. The orange and pink dotted lines indicate that the magnetization loop is the superposition of two hysteresis loops with two different coercivities. The arrows depict the two total magnetic moments corresponding to the two hysteresis loops. (b) Sketch of the sample (grey) with the IL and glass plate on top (light blue) and the electric contacts (wirebonds on the sample and gate contact on the ITO). Only the region below the glass plate (shaded in pink) is gated. The region between the edge of the glass plate and the electric contacts (shaded in orange) is also measured during the AHE measurements but was not gated. Sketch inspired by [140]. (c) Magnetization loop in the post-annealed state of the full sample (blue) and of only the gated region (purple). The inset shows the positions of the wirebonds, where the color of the wirebonds correspond to the magnetization loop in the same color. (d)–(e) Change of coercivity and EB shift for the three gating states, determined inside the gated region.

the gated region were not observed in the previous chapter, in which the as deposited samples showed in-plane magnetization. For samples with initially in-plane magnetization, the ungated region does not contribute additional signal in the measured AHE magnetization loops, which are only sensitive to OOP magnetization.

A remaining open question is why the magnetization loop after applying a gate voltage of -3.5 V does not exhibit a kink like after the post-annealing. This observation suggest that during IL gating the EB is modified throughout the entire sample region between the electrical contacts. To understand this differing behavior during IL gating compared to post-annealing, more experiments are required. This was not feasible within the scope of this thesis.

The change of the shift and coercivity in the gated region due to the post-annealing are presented in Figure 5.4 c. The coercivity increases significantly by approximately 25%. The

EB shift recovers almost to the value before the IL gating. Consequently, either only a small fraction of the oxygen at the Co/PtMn interface outlasts the post-annealing or the EB coupling can be established again despite the oxygen ions at the interface.

5.5 Summary and conclusion

Overall, I showed that the EB coupling can be manipulated by IL gating without losing the OOP anisotropy. For the sample stack Si/ SiO₂/ Ta (5 nm)/ Pt (2 nm)/ Co (0.9 nm)/ PtMn (6 nm)/ HfO₂ (2 nm), I demonstrated that oxygen ions can penetrate the 6 nm PtMn film and reach the Co/PtMn interface. This is notable because PtMn is a conductive layer and thus screens the applied electric field. By applying -3.5 V gate voltage, the EB shift can be diminished by almost 30 %. By post-annealing the sample in an OOP magnetic field of 800 mT in 300 °C for 2 h, the EB shift could be almost fully recovered. The AHE curves show the superposition of the magnetization loops inside and outside the gated region. Thereby, they also revealed that the EB in the ungated region is slightly larger compared to the gated region, indicating that some oxygen remained at the Co/PtMn interface after post-annealing.

To optimize these results further, a better understanding of the oxygen distribution inside the stack and the influence of the IL gating on the oxygen distribution is required. This will be discussed in the next chapter.

Understanding IL gating induced oxygen migration

6.1 Introduction

In the following section, all text marked with a line at the left is reprinted from [141]:

B. Bednarz and M. Wortmann et al.
“Depth Profiling of Oxygen Migration in Ta/HfO₂ Stacks During
Ionic Liquid Gating”
ACS Appl. Mater. Interfaces **18**, 6200–6209 (2026).

The paper is published under a Creative Commons CC-BY 4.0 license. The text is reprinted here literally according to the submitted version, except for the numbering of the citations. I wrote the initial draft of the paper, including the text which is reprinted here, and also incorporated all feedback for these paragraphs.

The oxidation of materials is one of the very early research fields. Initially, the process of oxidation was only known from the combustion of metals in air. Lavoisier found that such a combustion yielded an acidic product which was heavier than the initial metal [142]. He concluded that the metal must be reacting with something in the air. In the late 1770s he coined the name “oxygen”, derived from Greek meaning “acid former”, for the part of the air which was responsible for the combustion [142, 143]. In the following centuries, the knowledge of oxidation evolved further, following the discovery, that not all acids contain oxygen [143]. It was found that also other substances like halogen atoms can cause reactions very similar to the one with oxygen [144]. Nowadays, oxidation is described as the process of electron transfer from the material which gets oxidized to the oxidizing agent which gets reduced thereby [144].

For metals, their tendency to oxidize is given by the standard electrode potential [145]. The potentials represent that metals are more likely to get oxidized the less noble they are. The standard electrode potentials are determined by measuring the potential difference between the metal and a standard hydrogen electrode, when both are placed inside an electrolyte in a galvanic cell setup.

How far oxygen ions can penetrate into the metal depends on the temperature and the properties of the formed oxide [146]. Only if the oxide forms a stable, continuous layer with low ion conductivity, it can be passivating [147]. If it e.g. forms a porous layer or flakes off, the corrosion of the metal continues.

The process, how natural oxide layers are formed in the vicinity of oxygen, can be described by the Cabrera-Mott model [146]. Cabrera and Mott observed that at low enough temperatures

most metals show an initially very rapid formation of an oxide layer. This growth, however, becomes very slow or ceases completely when an oxide thickness of usually a few nm is reached. They proposed that when oxygen ions adsorb on the surface of a metal and oxidize the neighboring metal ions, a voltage builds up across the interface. This voltage persists for thin oxide films due to tunneling of the electrons from metal through the oxide to the adsorbed oxygen ions. The resulting electric field was suggested to pull the metal cations through the oxide. This causes an exponentially decaying growth rate of the oxide with increasing oxide thickness. After this initial phase, they describe several possible growth pathways, depending on temperature, oxide-layer thickness, and the ion and electron conductivity of the oxide [146].

Ionic liquids (ILs) are well-known for their unique combination of high electrochemical capacitance, usually low toxicity, negligible volatility, and broad thermal stability range [108]. Their use in ionic gating enables the application of extremely large electric fields (10–100 MV/cm) [36], far exceeding the dielectric breakdown limits of conventional SiO₂-based metal–oxide–semiconductor field-effect transistors (MOSFETs) [36]. These strong electric fields allow for field-driven ion motion, enabling reversible tuning of electronic, magnetic, optical, and structural properties [36, 123, 148, 149, 150]. In this regard, IL gating complements solid-state gating [38, 151, 152], which typically requires comparatively thick dielectric layers to ensure electric insulation. The electric double layer of an IL is only about 1 nm thick, which enables the large electric fields characteristic of IL gating [36]. Similarly to solid-state gating, IL gating has proven effective in controlling a wide range of magnetic interactions, including magnetic anisotropy [37, 82], exchange bias [39], Dzyaloshinskii–Moriya interaction [125], and Ruderman–Kittel–Kasuya–Yosida coupling [153]. This expanding toolbox of electric-field control over magnetic states opens possible pathways to ultra-low-power data storage, neuromorphic hardware, and spin-based sensors [21, 32, 33, 82, 121, 122].

Among various mobile species, oxygen ions are particularly attractive for magneto-ionic control due to their reactivity with a broad range of materials and the availability of multiple oxygen donor layers. Despite the widespread use of voltage-induced oxygen migration in functional magnetic stacks, the spatial profile of oxygen incorporation remains unknown. This is critical because the penetration depth, concentration profile, and sharpness of the resulting oxide/metal interface influence bulk magnetic and electronic properties through changes in oxidation state or chemical composition [82]. The oxygen depth profile might also affect adjacent functional layers in ultrathin or multilayer architectures. For instance, in exchange bias systems or synthetic antiferromagnets, magnetic properties are set at buried interfaces. Information on the oxygen penetration depth is essential for determining the optimal thickness of layers above the critical interface to either modulate or protect the interface. Additionally, recent work has shown that introducing a thin tantalum (Ta) insertion layer below the IL can significantly enhance the cyclability of oxide-based magneto-ionic devices [154], suggesting that the oxygen incorporation profile in such layers may play a key role in device stability and performance. However, it is neither known which amount of oxygen ions penetrates far down into the material and how the oxygen profile looks after IL gating, nor which process underlies the migration. A more detailed understanding of the oxygen distribution is therefore key to enabling precise and stable control in magneto-ionic systems.

In this chapter, the oxidation of metals upon the application of an external electric field will be investigated. To characterize the oxidation states, as well as the oxide penetration depth and profile, XPS and XRR were used. To allow for a high quality data analysis, the XPS analysis was evolved and refined during this thesis. In the following section, these advances will be described, including an error discussion of the refined XPS method in comparison to standard XPS analysis. In the subsequent section, the resulting oxide depth profiles in a Ta thin film capped with HfO₂ will be discussed as a function of IL gate voltage and HfO₂ thickness.

6.2 Advances in XPS depth profiling

XPS allows for a determination of composition and chemical state of materials and is therefore commonly used for surface analysis [88]. Depth profiling using XPS can be performed via surface ablation using ion etching, which can, however, induce significant intermixing and roughening, or via angle- or energy-resolved XPS [155]. In this thesis, I contributed to refining an analysis method which combines angle- and energy-resolved XPS. The method is based on the multiple energies approach which was developed previously by M. Wortmann et al. [95, 97]. In this approach several XPS core-level spectra get analyzed. The proposed analysis method assumes a metal covered by its corresponding oxide with a continuous interface in between of the form of an error function (see Chapter 3.3). The corresponding equation to obtain the average oxide layer thickness d and interface width σ is, according to reference [95]:

$$\frac{I_{\text{ox}}}{I_{\text{met}}} = \frac{N_{\text{ox}}}{N_{\text{met}}} \frac{\text{erfc}\left(-\frac{d}{\sqrt{2}\sigma}\right) - \text{erfc}\left(\frac{\sigma}{\sqrt{2}\lambda_{\text{av}} \cos \theta} - \frac{d}{\sqrt{2}\sigma}\right) \exp\left(\frac{\sigma^2}{2(\lambda_{\text{av}} \cos \theta)^2} - \frac{d}{\lambda_{\text{av}} \cos \theta}\right)}{\text{erfc}\left(\frac{d}{\sqrt{2}\sigma}\right) + \text{erfc}\left(\frac{\sigma}{\sqrt{2}\lambda_{\text{av}} \cos \theta} - \frac{d}{\sqrt{2}\sigma}\right) \exp\left(\frac{\sigma^2}{2(\lambda_{\text{av}} \cos \theta)^2} - \frac{d}{\lambda_{\text{av}} \cos \theta}\right)} \quad (6.1)$$

Thereby, I_{ox} and I_{met} are the peak intensities of the oxide and metal peak, N_{ox} and N_{met} are the number densities of the oxide and metal and λ_{av} is the IMFP average between oxide and metal layer. The measure k for the interface width from [95] was substituted here by $k = 1/(\sqrt{2}\sigma)$ with the interface roughness σ in nm which is defined equivalently as in XRR (see Chapter 3.3).

This equation gives reliable results, if the IMFPs of oxide and metal are similar and elastic scattering plays a negligible role. This was, however, not the case for the samples investigated in this thesis. Therefore, we refined the model by using the EAL L instead of the IMFP λ , thereby accounting for elastic scattering. For this purpose, I performed a literature study to determine how to implement the EAL. Since the oxidized overlayer is not a pure element, a method applicable to composite materials was required. Therefore, we chose the universal curve proposed by Seah, denoted as S3 [156]:

$$L = \frac{(5.8 + 0.0041 \cdot Z^{1.7} + 0.088 \cdot E_{\text{kin}}^{0.93}) a^{1.82}}{Z^{0.38}(1 - 0.02 \cdot E_g)} \quad (6.2)$$

It is defined for binary compounds $G_g H_h$ of the elements G and H with stoichiometry coefficients g and h . To apply the equation to pure elements either g or h has to be set to zero and the other one to one. Using this notation, Z denotes the average atomic number, given by the weighted average of the atomic numbers Z_g and Z_h of the elements G and H (Eq. 6.3). E_{kin} is the kinetic energy of the photoelectrons and E_g the band gap. a is defined as the thickness per monolayer, calculated from the total molecular weight M of the compound, its mass density ρ and the Avogadro constant N_A (Eq. 6.4). To obtain L in nm, also a has to be inserted in nm and E_{kin} and E_g in eV.

$$Z = \frac{gZ_g + hZ_h}{g + h} \quad (6.3)$$

$$a = \sqrt[3]{\frac{M}{\rho N_A (g + h)}} \quad (6.4)$$

Equation 6.2 was derived empirically by Seah with the goal to establish a universal curve applicable to non-stoichiometric compounds for which the parameters required in other equation for the EAL are not available. He derived the equation by examining from experimental

data which material parameters play an important role. These parameters were included into the equation with initially unknown exponents [157]. The resulting equation was fitted to experimental data for elements, inorganic and organic compounds in the energy range between 100 and 30 000 eV to obtain the exponents. He found the resulting root mean square deviation between the final equation and the experimental data to be 8 % [156].

Important to consider is that Equation 6.2 was derived for the case of an emission angle of 45°. However, in the range up to 65°, the EAL can be assumed to be almost constant, while it starts to increase significantly at higher emission angles [98]. Therefore, Equation 6.2 only holds for emission angles up to 65°.

In the revised version of Equation 6.1, we included the EAL for oxide (L_{ox}) and metal (L_{met}) separately without averaging. The corresponding integrals were solved by the mathematician Klaus Viertel. Details on the integrals which had to be solved can be found in Chapter 3.3. The resulting expression is given by Equation 6.5 and was published in the paper by M. Wortmann and B. Bednarz et al. [97]:

$$\frac{I_{\text{ox}}}{I_{\text{met}}} = \frac{N_{\text{ox}}L_{\text{ox}}}{N_{\text{met}}L_{\text{met}}} \exp\left(\frac{d}{L_{\text{ox}} \cos \theta} - \frac{d}{L_{\text{met}} \cos \theta}\right) \cdot \frac{\operatorname{erfc}\left(-\frac{d}{\sqrt{2}\sigma}\right) - \operatorname{erfc}\left(\frac{\sigma}{\sqrt{2}L_{\text{ox}} \cos \theta} - \frac{d}{\sqrt{2}\sigma}\right) \exp\left(\frac{\sigma^2}{2(L_{\text{ox}} \cos \theta)^2} - \frac{d}{L_{\text{ox}} \cos \theta}\right)}{\operatorname{erfc}\left(\frac{d}{\sqrt{2}\sigma}\right) + \operatorname{erfc}\left(\frac{\sigma}{\sqrt{2}L_{\text{met}} \cos \theta} - \frac{d}{\sqrt{2}\sigma}\right) \exp\left(\frac{\sigma^2}{2(L_{\text{met}} \cos \theta)^2} - \frac{d}{L_{\text{met}} \cos \theta}\right)} \quad (6.5)$$

This equation is a function of the emission angle θ and the two EALs L_{ox} and L_{met} which are binding energy dependent and therefore change when analyzing multiple emission peaks. When performing an angle and energy dependent analysis, as done in this thesis, the equation therefore has to be fitted as a function of three variables to obtain the fit parameters d and σ . Since the previously used analysis procedure in Origin was limited to two-dimensional equations with only two variables (θ and λ_{av}) and could not be easily extended, I developed a new analysis software using Python.

The new method, to use Equation 6.5 with the unaveraged EALs and fit it using several emission angles as well as emission peaks, allows to significantly reduce the uncertainty of the obtained values for d and σ . In the following, the remaining uncertainties and the improvement compared to previous methods will be discussed for the example of SnTe with an SnO overlayer. More details on this material system can be found in the paper by M. Wortmann and B. Bednarz et al. [97].

6.2.1 Improvements in uncertainty

In the following section, all text, figures and equations marked with a line at their left are reprinted from [97]:

M. Wortmann and B. Bednarz et al.

“Oxidation state depth profiling by self-consistent fitting of all emission peaks in the X-ray photoelectron spectrum of SnTe”

Appl. Surf. Sci. **713**, 164356 (2025).

The paper is published under a Creative Commons CC-BY 4.0 license. The text, figures and equations marked with a solid line are reprinted here literally according to the submitted version, except for the numbering of the figures, equations, citations and cross-references. Modifications to the cited text are indicated by square brackets. Figures with a dotted line are modified

compared to the submitted and published version. The details of the modification can be found in Appendix A.

In the following reprinted paragraphs, I calculated the uncertainties of the EALs L , number densities N , as well as the uncertainty caused by fitting with Equation 6.5. In particular, all data shown in Figure 6.1 was calculated by me. The final layout of the figure was created by M. Wortmann. The uncertainty on the peak fitting was determined from the joint fitting experience by Martin Wortmann and me. The text was co-written by Martin Wortmann and me and revised by all co-authors.

There are multiple sources of uncertainty u_n contributing to the combined standard uncertainties $u_{c,d}$ and $u_{c,\sigma} = \sqrt{\sum_n (u_n)^2}$ of the parameters d and σ . Given the correctness of the underlying model assumptions (i.e., a smooth, continuous, and homogeneous overlayer with a symmetric concentration gradient at the metal-oxide-interface), the most significant sources of uncertainty are: i) the peak fitting, ii) the EALs, iii) the atomic number densities, and iv) the fit uncertainty of the model (e.g. Eq. 6.5). In the following, we simplify all uncertainties as symmetrically normal distributed. To assess the improvement of our model (using both Sn 3d and 4d), over standard single-energy ARXPS (only 3d), we quantify and compare the uncertainties for both approaches.

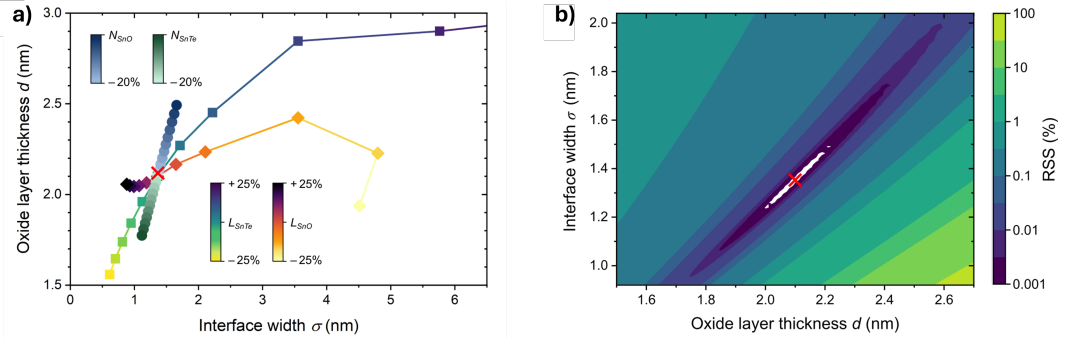


Figure 6.1: Uncertainties: (a) Fit parameters d and σ for $\pm 25\%$ variation of L_{SnO} and L_{SnTe} , and up to -20% variation of N_{SnO} and N_{SnTe} . The original values used in the modeling are marked with a red cross. The underlying fits are based only on the Sn 3d and Sn 4d intensity ratios. All input parameters have each been varied individually while keeping the other ones fixed at the original value. The values have been varied in steps of 5% for L and steps of 2% for N . (b) residual sum of squares (RSS) as a function of the fit parameters d and σ , calculated as the sum of squared differences between the weighted intensity ratios and the fit of Eq. 6.5 for Sn 3d and Sn 4d. The resulting RSS values were divided by their maximum and multiplied with 100 to get the RSS in $\%$. The original values used in the modeling are marked with a red cross. The white region indicates $\text{RSS} < 0.001\%$.

- i) The uncertainty of peak fitting is difficult to quantify, as it depends on the assumed background, line shapes, and the criteria for an acceptable goodness-of-fit. Fitting only a single energy region can result in substantial uncertainties, whereas using multiple energies and angles markedly reduces the overall ambiguity. In this work, based on extensive iterative fitting, we estimate the range of parameters reasonably compatible with the spectral data as $u_{i,d} = \pm 0.2 \text{ nm}$ and $u_{i,\sigma} = \pm 0.3 \text{ nm}$. For other materials, these values may differ, depending on factors such as the chemical shift between component peaks and the availability of reference data. Due to the interdependence of the 3d and 4d peak regions, the combined uncertainty is smaller than for either peak region

individually. When varying line shapes of Sn 3d [...] and applying the single energy ARXPS approach with Eq. 6.5, we estimate uncertainties of $u_{i,d} = \pm 0.3 \text{ nm}$ and $u_{i,\sigma} = \pm 0.5 \text{ nm}$. If a sharp interface is assumed (i.e., a step function), the error in σ equals the actual interface width.

- ii) Several material parameters of a real sample may deviate from nominal bulk values reported in the literature, affecting the calculation of the input parameters L_{SnTe} , L_{SnO} , N_{SnTe} , and N_{SnO} . Such parameters include bandgap, density, and the number of electrons contributing to scattering (often approximated by the number of valence electrons). As shown in Figure 6.1 a, we examined the fit parameters d and σ for $\pm 25\%$ variations in L_{SnTe} and L_{SnO} , roughly corresponding to the difference between the EAL and IMFP. The IMFP, however, neglects elastic scattering and is therefore not regarded as a reliable value. The results indicate that the fit is considerably more sensitive to changes in L_{SnTe} than in L_{SnO} . In general, substrate-layer properties (L_{SnTe}) are better defined than those of the oxide layer (L_{SnO}). The equation used to calculate the EAL (Eq. 6.2) shows a root-mean-square deviation of 8% compared with values from optical measurements [156], which we consider a reasonable estimate of the EAL uncertainty. This corresponds to a maximum combined uncertainty for the 3d and 4d peak regions of $u_{ii,d} = \pm 0.28 \text{ nm}$ and $u_{ii,\sigma} = \pm 0.64 \text{ nm}$. For single energy ARXPS, the uncertainty depends on the energy of the emission peak. The uncertainty is slightly larger for the 3d region and smaller for the 4d region, leading to approximately the same average uncertainty for ARXPS when using a single peak region. For both methods, the EAL increases at high emission angles due to elastic scattering; for $\theta > 60^\circ$, EAL values are generally considered unreliable [98].
- iii) We then examined d and σ for up to -20% variation in N_{SnTe} and N_{SnO} , both being proportional to the respective density. Positive variations from the nominal bulk values were not considered, as these appear highly unlikely. In the absence of direct density measurements, an uncertainty of up to 10% seems realistic in a thin film. When both layers deviate equally to lower values, the effect cancels out, because the parameters are affected equally and opposite. However, when considering that a density deviation is more likely to occur in the oxide layer, an uncertainty of up to 5% appears to be a reasonable estimate, corresponding to $u_{iii,d} = \pm 0.08 \text{ nm}$ and $u_{iii,\sigma} = \pm 0.06 \text{ nm}$. This uncertainty is independent of the peak region and therefore remains unchanged when considering only a single peak region.
- iv) The fit uncertainty of Eq. 6.5 is shown in Figure 6.1 b as the residual sum of squares (RSS). The RSS is generally very low because the set of intensity ratios was optimized to fit Eq. 6.5 [...]. However, there is a clear minimum in the RSS and the range of parameters resulting in a good fit (e.g. $\text{RSS} < 0.001\%$ above which the deviation between fit and data becomes apparent) is about $u_{iv,d} = \pm 0.2 \text{ nm}$ and $u_{iv,\sigma} = \pm 0.3 \text{ nm}$ for the combined fit of the 3d and 4d peak regions. This basically quantifies how unique a parametrization is for a given set of intensity ratios. Furthermore, the equipotential lines are almost linear, indicating a strong correlation between d and σ . The error becomes significantly smaller, if one of the two is known. For single energy ARXPS, in addition to the uncertainty caused by the correlation between d and σ , fewer data points contribute to the fit. When considering only one instead of two peak regions with a similar reliability of the peak fitting, the uncertainty on the fit using Eq. 6.5 increases by a factor of $\sqrt{2}$. Therefore, it can be estimated to be $u_{iv,d} = \pm 0.3 \text{ nm}$ and $u_{iv,\sigma} = \pm 0.4 \text{ nm}$.

We estimate a combined standard uncertainty of the multiple energy approach of $u_{c,d} = \pm 0.4 \text{ nm}$ for the overlayer thickness and $u_{c,\sigma} = \pm 0.8 \text{ nm}$ for the interface width [...]. When

applying Eq. 6.5 to ARXPS data using only a single peak region, the estimated uncertainties increase to approximately $u_{c,d} = \pm 0.5$ nm and $u_{c,\sigma} = \pm 0.9$ nm. The single energy approach therefore yields uncertainties that are 25 % higher for $u_{c,d}$ and 12.5 % higher for $u_{c,\sigma}$. When the interface distribution is simplified by a step function, which is often done, the error on σ is identical to the true value of σ (in the case of SnO/SnTe $u_{c,\sigma} = 1.4$ nm). However, the stated uncertainties are only estimates and may differ for other materials or samples. For example, the uncertainty in fitting spectral data may be less ambiguous for other materials, and will reduce as progress is made in understanding the XPS spectrum. Samples with well-defined overlayers can be used to improve peak fitting accuracy in general.

6.3 Depth profiling of oxygen migration during IL gating

In the following section, all text, figures and equations marked with a line at their left are reprinted from [141]:

B. Bednarz and M. Wortmann et al.
 “Depth Profiling of Oxygen Migration in Ta/HfO₂ Stacks During
 Ionic Liquid Gating”
 ACS Appl. Mater. Interfaces **18**, 6200–6209 (2026).

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This project was a collaboration combining the IL gating technique with the multiple-angle XPS analysis method. I developed it together with Martin Wortmann and Timo Kuschel. Thereby, I contributed the knowledge on the requirements for IL gating as well as the most compelling questions from a gating perspective. The samples were then grown by Fabian Kammerbauer. All IL gating experiments were performed by me, as were the XRR characterization and longitudinal resistance measurements. For the XPS analysis, the peak models were developed jointly by Martin Wortmann and me. All the peak fitting as well as the subsequent data analysis was performed by me. For the figures, I contributed the data and Martin Wortmann made the final images. The first draft of the manuscript was written by me.

In this study, we combine X-ray reflectivity (XRR) with angle- and energy-resolved X-ray photoelectron spectroscopy (XPS) to study the oxygen depth distribution in Ta as a function of the IL gate voltage in two systems with different hafnium oxide (HfO₂) capping layer thicknesses (see Fig. 6.2a). Ta was chosen as the investigated metal due to its very smooth growth, making it an ideal model system for the investigation of homogeneous metallic films. Because of this very smooth growth and its ductility and corrosion resistance, Ta is both a common seed layer as well as an important coating in a variety of applications [45, 46]. The Ta thickness was set to 15 nm to significantly exceed the XPS information depth, as approximately 95 % of the XPS signal originates from the upper 4.5 nm of the Ta layer (three times the effective attenuation length (EAL), see Appendix B.5). This ensures a clean signal without any influence of the substrate layer. HfO₂ was selected as a capping layer due to its high- κ dielectric properties and high oxygen ion mobility, making it a common component in IL gating stacks [118]. Oxygen ions were driven into the Ta layer by applying gate voltages between -1.0 and -3.0 V using IL gating.

More experimental details can be found in Appendix B.1.

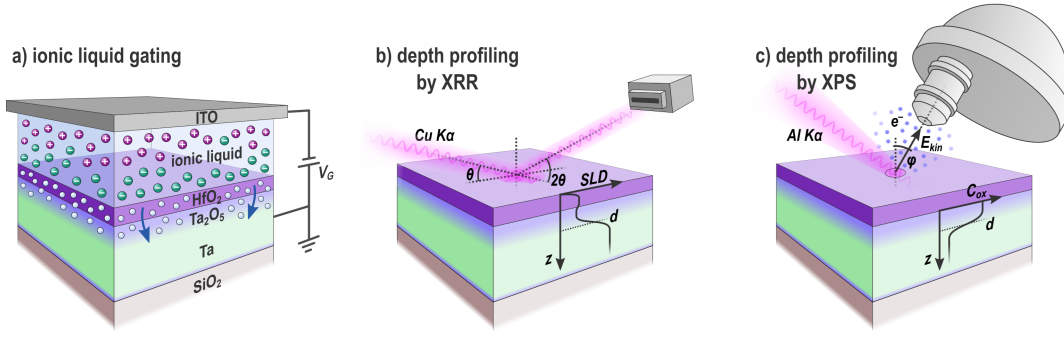


Figure 6.2: a) Schematic of the investigated material stack during IL gating. By applying a negative gate voltage (V_G) the IL is polarized and transmits the gate voltage to the sample. There, oxygen ions (white spheres) are pushed from the HfO_2 into the Ta layer, forming a Ta_2O_5 layer at the interface. (b) Sketch of the XRR setup. By shining X-rays at grazing angles onto the sample and measuring their reflection in a specular geometry, information on the average layer thickness and interface width of the different layers can be obtained. The quantity which defines the scattering is the scattering length density (SLD, see Appendix B.9 for more details). (c) Sketch of the XPS setup, in which the photoelectrons are detected as a function of their emission angle φ . From their kinetic energy E_{kin} , the binding energy of the respective element can be obtained, which provides information about the element and its oxidation state. By varying the investigated emission angle, the depth distribution from which the photoelectrons stem changes. Using this, a depth profile of the concentration of oxidized Ta atoms (C_{ox}) can be deduced.

To resolve the oxygen distribution within the Ta layer, we first carried out XRR measurements (Fig. 6.2b). The results for the samples with a 2 nm HfO_2 capping layer are shown in Figure 6.3. The XRR fits and corresponding scattering length density (SLD) graphs are exemplarily shown for the as-deposited state (Fig. 6.3a) and after 10 minutes of maximum gate voltage of -3 V (Fig. 6.3b). All other fits can be found in the supporting information (Appendix B.3). For the fit model, we considered the HfO_2 capping layer, an oxidized Ta_2O_5 layer, which is the only stable oxide of Ta [144], the metallic Ta layer, a thin bottom Ta_2O_5 layer between the Ta and the SiO_2 , as well as the SiO_2 substrate.

The SLD profiles of the samples depict a clear and only a few Å wide interface between the Ta and the upper, gating-induced Ta_2O_5 . The two oxide layers above the Ta (in the applied fit model Ta_2O_5 and HfO_2) cannot be clearly distinguished, as can be seen from the very broad transition in SLD between the two in the inset of Figure 6.3b. The reason is the very similar density and therefore similar SLD of Ta_2O_5 ($\rho = 8.2 \text{ g/cm}^3 \hat{=} \text{SLD} = 1.95 \text{ r}_e/\text{\AA}^3$) and HfO_2 ($\rho = 9.7 \text{ g/cm}^3 \hat{=} \text{SLD} = 2.27 \text{ r}_e/\text{\AA}^3$). For the same reason, additional intermediate TaO_x compositions cannot be excluded if their densities lie close enough to the densities of Ta_2O_5 and HfO_2 . However, the XPS spectra reveal no spectroscopically resolvable evidence for additional intermediate oxides, and a model including only the dominant oxidation states already provides an adequate description of the data as shown further below. While the presence of minor amounts of intermediate Ta oxides below the detection limit cannot be completely excluded, they would be energetically less favorable than Ta_2O_5 [144].

To disentangle the Ta_2O_5 and HfO_2 layer thicknesses, the HfO_2 thickness was fixed to its value in the as-deposited state for all further gating steps. This is a reasonable assumption as the HfO_2 layer shows no sign of an induced metallic phase after gating, as demonstrated by XPS (Figs. 6.5 and 6.6). The possible error on the Ta_2O_5 thickness, which is induced by this assumption, is included in its uncertainty (see Appendix B.2 for more information on the estimated uncertainties).

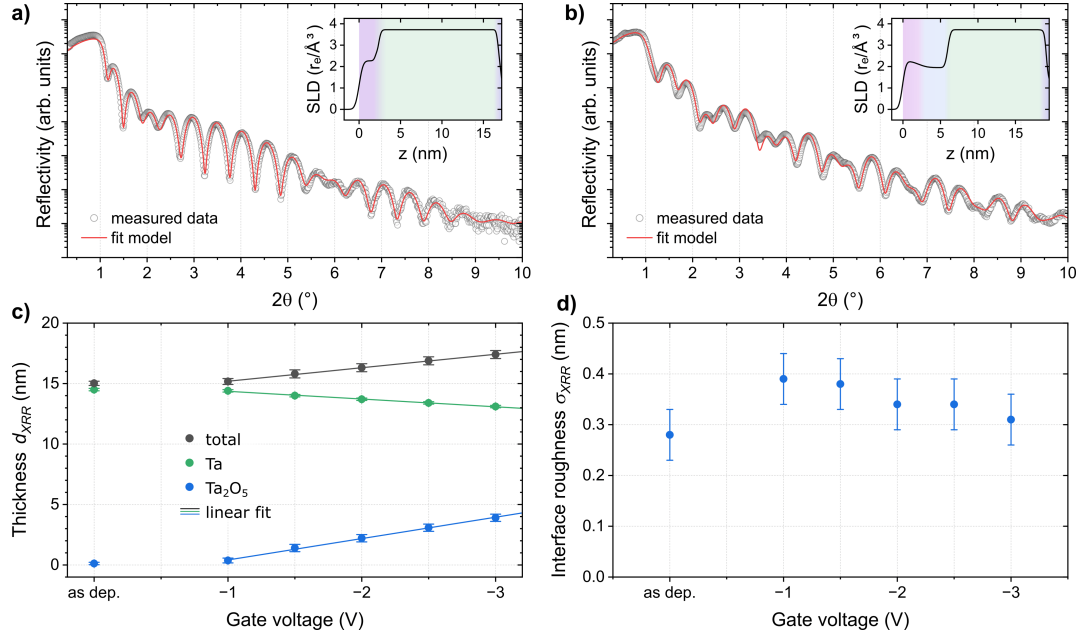


Figure 6.3: XRR analysis of the sample Si/ SiO₂/ Ta (15)/ HfO₂ (2) as a function of the applied gate voltage. (a), (b) XRR fits for the samples in the as-deposited state and after applying -3.0V for 10 min. The fit residuals are calculated as $\log(\text{model}) - \log(\text{data})$ and plotted on a linear scale below the graphs. The insets show the corresponding SLD profiles (starting from air with SLD = 0, to HfO₂ marked in purple, Ta₂O₅ in blue, Ta in green and the bottom Ta₂O₅ due to the interface with SiO₂ in blue again). (c) Evolution of the thicknesses of Ta, Ta₂O₅ and the total thickness (sum of Ta, Ta₂O₅ and the Ta₂O₅ below the Ta) as a function of the gate voltage, applied for 10 minutes each. (d) Interface width σ at the upper Ta₂O₅/Ta-interface. The XRR fits and SLD profiles at the other gate voltages, as well as details on the fits and all estimated uncertainties can be found in appendices B.2 and B.3.

Similarly, the thickness and interface width of the bottom Ta₂O₅ were fixed to the value obtained from the as-deposited state, assuming that the applied electric field is screened by the Ta layer and does not influence the bottom Ta₂O₅ layer. In the following, Ta₂O₅ will therefore always refer to the upper Ta₂O₅ layer induced by the IL gating.

Figure 6.3c shows the change of thickness of the upper Ta₂O₅ layer, the metallic Ta, as well as the total thickness of the Ta layers, including the metallic Ta and the Ta₂O₅ layers above and below, as a function of the applied gate voltage. A threshold voltage of approximately -1.0 V is required to oxidize Ta. Above this voltage, the average Ta₂O₅ thickness increases linearly with the applied gate voltage, as expected [158], reaching a thickness of (3.9 ± 0.3) nm after -3.0 V gating. In parallel, the Ta thickness reduces from (14.5 ± 0.1) to (13.1 ± 0.1) nm. This is notably less compared to the increase in the Ta₂O₅ thickness. The reason is the significantly lower mass density of Ta₂O₅ compared to metallic Ta. The total thickness therefore increases.

Figure 6.3d presents the evolution of the interface width at the upper Ta₂O₅/Ta interface with increasing gate voltage. In XRR simulations, the interface width corresponds to the fitted roughness value. However, such broadening can originate either from topographical roughness or from a gradual concentration gradient across the interface, which are virtually indistinguishable in specular XRR. Therefore, we refer to this parameter more generally as the interface width. Overall, the extracted interface width remains very small, especially

when compared to the layer thickness. At low gate voltages, the XRR-derived oxide thickness and interface width are effective parameters describing a gradual oxidation profile rather than layer-by-layer growth of a fully developed Ta_2O_5 . During the initial gating, the data suggests a slight increase in interface width. At higher gate voltages, it appears to level off or even decrease slowly, which, however, remains within the experimental uncertainty and requires further confirmation. The initial increase likely originates from the structural reorganization of the topmost Ta layer and the density change accompanying the formation of the first Ta_2O_5 layer. The subsequent leveling, or possibly slight decrease, indicates smooth and uniform growth of the additional oxide layers. Overall, the interface width changes by only about (0.1 ± 0.05) nm, which is less than the thickness of a single Ta monolayer (the metal atomic radius of Ta is 0.14 nm [144]).

6.3.1 Influence of gate voltage and time, stability and reversibility

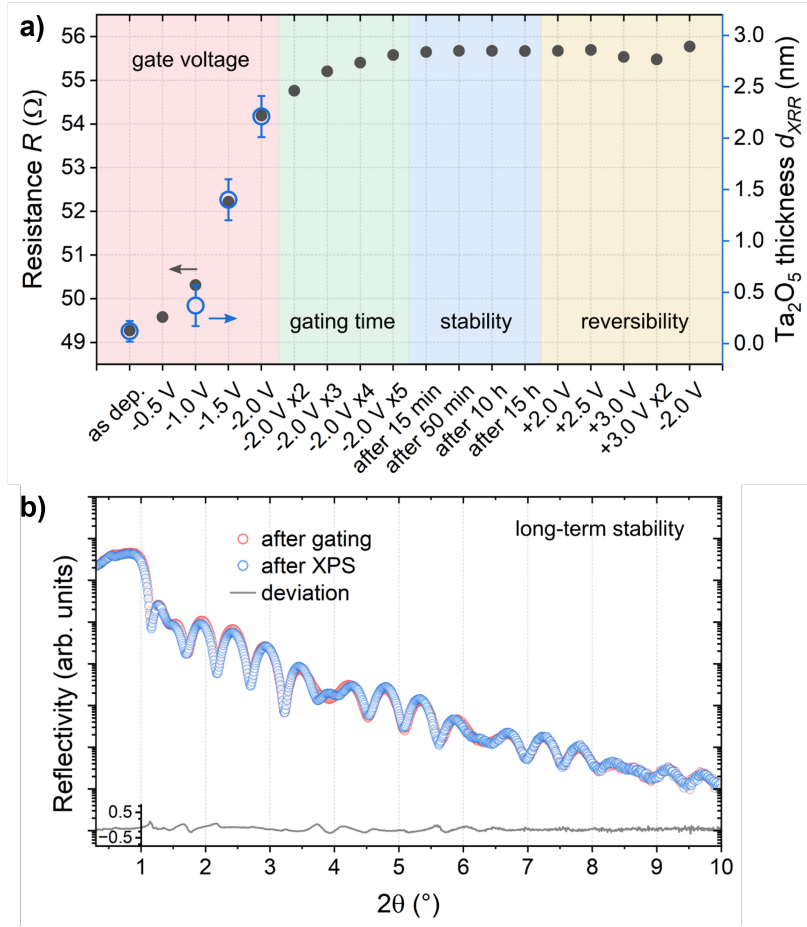


Figure 6.4: (a) Influence of gate voltage and gating time, as well as stability and reversibility of the gating-induced oxidation. All measurements were performed consecutively on the same sample by applying the gate voltages for 10 minutes each and measuring the longitudinal resistance right after turning off the voltage, without removing the IL or top electrode. For comparison, the Ta_2O_5 thicknesses determined by XRR are shown as blue open circles for the gate voltages at which XRR measurements were performed. (b) Comparison of an XRR measurement performed right after gating at -1.5 V for 10 minutes to one recorded after XPS (two months later).

To assess the influence of gate voltage, gating time, and the stability and reversibility of the induced oxidation, Figure 6.4a shows the evolution of the longitudinal resistance during consecutive gating steps and over time. The longitudinal resistance reflects the amount of conductive Ta and thus serves as an estimate of the degree of oxidation. This method enables immediate measurements on the same holder as used for IL gating – starting the measurement typically within 3 minutes after switching off the gate voltage – without removing the IL or top electrode.

With increasing gate voltage (red region in Fig. 6.4a), the resistance follows the same trend as the Ta_2O_5 thickness obtained from XRR (blue open circles), confirming the correspondence between the two methods. Changes induced by longer gating times (repeated -2.0 V steps) are significantly smaller than those from increasing the gate voltage. This is why we focused on voltage variation in this study. Although the additional oxidation decreases with repeated gating, full saturation is not reached within the 50 minutes of gating applied here in total. The oxidation state remains highly stable after gating. Both short-term monitoring over 15 h (blue region in Fig. 6.4a) and a long-term control measurement after 2 months (Fig. 6.4b) show negligible changes. The XRR measurements shown in Figure 6.4b also confirm that neither several hours of X-ray exposure during high resolution X-ray scans nor the exposure to atmosphere alter the thickness and roughness of the layers. Finally, reversibility tests (yellow region in Fig. 6.4a) reveal that the oxidation cannot be recovered by reversing the gate voltage from -2.0 V to +2.0 V. Only at the maximum accessible voltage of +3.0 V, a marginal decrease in resistance is observed, which can be reversed again by applying a negative voltage of -2.0 V.

6.3.2 Chemical analysis using XPS

To obtain more information about the chemical processes during IL gating and to validate the results from XRR, we performed XPS measurements. First of all, the nonvolatility of the oxidation was confirmed by repeating the XPS measurement of the sample with 2 nm HfO_2 gated at -2.0 V after 5 months. By analyzing the spectra from different emission angles (angle-resolved XPS) as well as peak regions (multiple-energies approach), information on the depth distribution of the elements can be obtained (see Fig. 6.2c and reference [97]). Therefore, we fitted all four available Ta peak regions, Ta 4f, Ta 5s, Ta 4d and Ta 4p at six different emission angles, 0°, 15°, 25°, 35°, 45°, and 55° relative to the sample normal. For larger angles, the error on the EAL, which determines the probability that a photoelectron reaches the sample surface without scattering, becomes significantly larger [98]. Therefore, no angles larger than 55° were considered. The results from XRR were used as starting parameters for the fitting of all XPS peaks. More details on the fit parameters and procedure can be found in SI B.4 to B.6.

Figures 6.5 and 6.6 show a subset of the fitted data for the sample with 2 nm HfO_2 capping. To investigate the effect of gating, the spectrum of the as-deposited state (Fig. 6.5) is compared to the state after applying the maximum gate voltage of -3.0 V for 10 minutes (Fig. 6.6). The survey spectra in Figures 6.5 a1 and 6.6 a1 display the full energy range containing Ta and Hf peaks (survey spectra showing the complete measured energy range can be found in Appendix B.7). The three different energy regions with the clearest distinction between the metallic Ta (Ta^0 , green) and oxidized Ta_2O_5 (Ta^{5+} , blue) peaks are shown in the close-ups below the surveys (Figs. 6.5 a2-4 and 6.6 a2-4). In the as-deposited state, only the metallic Ta^0 and Hf^{4+} (HfO_2 , purple) show pronounced peaks. Almost no oxidized Ta^{5+} is present. In contrast, after gating at -3.0 V for 10 minutes, the Ta^0 peaks get significantly smaller while Ta^{5+} now shows large, distinct peaks, confirming a significant oxidation of the Ta layer.

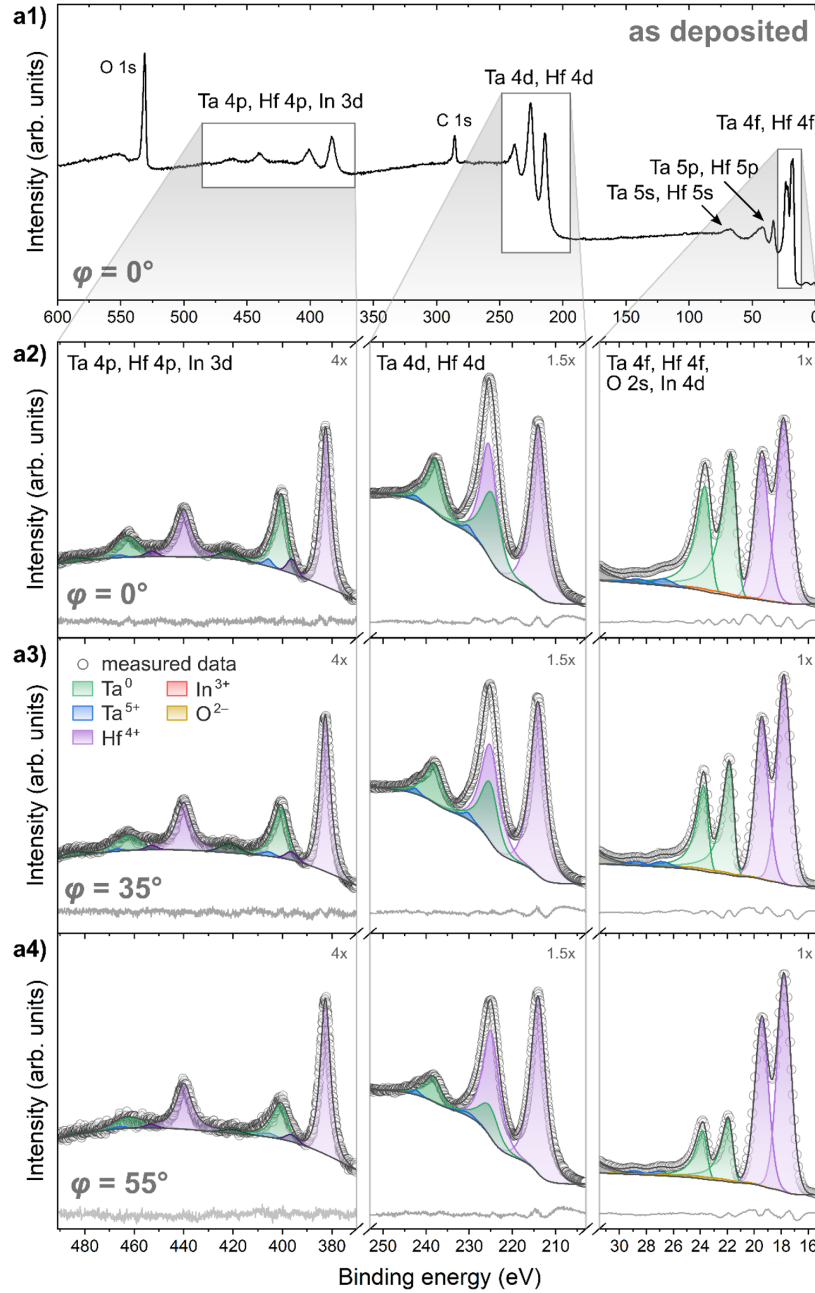


Figure 6.5: XPS spectra for the sample with 2 nm HfO₂ in the as-deposited state. (a1) Survey spectra and (a2-4) fitted elemental spectra for the peak regions Ta 4p, 4d, and 4f for three different emission angles (0°, 35°, and 55° respectively to the surface normal, for which $\cos(35^\circ)$ is approximately in the middle between the cosines of the other two angles). The fitted elemental spectra for the regions Ta 5s and O 1s, as well as the other angles and gating steps, can be found in Appendix B.8. The Ta 5p region (starting at 31 eV toward higher binding energies) was not fitted because of the high number of peaks with large overlap and the resulting high uncertainty of the fitting. However, since this region lies right next to the Ta 4f peak region, a dummy peak (gray) was fitted into the first peak of the Ta 5p region to account for the residual signal.

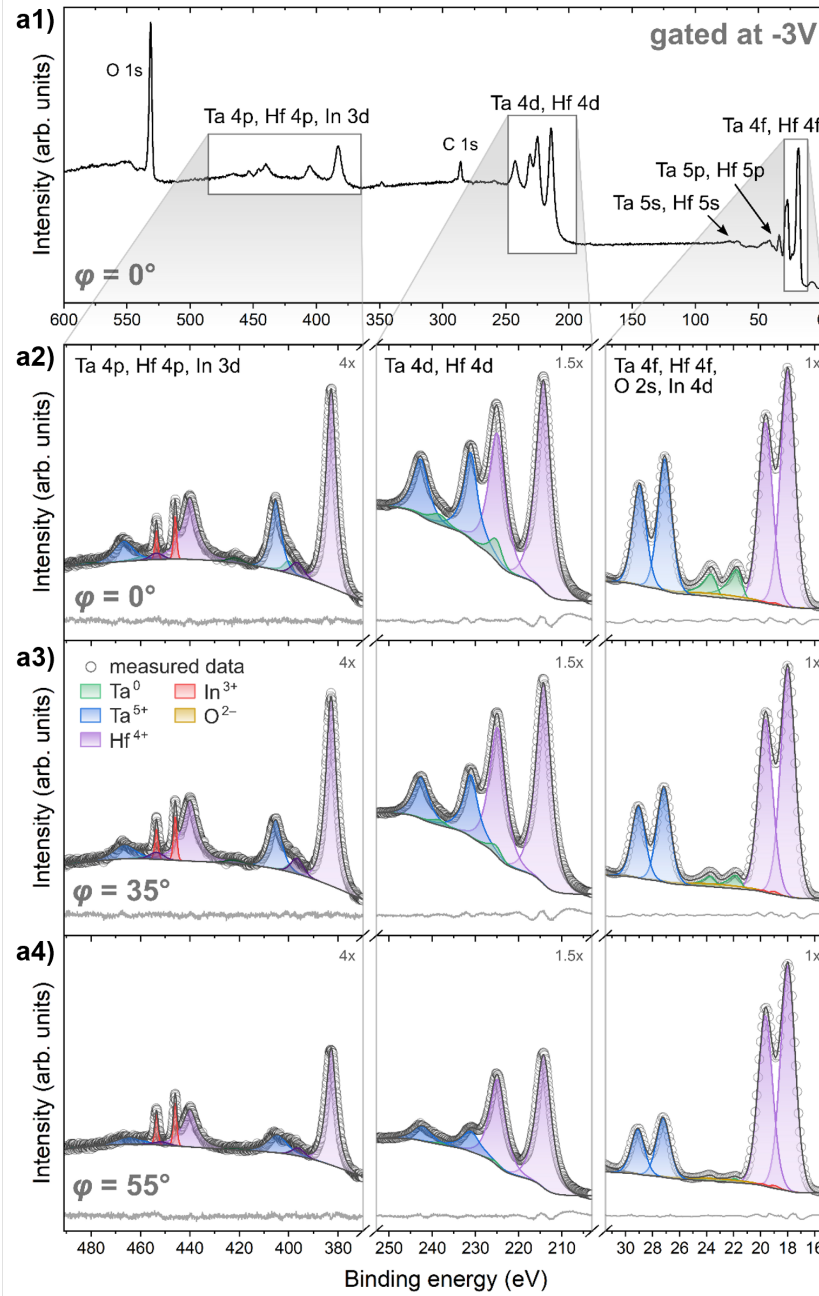


Figure 6.6: XPS spectra for the sample with 2 nm HfO₂ after the maximum applied gate voltage of -3.0 V. (a1) Survey spectra and (a2-4) fitted elemental spectra for the peak regions Ta 4p, 4d, and 4f for three different emission angles (0°, 35°, and 55° respectively to the surface normal, for which $\cos(35^\circ)$ is approximately in the middle between the cosines of the other two angles). The fitted elemental spectra for the regions Ta 5s and O 1s, as well as the other angles and gating steps, can be found in Appendix B.8. Like in Figure 6.5, the Ta 5p region was not fitted because of its high uncertainty of the fitting.

Notably, no additional peaks from intermediate Ta oxidation states are visible. Such peaks would be expected between the Ta^0 and Ta^{5+} peaks, as was, for example, observed at the interface between Si and SiO_2 [159]. As none of the gating steps show such peaks (see Appendix B.8), we conclude that an atomically sharp interface from Ta to Ta_2O_5 forms and propagates upon gating. This also matches the XRR results, which showed a sharp interface at all gate voltages.

6.3.3 Source of oxygen and suggested mechanism

When examining the HfO_2 spectra, it is noteworthy that no metallic Hf^0 peaks appear after gating. This indicates that the Hf–O bonds remain intact, consistent with the high energetic cost of bond dissociation. Possible oxygen sources therefore include interstitial or defect-bound oxygen within the HfO_2 layer, oxygen dissolved in the IL, or atmospheric oxygen entering from ungated edge regions of the HfO_2 . Prior work by An et al. demonstrated the supply of oxygen ions from a comparable IL into adjacent metallic layers by doping the IL with H_2^{18}O and tracking the migration of the ^{18}O under gating [160]. Based on this evidence, oxygen supplied by the IL is likely the dominant source in the present system. The applied electric field transports these O^{2-} anions inward through the dielectric stack. The following Ta oxidation process is likely comparable to atmospheric passivation, for which a self-generated electric field – the so-called Mott potential – drives ion motion. The Mott potential is of comparable magnitude to the electric field required for IL gating, on the order of 10^6 – 10^7 V/cm [146, 161]. As the oxide thickens, this electric field progressively weakens until it can no longer sustain either the required electron tunneling or ion transport, resulting in an equilibrium oxide thickness [146]. Depending on the defect chemistry, many passivation models assume that the metal cation migration can play a dominant role in oxide growth [146, 158]. However, since no intermixing of Hf^{4+} and Ta^{5+} is detected at the $\text{HfO}_2/\text{Ta}_2\text{O}_5$ interface (Appendix B.10), Ta^{5+} migration through the HfO_2 layer can be excluded. Consequently, oxygen can be identified as the primary mobile species, migrating inward through the HfO_2 and Ta_2O_5 as anions or equivalently outward as oxygen vacancies.

6.3.4 Deposition of indium on sample surface

Another noteworthy change after gating is the appearance of sharp indium peaks (In^{3+} , red) in the spectrum of Ta 4p and Hf 4p (Fig. 6.6 a2–4). Since this In is not present in the as-deposited state, it has to originate from the ITO coating of the glass plate, which is used as the top gate contact. Apparently, some of this In is released from the ITO during gating. The standard electrode potential of In^{3+} to In^0 is -0.34 V vs. a standard hydrogen electrode, which is lower than the applied voltage. Therefore, likely In is reduced to In^0 , and deposits on the sample surface. After gating, it oxidizes back to In^{3+} . The intensity of the In peaks does not significantly change for different emission angles, in contrast to the Ta peaks, which become significantly smaller for larger angles. Even the adjacent Hf peak decreases slightly in size for increasing angles in contrast to the In peaks. Hence, the In atoms were deposited only at the surface of the sample and did not penetrate the HfO_2 .

6.3.5 Modeling the Ta/ Ta_2O_5 interface

Based on the finding that there are no spectroscopically resolvable intermediate oxidation states at the interface between Ta and Ta_2O_5 , we can model the interface assuming a symmetric transition between Ta and Ta_2O_5 of the form of an error function. This is the common assumption for metallic interfaces, as also applied in XRR. The thickness d of the Ta_2O_5 layer and width σ of the interface between Ta and Ta_2O_5 can then be calculated using Equation 6.6.

$$\begin{aligned}
& \frac{I_{\text{Ta}^{5+}} \cdot N_{\text{Ta}^0}}{I_{\text{Ta}^0} \cdot N_{\text{Ta}^{5+}}} (L_{\text{Ta}_2\text{O}_5}, L_{\text{Ta}}, \varphi) \\
&= \frac{L_{\text{Ta}_2\text{O}_5}}{L_{\text{Ta}}} \cdot \exp \left(\frac{d}{L_{\text{Ta}_2\text{O}_5} \cos \varphi} - \frac{d}{L_{\text{Ta}} \cos \varphi} \right) \\
& \cdot \frac{\operatorname{erfc} \left(-\frac{d}{\sqrt{2}\varphi} \right) - \operatorname{erfc} \left(\frac{\sigma}{\sqrt{2}L_{\text{Ta}_2\text{O}_5} \cos \varphi} - \frac{d}{\sqrt{2}\varphi} \right) \cdot \exp \left(\frac{\sigma^2}{2(L_{\text{Ta}_2\text{O}_5} \cos \varphi)^2} - \frac{d}{L_{\text{Ta}_2\text{O}_5} \cos \varphi} \right)}{\operatorname{erfc} \left(\frac{d}{\sqrt{2}\sigma} \right) + \operatorname{erfc} \left(\frac{\sigma}{\sqrt{2}L_{\text{Ta}} \cos \varphi} - \frac{d}{\sqrt{2}\sigma} \right) \cdot \exp \left(\frac{\sigma^2}{2(L_{\text{Ta}} \cos \varphi)^2} - \frac{d}{L_{\text{Ta}} \cos \varphi} \right)} \quad (6.6)
\end{aligned}$$

Thereby, $\frac{I_{\text{Ta}^{5+}} \cdot N_{\text{Ta}^0}}{I_{\text{Ta}^0} \cdot N_{\text{Ta}^{5+}}}$ denotes the normalized intensity ratio of the metallic and corresponding oxidized Ta peak inside the same peak region. The peak intensities $I_{\text{Ta}^{5+}}$ and I_{Ta^0} of the oxidized and metallic Ta peaks are normalized to the atomic number densities $N_{\text{Ta}^{5+}}$ and N_{Ta^0} of Ta^{5+} and Ta^0 atoms per unit volume of the pure compounds, respectively. The intensity ratio depends on the emission angle φ , as well as on the EALs $L_{\text{Ta}_2\text{O}_5}$ and L_{Ta} in Ta_2O_5 and Ta, respectively, which are functions of the kinetic energy E_{kin} of the photoelectrons of the respective peak region. More details on the equation and the required parameters can be found in Appendix B.4 as well as in references [97] and [95].

For all peak regions, the normalized intensity ratios have to correspond to the same values of d and σ . Therefore, all fits were optimized accordingly. Figures 6.7 a1 and b1 show the results of the weighted intensity ratios [derived from the data in Figures 6.5 and 6.6] and the 3D fit of Equation 6.6 as a function of φ and $L_{\text{Ta}_2\text{O}_5}(E_{\text{kin}})$. From the corresponding results of the fit for d and σ , we obtained the Ta^0 and Ta^{5+} depth profiles (Figs. 6.7 a2 and b2). Both d and σ were thereby consistent with the XRR results, such that the values obtained from both methods are identical.

Figure 6.7c shows the comparison between the SLD profile obtained from XRR and the depth profiles obtained from XPS, given by the depth z dependent number densities $N(\text{Ta}^0) = \frac{N_{\text{Ta}^0}}{2} \operatorname{erfc} \left(\frac{d-z}{\sqrt{2}\sigma} \right)$ and $N(\text{Ta}^{5+}) = \frac{N_{\text{Ta}^{5+}}}{2} \operatorname{erfc} \left(\frac{z-d}{\sqrt{2}\sigma} \right)$, after gating at -3.0 V.

When normalized and expressed in percent, $N(\text{Ta}^{5+})$ is identical to the Ta^{5+} depth profile, as plotted in Figures 6.8a and b. For a more direct comparison between the results from XRR and XPS, the SLD-XPS profile was calculated from $N(\text{Ta}^0)$ and $N(\text{Ta}^{5+})$ at the energy of Cu $K\alpha$ radiation. Details on the calculation can be found in Appendix B.9. In XPS, we only investigated the interface between Ta and Ta_2O_5 , so the SLD-XPS was only calculated for that interface. The SLD profiles obtained from XPS and XRR are almost perfectly congruent at that interface. This reflects that both methods model the interface in the same way, using an error function, and yield the same average position and width of the interface. To focus on the $\text{Ta}_2\text{O}_5/\text{Ta}$ interface, we will use the Ta^{5+} depth profiles from XPS in the following to discuss the evolution of interface position and width under gating, as well as the effect of HfO_2 thickness.

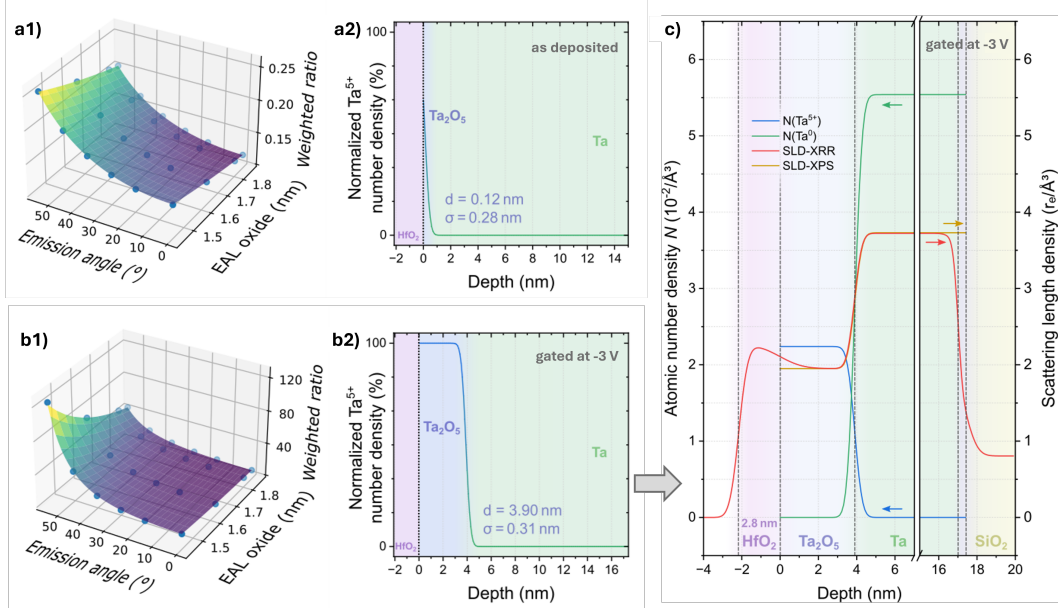


Figure 6.7: (a1, b1) Weighted $Ta^{5+}:Ta^0$ peak ratios, derived from the data shown in Figures 6.5 and 6.6, for all angles and peak regions, and fitted by Equation 6.6. Since the EALs for Ta and Ta_2O_5 are interdependent and defined by the kinetic energy of the photoelectrons, only the EAL of Ta_2O_5 is representatively plotted on the axis. (a2, b2) Ta^{5+} depth profiles, corresponding to d and σ obtained from the fit in (a1, b1), respectively. The Ta^{5+} number densities were normalized to their respective nominal maximum values. (c) Comparison of the scattering length density (SLD) as obtained from XRR and the depth profiles as well as corresponding SLD (calculated for the energy of Cu K α radiation to compare to XRR, details can be found in Appendix B.9) as obtained from XPS for the sample with 2 nm HfO_2 capping and gated at -3.0 V.

6.3.6 Influence of HfO_2 capping layer thickness

The Ta^{5+} depth profiles are depicted in Figure 6.8a and b as a function of the gate voltage, for two different HfO_2 thicknesses. The results are qualitatively the same for both HfO_2 thicknesses, showing a sharp interface between Ta and Ta_2O_5 , which is pushed deeper into the Ta layer with increasing gate voltage. Figure 6.8c shows the comparison of the corresponding average oxide layer thicknesses d for all samples. For both HfO_2 thicknesses, the threshold voltage required to significantly oxidize the Ta is around -1.0 V. Above this voltage, the average oxide layer thickness increases linearly with the applied gate voltage in the investigated range. Overall, the oxide layer thickness is larger for all gate voltages when a thinner HfO_2 capping of only 2 nm is used. This is most likely due to the larger electric field created by applying an identical gate voltage over a thinner dielectric material.

In the inset (Fig. 6.8c), the average oxide layer thickness is therefore plotted as a function of the electric field, calculated by assuming an IL electric double layer thickness of 1 nm. This value corresponds approximately to the combined thickness of one negatively and one positively charged ion layer, across which the voltage drop in the IL occurs. The relation between d and E is very similar for both HfO_2 thicknesses, with the same initial threshold electric field of ≈ -2.8 MV/cm to start oxidizing the Ta.

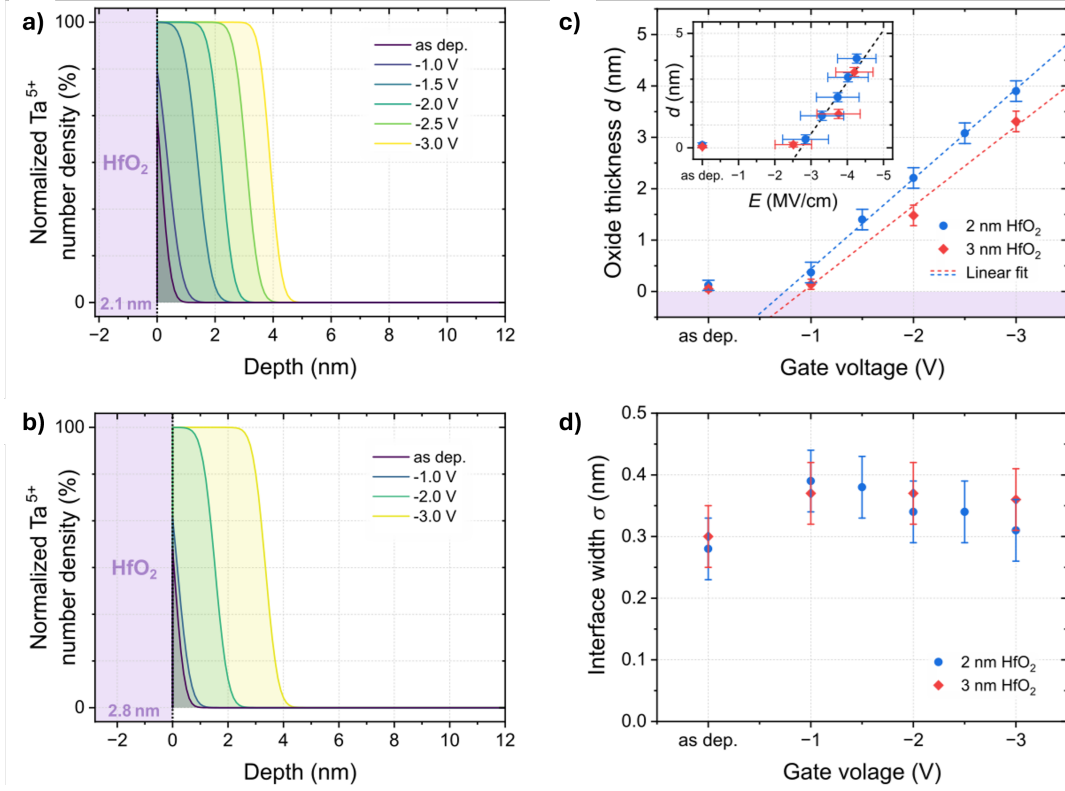


Figure 6.8: (a, b) Ta⁵⁺ depth profiles for the samples with (a) 2 nm and (b) 3 nm nominal HfO₂ capping as a function of the gate voltage. (c) Average Ta₂O₅ layer thicknesses obtained from the depth profiles in (a) and (b) as a function of the gate voltage. The inset shows the same thicknesses as a function of the applied electric field (assuming an electric double layer of the IL of 1 nm, added up with the HfO₂ and Ta₂O₅ thicknesses). The error bar reflects the difference resulting from assuming an electric double-layer thickness of 2 nm. (d) Interface width at the Ta₂O₅/Ta interface as a function of the gate voltage as obtained from the depth profiles in (a) and (b).

Remarkably, the required electric field increases by ≈ -0.45 MV/cm for every additional nm of Ta₂O₅. This shows that the threshold electric field needed to drive oxygen ions from HfO₂ to the Ta₂O₅/Ta interface is not constant – as might be expected – but grows with oxide thickness. Even when considering the saturated film thickness, which can be estimated from Figure 6.2e to be approximately 2.9 nm for the -2.0 V gating step, the required electric field still increases with oxide thickness. One possible explanation is the self-passivating nature of Ta, for which the energetic cost of further oxidation increases with depth [95]. This is also consistent with temperature-dependent oxide growth reported in the literature [162]. A voltage-dependent increase in the IL's electric double-layer thickness might also contribute, but would likely be too small to account for the observed slope.

The Ta₂O₅/Ta interface width shows very similar behavior regardless of the HfO₂ thickness (Fig. 6.8d). For both samples, an initial slight increase is observed, followed by leveling or a possible minor decrease at higher gate voltages. Importantly, the interface remains extremely sharp, with a width of only a few Å.

6.3.7 Conclusion

Our results demonstrate that oxygen ions can be driven several nm into metallic films. In Ta, penetration depths up to 4 nm were achieved by applying -3 V for 10 minutes. This depth exceeds the typical thickness of magnetic thin films, which are usually 0.8–0.9 nm for out-of-plane magnetized layers and 1.0–2.5 nm for in-plane layers. Spacer layers, such as in synthetic antiferromagnets or magnetic tunnel junctions, can be even thinner. Thus, the observed oxygen penetration depth is sufficient to alter the properties of buried layers or interfaces. Depending on the application, this effect can be exploited deliberately or must be carefully managed when preservation of lower interfaces is required.

Furthermore, we find that the Ta₂O₅/Ta interface propagates linearly with applied voltage into the Ta film. The required electric field between IL and Ta electrode is of comparable strength as the Mott potential in passivation processes. Our results demonstrate that oxygen anions, rather than metallic cations, are the primary mobile species underlying the oxide growth. Notably, the interface remains atomically sharp (few Å) at all voltages, indicating that complete Ta₂O₅ layers form sequentially. This behavior is consistent with electric-field screening. The sharpness of the interface further shows that oxidation occurs uniformly across the analyzed sample region, which reflects the high uniformity of the sputtered Ta film. In other materials, additional effects such as grain boundary diffusion may play a role. For example, Gilbert et al. reported that solid-state gating in Pd/Co/AlO_x/GdO_x stacks leads to two distinct magnetic phases [163]. They attributed this to preferential oxygen transport along grain boundaries combined with slower diffusion within grains. In such cases, the process inside each grain or homogeneous region will likely resemble the behavior identified in this study. Thus, our findings provide a framework to interpret oxide depth profiles and disentangle competing physical effects in a broad range of systems.

When choosing the thickness of the dielectric capping layer, it is important to note that thinner HfO₂ enhances oxidation by increasing the electric field. Still, for reliable IL gating, a continuous capping layer is essential. The minimum thickness is therefore limited by the width of the underlying interface and growth characteristics of the capping layer.

Finally, we observe the migration of indium atoms from the ITO electrode onto the sample surface during gating. This is important to consider for all applications requiring a well-defined surface, e.g. when post-processing the sample after removal of the IL and gate.

The results from XRR and XPS showed very good agreement, thereby validating the derived depth profiles. In the present case, XRR provided depth profiles with lower uncertainty while requiring less experimental effort. However, the uncertainty of the extracted depth profiles is material-dependent, and the relative advantages of the two techniques may shift for different systems. Specifically, XRR yields more reliable results in cases of pronounced electron density contrasts, while XPS achieves higher sensitivity when several well-separated emission peaks with large chemical shifts are present. Beyond depth profiling, the evaluation of the full XPS spectrum using the multiple-energies approach provided valuable insights into oxidation states and enabled the detection of indium on the sample surface. Hence, the two techniques offer complementary strengths for a more robust assessment of interfacial structure and composition.

The presented results elucidate the mechanism of oxygen migration and Ta₂O₅ formation during IL gating, providing quantitative design rules for magneto-ionic stacks. This understanding is key for advancing low-power nanoelectronic, spintronic and neuromorphic devices.

Conclusion and Outlook

7.1 Conclusion

In this thesis, magneto-ionic control of magnetism was investigated from both fundamental and applied perspectives. By enabling ultra-low power manipulation of magnetic properties, magneto-ionics offers a promising route to address the rapidly growing energy demand of information and communication technology.

I investigated the magneto-ionic control of magnetic metals using oxygen ions, which are advantageous due to their high reactivity with a wide range of materials and the large number of possible oxygen donor layers. To be able to perform the experiments in Mainz, I built a gating setup. It uses an IL as an insulating barrier, enabling the reliable and highly reproducible application of electric fields. Voltages of up to -3 V and $+4\text{ V}$ are accessible, corresponding to electric fields on the order of a few MV/cm for an electric double layer thickness of the IL of about 1 nm and an insulating capping layer of 2–3 nm. To detect possible time evolution of the magnetization, a characterization of the magnetic state within minutes after gate voltage application was desired. Accordingly, the sample holder of the IL gating setup was designed such that AHE measurements could be performed without removing the top electrode or the IL.

Using this setup, I investigated the effect of IL gating on exchange coupled PtMn/Co bilayers capped with HfO_2 . It was demonstrated that OOP magnetization with OOP EB can be stabilized in an initially IP system. This is particularly useful for applications in which specific areas of a sample need to be set to OOP magnetization in a postprocessing step, e.g. to program 3D magnetization sensors. The set OOP state was shown to be very stable over time and became the preferred energetic configuration once first reached. When subsequently bringing the sample back to an IP state, the magnetization direction evolves back toward the OOP direction within less than a day. XPS, AHE and SQUID measurements revealed that the change in anisotropies was due to an oxidation of the Co film which results in an increased interfacial PMA. At moderate negative voltages up to -2.5 V , the demagnetization energy remains nearly constant, revealing that the thickness of the magnetic Co layer does not change significantly. The interfacial PMA, however, changes significantly, causing the rotation of the magnetization toward the OOP direction. At higher voltages of -2.9 V , an overoxidized state is reached. In this state, both the demagnetization energy and the interfacial PMA are diminished. Furthermore, I showed that reducing the Co thickness alone is not sufficient to induce the OOP magnetization in this material system. Notably, at gate voltages of -2.7 V , the oxygen ions reach the Co/PtMn interface, which is evidenced by the oxidation of Mn observed in XPS. This oxidation however does not erase the EB.

When increasing the PtMn thickness from 8 nm to 20 nm, the EB increases significantly, stabilizing in a state with fully shifted magnetization loop. However, it takes longer until this state is reached, requiring more than one gating cycle. This is most likely due to the increased crystallinity of the Co layer when grown on a thicker PtMn film, demonstrating the importance of the properties of the underlayer during IL gating.

When inverting the order of the Co and PtMn layer by growing PtMn on top of the Co, the Co shows an OOP magnetization in the as-deposited state. In this growth order, the Co/PtMn interface, which sets the EB, is the upper interface of the Co while the PMA is sustained by the bottom interface of Co when grown on a Pt seed layer. In this way, the interface responsible for the EB is reached first when applying IL gating. Indeed, I could show that the EB shift gets diminished by over 25 % after applying a negative gate voltage of -3.5 V in a sample with 6 nm PtMn grown on 0.9 nm Co. The OOP magnetization is retained during all gating steps. This demonstrates that oxygen ions can penetrate the 6 nm metallic PtMn layer and reach the Co/PtMn interface. After post-annealing, the EB increases again, almost recovering the initial state.

These experiments demonstrate, that a profound understanding of the oxygen penetration depth and its depth profile is essential to be able to exploit the voltage-induced oxidation for applications. Depending on the application, buried layers may need to be protected from oxidation or an oxidation may be desired. Therefore, the oxygen profiles in metallic thin films were investigated as a function of the gate voltage by performing an extensive XPS and XRR characterization. To get high quality depth profiles, I contributed to improving and refining the XPS analysis procedure and wrote the required analysis software to obtain the average oxide layer thickness and interface width from the XPS fits. Ta, grown on thermally oxidized Si and capped with HfO_2 , served as the model system because of the very smooth and homogeneous Ta growth. The application of voltages across the IL and HfO_2 layer was demonstrated to cause the formation of a Ta_2O_5 layer. For electric fields above a threshold electric field of $\approx -2.8 \text{ MV/cm}$, the average thickness of the Ta_2O_5 layer grows linearly with increasing gate voltage. However, the growth of every additional nm of Ta_2O_5 requires an increasing electric field, reflecting the self-passivating nature of Ta. The presence of a threshold electric field and its strength, which is of the same order of magnitude as the Mott potential for natural passivation, indicate that a similar process as during natural passivation could be underlying. This would imply that the threshold electric field is set either by the electric field required to move the mobile ions (oxygen anion into the stack or metal cation toward the surface) or for the electrons to tunnel through the oxide layer. Furthermore, in XPS measurements no intermixing between Ta and HfO_2 was observed, implying that the oxygen anions are moving and not the metal cations.

Since the HfO_2 peaks show no sign of reduction in XPS during IL gating, the Hf-O bonds most likely stay stable. This is reasonable because the energy of bond dissociation for Hf-O is very high. Most likely, the dominant oxygen supply is via H_2O or O_2 dissolved in the IL, possibly with additional oxygen supply via interstitial or defect-bound oxygen within the HfO_2 layer or atmospheric oxygen entering from ungated edge regions of the HfO_2 .

It is noteworthy that the Ta/ Ta_2O_5 interface exhibits atomic-scale sharpness under all gating conditions with negative voltage. Hence, complete oxide layers form before the oxygen ions penetrate further down into the metallic Ta film. The maximum Ta_2O_5 thickness, reached at -3 V gating, was 4 nm. This is significantly more than the typical thickness of many functional layers in magnetic stacks. Therefore, a careful stack design and choice of gate voltages enable the manipulation of magnetic layers down to several nm depth. It should be noted that the oxide layer formation might be less homogeneous for more granular samples than Ta. The results presented here should be considered as a framework for the understanding of the oxidation process during IL gating. Most likely, the oxidation of homogeneous regions, like individual crystal grains, is similar in other materials systems, with increased oxidation speed in grain boundaries.

Furthermore, for the design of the magnetic stacks, the thickness of the HfO_2 capping layer can be tuned. Thinner HfO_2 results in larger electric fields at equal gate voltage and therefore allows for stronger oxidation. There is no sign of diminishing oxygen supply for thinner HfO_2 capping layers, in accordance with the finding that the dominant source of oxygen is most likely oxygen dissolved in the IL. When using ITO as the top gate electrode, as done in this thesis, it should be noted that indium ions from the ITO diffuse down onto the sample surface during IL gating. This aspect is particularly relevant for surface sensitive applications.

To crosscheck oxide depth profiles or disentangle changes in interstitial oxide concentration versus bound oxygen, a comparison of XRR and XPS can be very helpful. I demonstrated that reliable and high quality oxide depth profiles can be obtained with XRR, if the following three conditions are fulfilled at the relevant interfaces: the interfaces show a clear change of SLD, the topographical roughness of the interface is small compared to the width of the oxygen gradient, and an error function is a good approximation of the shape of the interfaces. For XPS, the quality of the oxide depth profile depends on the chemical shift between the metallic and oxidized peaks and the number of available peak regions which can be included into the fitting.

The gained understanding on the mechanisms underlying IL gating, together with the developed methodology to obtain high quality oxide depth profiles and the described design rules for optimized stacks, the results presented in this thesis will help paving the way for optimized magneto-ionic devices.

7.2 Outlook

The results presented in this thesis provide a foundation for a comprehensive understanding of the microscopic processes underlying IL gating in metals. Nevertheless, several questions remain open and warrant further investigation.

In this thesis, oxygen migration was investigated in Ta because of its very smooth growth. A natural next step is to extend this study to a magnetic metal such as Co and to compare the results. Due to its higher crystallinity, Co is expected to exhibit enhanced oxygen migration along grain boundaries. Knowledge of the resulting oxide penetration depths and depth profiles is fundamental to be able to protect buried layers or actively manipulate them using the oxygen. For the stack design it should be noted that the higher crystallinity also leads to increased surface roughness. Initial tests on 15 nm thick Co films capped with HfO_2 revealed that such topographical roughness poses a challenge to achieving stable IL gating. To determine the optimal Co film thickness, the following points should therefore be considered: The Co thickness has to be sufficiently large to differentiate between metallic and oxidized Co, as well as between fully oxidized layers and oxygen which diffused deeper into the bulk along the grain boundaries. For the XRR analysis, it is important that the Co film thickness is significantly larger than the interface width and that the topographical roughness is as small as possible. For the XPS analysis, it is advantageous if the signal only stems from Co and its capping and not from the underlayers. The depth from which the detected photoelectrons originate is determined by the EALs of the materials. For Co, a thickness of approximately 3 nm is sufficient to ensure that roughly 95 % of the photoelectrons originate from the Co layer, with only 5 % originating from the underlying layers. Furthermore, it should be noted that Co has multiple stable oxides, so oxidized layers with different oxidation states might be possible.

Another important question is what determines whether a material shows reversible or irreversible effects during IL gating. Previous work by Bhatnagar-Schöffmann et al. indicated that reversible changes are due to interstitial, unbound oxygen [164]. They suggested that the oxygen ions only move gently during gating. With the method used in this thesis, comparing XRR and XPS, it is possible to distinguish between interstitial and bound oxygen. Thereby, XRR is a measure of the density of oxygen atoms, while XPS gives the amount of oxidized material. The difference between the two therefore yields the amount of unbound, interstitial oxygen atoms.

This allows for a more in-depth understanding of the origin of reversible and irreversible gating effects. Thus, it helps to choose materials and design devices with the desired properties. Additionally, an investigation of the changes in oxide depth profiles for different capping and underlayers would allow to understand why and how these layers modify the results obtained with IL gating.

For practical applications, it would be highly desirable to enhance the oxidation achieved with a fixed gate voltage. I already demonstrated that this can be achieved by decreasing the capping layer thickness to increase the electric field. Additionally, increasing the supply of oxygen ions would be beneficial. My results suggest that the main source of oxygen is the IL. However, the IL used in this thesis is a hydrophobic IL with $< 0.5\%$ water according to the data sheet. Therefore, it would be very interesting to test a hydrophilic IL and check whether the gating efficiency increases. To verify whether the IL is the main source of mobile oxygen, a sample with an additional insulating layer between HfO_2 and the IL could be investigated. If the source of mobile oxygen is the IL, this will cut the oxygen supply reaching the layer below the HfO_2 .

Building on the experiments presented in this thesis on the control of EB, it would be interesting to investigate whether strain induced by IL gating could be used to manipulate the magnetic order of PtMn. In my experiments on Ta, I observed that the total film thickness increases significantly after the insertion of oxygen atoms, due to the lower mass density of Ta_2O_5 compared to Ta. Equivalently, an insertion of oxygen ions into PtMn would strain the PtMn lattice. Yan et al. demonstrated experimentally that strain can alter the magnetic structure of $\text{Pt}_{51.7}\text{Mn}_{48.3}$ and, in turn, the EB of an adjacent FM [165]. According to the first principles calculations of Park et al., the Néel vector of $\text{Pt}_{50}\text{Mn}_{50}$ points in the OOP direction in the absence of strain. A tensile strain, so a larger distance between Mn atoms, causes the Néel vector to rotate into the plane [166]. Achieving such a rotation of magnetization via the application of IL gating would present a significantly easier method compared to the growth on a piezoelectric substrate. A phase diagram of PtMn as a function of the Pt concentration and temperature can be found in [167]. A composition close to the transition between IP and OOP magnetization should be chosen to minimize the strain required for the transition. Analogously, other materials which show a spin reorientation among strain are therefore also of interest.

Moreover, many more applications of IL gating for the control of magnetic properties are conceivable. In particular all interfacial properties determined within 4 nm below the top interface of the uppermost conductive layer can likely be manipulated using IL gating. Next to the EB and PMA, this makes the investigation of the effect of IL gating on e.g. the spin and orbital Rashba Edelstein effects or the magnetic proximity effect very promising. Furthermore, oxygen-induced properties, like altermagnetism in RuO_2 , merit further investigation with IL gating. This opens up a wide range of magnetic material systems which can be explored, both to advance fundamental understanding and to support device development.

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<https://doi.org/10.1038/s41567-022-01830-6>.

Authorship and credits for figures in the results chapters

A.1 Figures of Chapter 4 Stabilizing PMA with strong EB

Figure 4.1: Panel (a) is identical to Fig. 1a in Ref. [82].
Panel (b) was added and has not been published previously.
For both panels, the figures were created by me.

Figure 4.2: Subset of Fig. S3 from Ref. [82].
The data were evaluated and the figure was created by me.

Figure 4.3: Reprinted from Ref. [82] (Fig. S1) without modifications.
The data were evaluated and the figure was created by me.

Figure 4.4: Panels (a), (c), (d), (f) and (g) are reprinted from Fig. 2 of Ref. [82].
Panels (b) and (e) are adapted from Fig. S5 of [82].
For all panels, the data were evaluated and the figure was created by me.

Figure 4.5: Reprinted from Ref. [82] (Fig. S8) with a small adaption in the figure caption.
The data were evaluated and the figure was created by me.

Figure 4.6: Adapted from Ref. [82], with panels (a–e) corresponding to Fig. S3 b–f, panel (f) corresponding to Fig. 2f and panel (g) corresponding to Fig. S4.
The data were evaluated and the figure was created by me.

Figure 4.7: This figure was created for this thesis and is not published previously.
The data were evaluated and the figure was created by me.

Figure 4.8: Adapted from Fig. 3 of Ref. [82], whereby panel (a) was substituted by an adapted version of Fig. S6 b from [82] which includes the the curves at -2.3 and -2.9 V.
The data were evaluated and the figure was created by me.

Figure 4.9: Adapted from Ref. [82], with panel (a) adapted from Fig. S9 and panels (b–c) corresponding to Fig. 4a–b.
The data were evaluated and the figure was created by me.

A.2 Figures of Chapter 5

Controlling the EB with fixed PMA

Figure 5.1: This figure was created for this thesis and is not published previously.
The figure was created by me.

Figure 5.2: This figure was created for this thesis and is not published previously.
The data were evaluated and the figure was created by me.

Figure 5.3: This figure was created for this thesis and is not published previously.
The data were evaluated and the figure was created by me.

Figure 5.4: This figure was created for this thesis and is not published previously.
The data were evaluated and the figure was created by me.

A.3 Figures of Chapter 6

Understanding IL gating induced oxygen migration

Figure 6.1: Subset of Fig. S6 from Ref. [97].
The data were evaluated by me, the published figure was created by Martin Wortmann and adapted by me for this thesis.

Figure 6.2: Reprinted from Ref. [141] (Fig. 1) without modifications.
The figure was created by Martin Wortmann.

Figure 6.3: Adapted from Fig. 2 of Ref. [141].
The data were evaluated by me, the published figure was created by Martin Wortmann and adapted by me for this thesis.

Figure 6.4: Subset of Fig. 2 from Ref. [141].
The data were evaluated by me, the published figure was created by Martin Wortmann and adapted by me for this thesis.

Figure 6.5: Adapted from Fig. 3 of Ref. [141].
The data were evaluated by me, the published figure was created by Martin Wortmann and adapted by me for this thesis.

Figure 6.6: Adapted from Fig. 3 of Ref. [141].
The data were evaluated by me, the published figure was created by Martin Wortmann and adapted by me for this thesis.

Figure 6.7: Adapted from Ref. [141], with panels (a1), (a2), (b1) and (b2) corresponding to panels (a5), (a6), (b5) and (b6) of Fig. 3 in Ref. [141] and panel (c) adapted from to panel (a) of Fig. 4 in Ref. [141].
The data were evaluated by me. The figures in panels (a1) and (b1) were created by me using Python and the axes redesigned by Martin Wortmann. The figures in the other panels were created by Martin Wortmann and adapted by me for this thesis.

Figure 6.8: Subset of Fig. 4 from Ref. [141].
The data were evaluated by me, the published figure was created by Martin Wortmann and adapted by me for this thesis.



Supporting information for oxygen depth profiling

In the following section, all text marked with a line at the left is reprinted from [141]:

B. Bednarz and M. Wortmann et al.

“Depth Profiling of Oxygen Migration in Ta/HfO₂ Stacks During Ionic Liquid Gating”

ACS Appl. Mater. Interfaces **18**, 6200–6209 (2026).

The paper is published under a Creative Commons CC-BY 4.0 license. The text, figures and equations marked with a solid line are reprinted here literally according to the submitted version, except for the numbering of the figures, tables, equations, citations and cross-references. Modifications to the cited text are indicated by square brackets.

B.1 Experimental details

B.1.1 Sample growth

The samples were grown on p-doped thermally oxidized Si/SiO₂ (100 nm SiO₂) at room temperature in an industrial Singulus Rotaris magnetron sputtering tool. The base pressure was 5×10^{-8} mbar. As a metallic film, Ta was grown using DC magnetron sputtering. HfO₂ was grown using RF magnetron sputtering, without introducing additional oxygen, in pure Ar atmosphere at a pressure of 6×10^{-3} mbar. In this way, a very high sample quality and homogeneity was achieved for both layers, as evidenced by the smooth growth observed by XRR. All samples with the same nominal HfO₂ thickness were grown together on the same wafer and afterward cut into 5×8 mm² large pieces.

B.1.2 IL gating

The IL 1-ethyl-3-methylimidazolium-bis-(trifluoromethylsulfonyl)-imide ([EMIM]⁺ [TFSI][−]) (CAS: 174899-82-2, SKU: 711691-100G, >98 % (HPLC), from Sigma-Aldrich) was used to apply the gate voltages. A drop of the IL was placed in each corner of the HfO₂ surface. A glass slide (area 5×7 mm²) coated with ITO, floating on top of the IL, was used as the top contact for the gate voltage. To ground the Ta, serving as the bottom contact, the Ta was wirebonded through the insulating layers on top. By applying negative gate voltages to this setup, oxygen ion species can be moved from HfO₂ into the Ta. Gate voltages between -1.0 and -3.0 V were applied at room temperature using a Keithley 2400. Thereby, the voltage was slowly increased, to minimize instabilities, up to the target voltage which was applied for 10 minutes. Afterward, the IL was washed off in acetone.

B.1.3 XRR measurement

XRR measurements were performed using a Bruker D8 X-ray diffractometer using Cu $K\alpha$ radiation. The primary beam was focused using a line focus of 12 mm length, followed by a Göbel mirror and a slit with a nominal width of 0.6 mm. The resulting X-ray beam incident on the sample is approximately rectangular with dimensions 12 mm x 0.6 mm. The secondary beam path had two parallel slits with a width of 0.6 mm each, to filter out off-specular X-rays. The geometric acceptance angle at the detector is approximately $\pm 0.05^\circ$. The XRR data was measured in the 2θ -range from 0.3° to 10° with a step size of 0.01° and a collection time of 1.0 s per step. The resulting instrument resolution is of the order of the step size. All densities, the HfO_2 thickness and the thickness and interface width of the bottom Ta_2O_5 layer were fixed in the XRR analysis. Detailed information on the reasons and implications can be found in B.2. The analysis was done using the software GenX version 3.7.4. All data was measured in a specular geometry. Therefore, the spec.nx mode of the advanced reflectivity plugin was used, which fits the data using the Parratt algorithm [87, 168]. The interface width is defined as the root mean square roughness at the top interface of the layer, assuming a Gaussian deviation from the ideal interface.

B.1.4 XPS measurements

XPS measurements were performed using an ESCA-unit Phi 5000 VersaProbe III photoelectron spectrometer. A monochromated raster scanned micro focused X-ray beam with Al $K\alpha$ radiation (1486.6 eV) and 25 W at 15 kV was used. The resulting analyzed area has a diameter of 100 μm . A 180° hemispherical electron energy analyzer with a scanning input lens was used, which is synchronized to the scanning X-ray beam. It has a work function of 4.39 eV and was positioned at a fixed angle of 45° toward the X-ray source. The energy resolution of the instrument, defined as the full width at half maximum (FWHM) of the Ag 3d $_{5/2}$ peak, is 0.7 eV at 55 eV pass energy. For each sample, a survey (pass energy 224 eV) as well as the O 1s and Ta 4p, 4d, 5s and 4f energy ranges (pass energy 55 eV) were recorded for electron emission angles φ between 0° and 55° relative to the surface normal by tilting the sample. The surveys were measured from the Fermi edge up to 1300 eV in steps of 0.4 eV and the individual peak regions were scanned in steps of 0.1 eV. The binding-energy scale was referenced to the Fermi-edge cutoff of the valence band [169]. The analysis was done using the software CasaXPS version 2.3.26PR1.0.

B.2 X-ray reflectivity (XRR) fit parameters

The XRR analysis was performed in GenX [168] (homepage: <https://aglavic.github.io/genx/>) version 3.7.4, using the following slab model: SiO₂ / Ta₂O₅ bottom / Ta / Ta₂O₅ top / HfO₂.

For all layers, literature densities were used. For HfO₂ and the top Ta₂O₅, the reason is their very similar mass density and correspondingly similar scattering length density (SLD). Therefore, they are nearly indistinguishable in XRR, which leads to unreasonable density values when fitted freely. For Ta, a free fit gave densities very close to the literature density (within 0.3 g/cm³), which, however, differed between the samples after the different gating steps. Since all samples with the same HfO₂ thickness were sputter-deposited together on the same wafer, their Ta densities cannot be different. Therefore, the literature density was set for all samples. For the bottom Ta₂O₅ layer, the thickness is too thin to fit the density freely.

Additionally, for the HfO₂ layer and the bottom Ta₂O₅ layer, the thicknesses were fixed according to their thickness in the corresponding as-deposited sample. For the bottom Ta₂O₅, the underlying assumption is that the Ta layer above screens the electric field and therefore the bottom Ta₂O₅ layer is not significantly affected by the gating. Also, the interface width of this layer was fixed according to the as-deposited state, using the knowledge that the roughness of the SiO₂ wafer is in the range of 1–3 Å. For HfO₂, the reason to fix the thickness is the indistinguishability between the HfO₂ and the top Ta₂O₅ layer because of their similar densities. Using the knowledge from XPS, that the HfO₂ does not get reduced to metallic Hf (no Hf⁰ peak and also no shoulder or other sign of a change due to gating appears in XPS), the assumption that the HfO₂ layer remains unaffected by gating seems justified. Still, this uncertainty was included in the error on the Ta₂O₅ thickness (see error discussion below).

Table B.1 shows the parameters fixed in the XRR fit. Tables B.2 and B.3 provide the corresponding results for the layer thickness d and interface width σ for the samples with 2 and 3 nm HfO₂, respectively. Figure B.1 shows the corresponding fits and SLD profiles for all samples.

Tables B.2 and B.3 also give the estimated uncertainties for all values. For the layer thicknesses, the uncertainty of the fits is estimated to be 0.1 nm. Additionally, the HfO₂ layer has an uncertainty due to the assumption that it is unaffected by gating. It was estimated to be 0.1 nm for all gating steps, leading to a total uncertainty on the HfO₂ thickness of 0.14 nm. This error gets propagated to the thickness of the upper Ta₂O₅ layer because of their similar densities, additionally to the fitting uncertainty. For the interface width, the basic fitting uncertainty is estimated to be 0.05 nm. However, toward the sample surface (for HfO₂) and the substrate (Ta₂O₅ bottom) the uncertainty is larger and estimated to be 0.1 nm. At the HfO₂/Ta₂O₅ interface, the error is significantly larger because of the similar densities.

Table B.1: Fixed parameters of XRR fits. Densities taken from literature values given by Merck KGaA and Kurt J. Lesker Company are used.

		HfO ₂	Ta ₂ O ₅ top	Ta	Ta ₂ O ₅ bottom	SiO ₂
Ta (15)/ HfO ₂ (2)	ρ (g/cm ³)	9.7	8.2	16.7	8.2	2.7
	d (nm)	2.14			0.4	
	σ (nm)				0.2	
Ta (15)/ HfO ₂ (3)	ρ (g/cm ³)	9.7	8.2	16.7	8.2	2.7
	d (nm)	2.84			0.4	
	σ (nm)				0.3	

Table B.2: Fitted parameters from XRR for the samples Si/ SiO₂/ Ta (15)/ HfO₂ (2) for all applied gate voltages. The values of the interface width σ , which can be caused either by topographical roughness or a gradual concentration gradient, are defined at the upper interface of each layer. The thickness d of the Ta₂O₅ layer and interface width σ at the Ta₂O₅/Ta interface, which are particularly discussed in the manuscript, are highlighted with a green background. The grey values were fixed (see table B.1) and are given here together with their estimated uncertainties. SiO₂ is not included because the substrate is assumed to have infinite thickness in XRR. The substrate interface width was fixed to the range 1–3 Å, which is the topographical roughness of the substrates.

		HfO ₂	Ta ₂ O ₅ top	Ta	Ta ₂ O ₅ bottom
As deposited	d (nm)	2.14 ± 0.10	0.12 ± 0.10	14.5 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	0.12 ± 0.05	0.28 ± 0.05	0.2 ± 0.1
-1.0 V	d (nm)	2.14 ± 0.14	0.4 ± 0.2	14.4 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	0.4 ± 0.2	0.39 ± 0.05	0.2 ± 0.1
-1.5 V	d (nm)	2.14 ± 0.14	1.4 ± 0.2	14.0 ± 0.1	0.4 ± 0.1
	σ (nm)	0.5 ± 0.1	0.5 ± 0.3	0.38 ± 0.05	0.2 ± 0.1
-2.0 V	d (nm)	2.14 ± 0.14	2.2 ± 0.2	13.7 ± 0.1	0.4 ± 0.1
	σ (nm)	0.5 ± 0.1	0.4 ± 0.3	0.34 ± 0.05	0.2 ± 0.1
-2.5 V	d (nm)	2.14 ± 0.14	3.1 ± 0.2	13.4 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	0.6 ± 0.5	0.34 ± 0.05	0.2 ± 0.1
-3.0 V	d (nm)	2.14 ± 0.14	3.9 ± 0.2	13.1 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	1.0 ± 0.7	0.31 ± 0.05	0.2 ± 0.1

Table B.3: Fitted parameters from XRR for the samples Si/ SiO₂/ Ta (15)/ HfO₂ (3) at all applied gate voltages, presented equivalently to table B.2 for the samples with 2 nm HfO₂.

		HfO ₂	Ta ₂ O ₅ top	Ta	Ta ₂ O ₅ bottom
As deposited	d (nm)	2.84 ± 0.10	0.05 ± 0.05	14.5 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	0.07 ± 0.05	0.30 ± 0.05	0.3 ± 0.1
-1.0 V	d (nm)	2.84 ± 0.14	0.14 ± 0.10	14.5 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	0.2 ± 0.1	0.37 ± 0.05	0.3 ± 0.1
-2.0 V	d (nm)	2.84 ± 0.14	1.5 ± 0.2	14.0 ± 0.1	0.4 ± 0.1
	σ (nm)	0.3 ± 0.1	0.4 ± 0.2	0.37 ± 0.05	0.3 ± 0.1
-3.0 V	d (nm)	2.84 ± 0.14	3.3 ± 0.2	13.2 ± 0.1	0.4 ± 0.1
	σ (nm)	0.4 ± 0.1	0.6 ± 0.4	0.36 ± 0.05	0.3 ± 0.1

B.3 Overview over all XRR fits

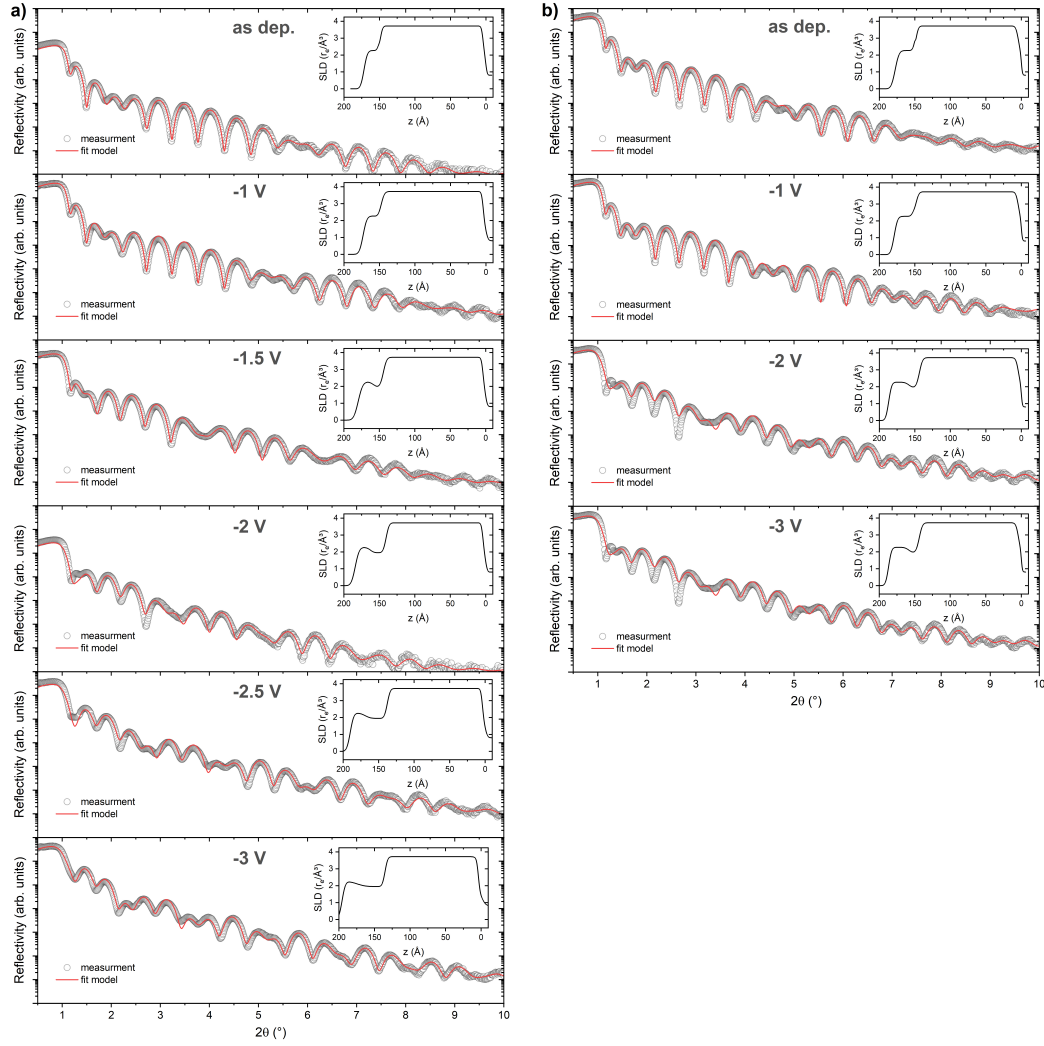


Figure B.1: XRR fits and corresponding SLDs for the samples with (a) 2 and (b) 3 nm HfO_2 , respectively, at all gate voltages. The narrow oscillation corresponds to the Ta thickness, while the wider oscillation with the visibly decreasing period corresponds to the combined thickness of HfO_2 and the top Ta_2O_5 .

B.4 Origin of the equation used to obtain d and σ from the XPS data

In XPS, the binding energy of the emitted photoelectrons provides information on the corresponding element and its oxidation state. The number of photoelectrons ΔI , which reach the surface without inelastic scattering, can be expressed according to the Beer-Lambert law, as

$$\Delta I = \Delta I_0 \exp\left(\frac{-z}{L \cos(\varphi)}\right) \quad \text{with} \quad \Delta I_0 \propto \Delta z \quad (\text{B.1})$$

with the excited number of photoelectrons ΔI_0 created in a thin layer with thickness Δz at a depth z below the surface, the distance $z/\cos(\varphi)$ traveled by the photoelectrons emitted at an angle φ toward the sample normal and the inelastic mean free path (IMFP) or effective attenuation length (EAL) L of the material (an explanation of the difference between the IMFP and EAL can be found in B.5). In this study, we consider a two-layer system with a Ta_2O_5 layer with an average thickness d on top of a Ta film. We assume a gradual interface with a width σ between the two layers, which can be approximated by a complementary error function $\text{erfc}\left(\frac{z-d}{\sqrt{2}\sigma}\right)$. In this case, the number of photoelectrons from the Ta_2O_5 layer $I_{\text{Ta}^{5+}}$ and from the Ta layer I_{Ta^0} can be expressed as

$$\Delta I_{\text{Ta}^{5+}} = \Delta I_{0,\text{Ta}^{5+}} \exp\left(\frac{-z}{L_{\text{Ta}_2\text{O}_5} \cos(\varphi)}\right) \quad (\text{B.2})$$

with $\Delta I_{0,\text{Ta}^{5+}} \propto N_{\text{Ta}^{5+}} \Delta z \text{erfc}\left(\frac{z-d}{\sqrt{2}\sigma}\right)$

$$\Delta I_{\text{Ta}^0} = \Delta I_{0,\text{Ta}^0} \exp\left(\frac{-(z-d)}{L_{\text{Ta}} \cos(\varphi)}\right) \exp\left(\frac{-d}{L_{\text{Ta}_2\text{O}_5} \cos(\varphi)}\right) \quad (\text{B.3})$$

with $\Delta I_{0,\text{Ta}^0} \propto N_{\text{Ta}^0} \Delta z \text{erfc}\left(\frac{d-z}{\sqrt{2}\sigma}\right)$

Thereby, $\Delta I_{0,\text{Ta}^{5+}}$ and $\Delta I_{0,\text{Ta}^0}$ are the excited number of photoelectrons reaching the detector from a thin layer with thickness Δz in the oxide and metal, respectively, $L_{\text{Ta}_2\text{O}_5}$ and L_{Ta} are the EALs of the oxide and the metal and $N_{\text{Ta}^{5+}}$ and N_{Ta^0} denote the number densities of oxidized or metallic Ta atoms, respectively. Integrating these two equations from $0 \leq z \leq \infty$ (assuming that the thickness of the Ta layer is much thicker than L_{Ta} yields the respective XPS peak intensities $I_{\text{Ta}^{5+}}$ and I_{Ta^0} . By calculating the quotient of the two and rearranging, we obtain Equation 6.6 from the main text

$$\begin{aligned} & \frac{I_{\text{Ta}^{5+}} \cdot N_{\text{Ta}^0}}{I_{\text{Ta}^0} \cdot N_{\text{Ta}^{5+}}}(L_{\text{Ta}_2\text{O}_5}, L_{\text{Ta}}, \varphi) \\ &= \frac{L_{\text{Ta}_2\text{O}_5}}{L_{\text{Ta}}} \cdot \exp\left(\frac{d}{L_{\text{Ta}_2\text{O}_5} \cos \varphi} - \frac{d}{L_{\text{Ta}} \cos \varphi}\right) \\ & \cdot \frac{\text{erfc}\left(-\frac{d}{\sqrt{2}\varphi}\right) - \text{erfc}\left(\frac{\sigma}{\sqrt{2}L_{\text{Ta}_2\text{O}_5} \cos \varphi} - \frac{d}{\sqrt{2}\varphi}\right) \cdot \exp\left(\frac{\sigma^2}{2(L_{\text{Ta}_2\text{O}_5} \cos \varphi)^2} - \frac{d}{L_{\text{Ta}_2\text{O}_5} \cos \varphi}\right)}{\text{erfc}\left(\frac{d}{\sqrt{2}\sigma}\right) + \text{erfc}\left(\frac{\sigma}{\sqrt{2}L_{\text{Ta}} \cos \varphi} - \frac{d}{\sqrt{2}\sigma}\right) \cdot \exp\left(\frac{\sigma^2}{2(L_{\text{Ta}} \cos \varphi)^2} - \frac{d}{L_{\text{Ta}} \cos \varphi}\right)} \end{aligned} \quad (\text{B.4})$$

Note that the peak region of each orbital corresponds to a different binding energy E_{BE} and corresponding kinetic energy E_{kin} of the electrons, with $E_{\text{kin}} = h\nu - E_{\text{BE}} - \Phi$ with photon energy $h\nu = 1486.6 \text{ eV}$ and work function of the electron analyzer $\Phi = 4.39 \text{ eV}$. This results

in a unique set of EALs $L_{\text{Ta}_2\text{O}_5}(E_{\text{kin}})$ and $L_{\text{Ta}}(E_{\text{kin}})$. Therefore, this equation is a function of the emission angle Φ as well as the kinetic energy E_{kin} of the electrons. The uncertainties on the oxide thickness d and interface width σ , obtained from fitting this equation, can be minimized by increasing the number of analyzed peak regions and emission angles. A detailed error discussion and more information on this equation can be found in reference [97]. The HfO_2 layer does not need to be explicitly considered in our XPS analysis, as Equation B.4 relies on relative signal intensities. Since the HfO_2 layer attenuates both the Ta^0 and Ta^{5+} signal intensities equally, its effect cancels out when calculating their ratio.

Calculation of the effective attenuation lengths (EALs) L and number densities N

Equation B.4 (which is equal to Equation 6.6 in the main text) requires the effective attenuation lengths (EALs) in Ta_2O_5 and Ta as an input parameter. The EAL is a measure of the attenuation of the photoelectrons inside the material, similar to the inelastic mean free paths (IMFPs). However, in contrast to the IMFP, the EAL also considers elastic scattering. Therefore, it is generally considered more reliable and was used in this analysis [98].

Details on the equation used to calculate the EALs can be found in Chapter 6.2.

The parameters used to calculate $L_{\text{Ta}_2\text{O}_5}$ and L_{Ta} and the resulting values for all peak regions investigated can be found in the following two tables B.4 and B.5.

Table B.4: Material meters used to calculate L_{Ta} and $L_{\text{Ta}_2\text{O}_5}$.

	$M(\text{u})$	$\rho(\text{g}/\text{cm}^3)$	$a(\text{nm})$	$E_g(\text{eV})$	Z
Ta	180.95	16.7	0.26	0	73
Ta_2O_5	441.90	8.2	0.23	3.8	26.6

Table B.5: Values obtained for L_{Ta} and $L_{\text{Ta}_2\text{O}_5}$ for each analyzed peak region. The kinetic energy E_{kin} is related to the binding energy E_{BE} via $E_{\text{kin}} = h\nu - E_{\text{BE}} - \Phi$ with $h\nu = 1486.6 \text{ eV}$ and $\Phi = 4.39 \text{ eV}$. For the binding energy, the energy of the larger peak of the doublets was used. For comparison, the IMFPs are calculated using the TPP-2M equation [170], both for the number of valence electrons N_V including 4f electrons (first value, $N_{V,\text{Ta}} = 19$, $N_{V,\text{Ta}_2\text{O}_5} = 68$), and excluding 4f electrons (second value, $N_{V,\text{Ta}} = 5$, $N_{V,\text{Ta}_2\text{O}_5} = 40$) [170].

Peak region	$E_{\text{kin,Ta}}(\text{eV})$	$E_{\text{kin,Ta}_2\text{O}_5}(\text{eV})$	$L_{\text{Ta}}(\text{nm})$	$L_{\text{Ta}_2\text{O}_5}(\text{nm})$	IMFP _{Ta} (nm)	IMFP _{Ta_2O_5} (nm)
Ta 4f	1460.6	1455.3	1.53	1.85	1.18–1.84	1.72–1.82
Ta 5s	1412.3	1409.0	1.49	1.80	1.32–2.05	1.93–2.04
Ta 4d	1257.3	1251.5	1.35	1.63	1.44–2.24	2.12–2.23
Ta 4p	1082.8	1076.8	1.21	1.44	1.48–2.29	2.17–2.29

Additionally to the EALs, Equation B.4 also requires the number densities $N_{\text{Ta}^{5+}}$ and N_{Ta^0} . They are defined as the number of Ta^{5+} or Ta^0 atoms per unit volume and are given in table B.6.

Table B.6: Values of $N_{\text{Ta}^{5+}}$ and N_{Ta^0} used in the XPS analysis.

	$N(10^{22}/\text{cm}^3)$
Ta	5.54
Ta_2O_5	2.23

B.6 XPS peak fitting

XPS peak fitting was performed in casaXPS version 2.3.26PR1.0. Referencing was done by aligning the Fermi cutoff in the valence band to a binding energy of 0 eV [169]. Symmetric peaks were fitted using the Gaussian/Lorentzian product formula $GL(p)$, for which $GL(0)$ is a pure Gaussian and $GL(100)$ a pure Lorentzian. All metallic peaks are asymmetric and were fitted with the Lorentzian asymmetric lineshape $LA(a, b, m)$. It is defined as a convolution of a Lorentzian, with a spread to the left and right defined by the parameters a and b , and a Gaussian with width m .

Where possible, backgrounds were subtracted using the Analytic Shirley background. It has the advantage of showing steps at each peak, which correspond to the additional inelastic scattering of the corresponding transition, equivalently to the Shirley background. Therefore, the background is also physically justified for regions with several peaks. To take account of broad underlying peaks in the background, the Analytic Shirley background has four cross-section parameters. Three of them define the linear, quadratic and cubic coefficients of a cubic polynomial with which the step height is modified. The fourth parameter is an offset in energy. However, the Analytic Shirley background always ends horizontally toward the lower binding energy side. For regions lying on a tilted background, this leads to errors which can significantly change the intensity ratios. Therefore, the backgrounds of the Ta 5s and O 1s regions, which require a tilted background and only span a small energy range, were subtracted using an Offset Shirley background [171]. In the case of the Ta 4p region, the peak region is large and lies on top of a very pronounced peak. Therefore, a Spline Tougaard background was used, which allows for the most flexibility to adapt the shape of the background [171].

For spin-orbit split peak doublets, the ratio of the peak intensities was fixed according to their degeneracy, given by $2J+1$: For the 4f-orbitals the intensity ratio is given by $I(4f_{7/2})/I(4f_{5/2}) = 4/3$, for 4d-orbitals it is $I(4d_{5/2})/I(4d_{3/2}) = 3/2$ and for 4p-orbitals it is $I(4p_{3/2})/I(4p_{1/2}) = 2/1$.

In the Ta 4f peak region, O^{2-} 2s (at 22.3 eV in the 2 nm HfO_2 samples) and In^{3+} 4d (at 18.9 and 19.7 eV in the 2 nm HfO_2 samples) peaks are buried below the other peaks. To minimize errors on the Ta^0 4f and Ta^{5+} 4f peak intensities, the intensities of the O^{2-} 2s and In^{3+} 4d peaks were estimated in the following way: First, the areas of the O^{2-} 1s and In^{3+} 3d peaks were determined in the O 1s and Ta 4p peak region, respectively, where these peaks can be fitted reliably (see tables B.7 and B.8). Then, the corresponding areas of the O^{2-} 2s and In^{3+} 4d peaks were calculated using the corrected relative sensitivity factor (RSF) values at 55 eV pass energy for our instrument. The resulting areas were then fixed in the Ta 4f peak region. For simplicity, the O^{2-} 2s peak was thereby only fitted with one asymmetric peak shape instead of the two symmetric peaks corresponding to the carbonate and hydroxide subpeaks.

Tables B.7 and B.8 provide an overview of all fit parameters of the samples with 2 and 3 nm HfO_2 , respectively. The binding energies and the full width at half maximum (FWHM) values were averaged over all emission angles and gate voltages and the average and standard deviation are given in the tables.

Table B.7: For sample Si/ SiO₂/ Ta (15)/ HfO₂ (2): Binding energies, line shapes, full width at half maximum (FWHM) and background types for the orbitals in all analyzed peak regions. For the binding energy and FWHM, the average and standard deviation of the values from all angles and all gate voltages are provided (if smaller than 0.1 eV, 0.1 eV is estimated as the uncertainty). Large uncertainties in the FWHM are typically caused by large differences in peak size after different gating steps (the smaller the peak, the smaller its FWHM).

Peak region	Orbital	Binding energy (eV)	Line shape	FWHM (eV)	Background type
Ta 4f	Hf ⁴⁺ 4f _{7/2}	17.8 ± 0.1	GL(40)	1.2 ± 0.1	Analytic Shirley
	Hf ⁴⁺ 4f _{5/2}	19.5 ± 0.2	GL(40)	1.2 ± 0.1	
	Ta ⁰ 4f _{7/2}	21.6 ± 0.1	LA(1,7,50)	0.8 ± 0.1	
	Ta ⁰ 4f _{5/2}	23.5 ± 0.1	LA(1,7,50)	0.8 ± 0.1	
	Ta ⁵⁺ 4f _{7/2}	26.9 ± 0.2	GL(40)	1.3 ± 0.2	
	Ta ⁵⁺ 4f _{5/2}	28.8 ± 0.1	GL(40)	1.3 ± 0.2	
	O ²⁻ 2s	22.3 ± 0.2	LA(1,7,150)	5.5 ± 0.1	
	In ³⁺ 4d _{5/2}	18.9 ± 0.2	GL(50)	0.7 ± 0.1	
	In ³⁺ 4d _{3/2}	19.7 ± 0.2	GL(50)	0.7 ± 0.1	
O 1s	O ²⁻ 1s	531.1 ± 0.2	GL(40)	1.4 ± 0.1	Offset Shirley
	O 1s (O-C)	532.6 ± 0.2	GL(40)	2.0 ± 0.1	
Ta 5s	Hf ⁴⁺ 5s	65.9 ± 0.2	GL(75)	4.6 ± 0.9	Offset Shirley
	Ta ⁰ 5s	69.9 ± 0.2	LA(1.4,6,80)	4.2 ± 1.2	
	Ta ⁵⁺ 5s	73.2 ± 0.2	GL(95)	3.9 ± 1.0	
Ta 4d	Hf ⁴⁺ 4d _{5/2}	214.0 ± 0.2	GL(80)	4.1 ± 0.1	Analytic Shirley
	Hf ⁴⁺ 4d _{3/2}	224.9 ± 0.2	GL(80)	4.6 ± 0.3	
	Ta ⁰ 4d _{5/2}	224.9 ± 0.2	LA(1.3,2,50)	3.6 ± 0.9	
	Ta ⁰ 4d _{3/2}	238.0 ± 0.2	LA(1.3,2,50)	4.0 ± 0.8	
	Ta ⁵⁺ 4d _{5/2}	230.7 ± 0.3	GL(95)	3.8 ± 0.6	
	Ta ⁵⁺ 4d _{3/2}	242.5 ± 0.1	GL(80)	3.8 ± 0.8	
Ta 4p	Hf ⁴⁺ 4p _{3/2}	382.7 ± 0.1	GL(85)	5.0 ± 0.1	Spline Tougaard
	Hf ⁴⁺ 4p _{1/2}	439.9 ± 0.1	GL(95)	7.3 ± 0.2	
	Hf ⁴⁺ (sat)	396.4 ± 0.2	GL(30)	5.8 ± 0.7	
	Hf ⁴⁺ (sat)	453.1 ± 0.5	GL(30)	6.0 ± 0.7	
	Ta ⁰ 4p _{3/2}	399.4 ± 0.2	LA(1,7,150)	4.7 ± 1.2	
	Ta ⁰ 4p _{1/2}	458.9 ± 1.1	LA(1,7,150)	7.7 ± 2.6	
	Ta ⁰ (sat)	421.1 ± 0.7	GL(30)	9.4 ± 1.6	
	Ta ⁰ (sat)	484.6 ± 1.7	GL(30)	8.7 ± 2.8	
	Ta ⁵⁺ 4p _{3/2}	405.4 ± 0.3	GL(77)	6.0 ± 1.1	
	Ta ⁵⁺ 4p _{1/2}	466.4 ± 0.4	GL(77)	8.8 ± 1.9	
	In ³⁺ 3d _{5/2}	445.9 ± 0.1	GL(50)	1.5 ± 0.1	
	In ³⁺ 3d _{3/2}	453.4 ± 0.2	GL(50)	1.5 ± 0.1	

Table B.8: For sample Si/ SiO₂/ Ta (15)/ HfO₂ (3): Binding energies, line shapes, FWHM and background types for the orbitals in all analyzed peak regions, equivalent to Table B.7 for the sample with 2 nm HfO₂.

Peak region	Orbital	Binding energy (eV)	Line shape	FWHM (eV)	Background type
Ta 4f	Hf ⁴⁺ 4f _{7/2}	18.1 ± 0.1	GL(30)	1.2 ± 0.1	Analytic Shirley
	Hf ⁴⁺ 4f _{5/2}	19.8 ± 0.1	GL(40)	1.2 ± 0.2	
	Ta ⁰ 4f _{7/2}	21.7 ± 0.2	LA(1,7,50)	0.7 ± 0.1	
	Ta ⁰ 4f _{5/2}	23.6 ± 0.2	LA(1,7,50)	0.7 ± 0.1	
	Ta ⁵⁺ 4f _{7/2}	27.2 ± 0.1	GL(40)	1.9 ± 0.7	
	Ta ⁵⁺ 4f _{5/2}	29.0 ± 0.1	GL(40)	1.9 ± 0.7	
	O ²⁻ 2s	22.1 ± 0.1	LA(1,7,150)	5.4 ± 0.3	
	In ³⁺ 4d _{5/2}	19.8 ± 0.1	GL(50)	1.0 ± 0.1	
	In ³⁺ 4d _{3/2}	20.6 ± 0.1	GL(50)	1.0 ± 0.1	
O 1s	O ²⁻ 1s	531.4 ± 0.1	GL(40)	1.4 ± 0.1	Offset Shirley
	O 1s (O-C)	532.9 ± 0.1	GL(40)	2.0 ± 0.1	
Ta 5s	Hf ⁴⁺ 5s	66.3 ± 0.2	GL(75)	4.8 ± 0.6	Offset Shirley
	Ta ⁰ 5s	70.3 ± 0.1	LA(1.4,6,80)	3.2 ± 0.9	
	Ta ⁵⁺ 5s	73.2 ± 0.2	GL(95)	2.8 ± 1.4	
Ta 4d	Hf ⁴⁺ 4d _{5/2}	214.4 ± 0.1	GL(80)	4.2 ± 0.1	Analytic Shirley
	Hf ⁴⁺ 4d _{3/2}	225.0 ± 0.1	GL(80)	4.9 ± 0.4	
	Ta ⁰ 4d _{5/2}	225.4 ± 0.2	LA(1.3,2,50)	3.0 ± 0.5	
	Ta ⁰ 4d _{3/2}	238.1 ± 0.2	LA(1.3,2,50)	4.1 ± 0.7	
	Ta ⁵⁺ 4d _{5/2}	230.9 ± 0.3	GL(95)	4.9 ± 0.6	
	Ta ⁵⁺ 4d _{3/2}	242.7 ± 0.3	GL(85)	3.3 ± 1.2	
Ta 4p	Hf ⁴⁺ 4p _{3/2}	383.0 ± 0.1	GL(85)	4.9 ± 0.1	Spline Tougaard
	Hf ⁴⁺ 4p _{1/2}	440.3 ± 0.1	GL(95)	7.5 ± 0.2	
	Hf ⁴⁺ (sat)	396.7 ± 0.1	GL(30)	6.0 ± 0.8	
	Hf ⁴⁺ (sat)	454.2 ± 0.4	GL(30)	5.5 ± 0.8	
	Ta ⁰ 4p _{3/2}	399.6 ± 0.3	LA(1,7,150)	5.1 ± 1.0	
	Ta ⁰ 4p _{1/2}	459.6 ± 0.6	LA(1,7,95)	7.6 ± 2.5	
	Ta ⁰ (sat)	420.7 ± 0.2	GL(30)	7.6 ± 1.4	
	Ta ⁰ (sat)	487.1 ± 0.9	GL(30)	3.6 ± 1.6	
	Ta ⁵⁺ 4p _{3/2}	405.6 ± 0.3	GL(77)	7.1 ± 1.2	
	Ta ⁵⁺ 4p _{1/2}	465.3 ± 0.8	GL(77)	7.9 ± 2.7	
	In ³⁺ 3d _{5/2}	446.2 ± 0.1	GL(50)	1.4 ± 0.1	
	In ³⁺ 3d _{3/2}	453.7 ± 0.1	GL(50)	1.4 ± 0.1	

B.7 XPS survey spectra showing the full measured energy range

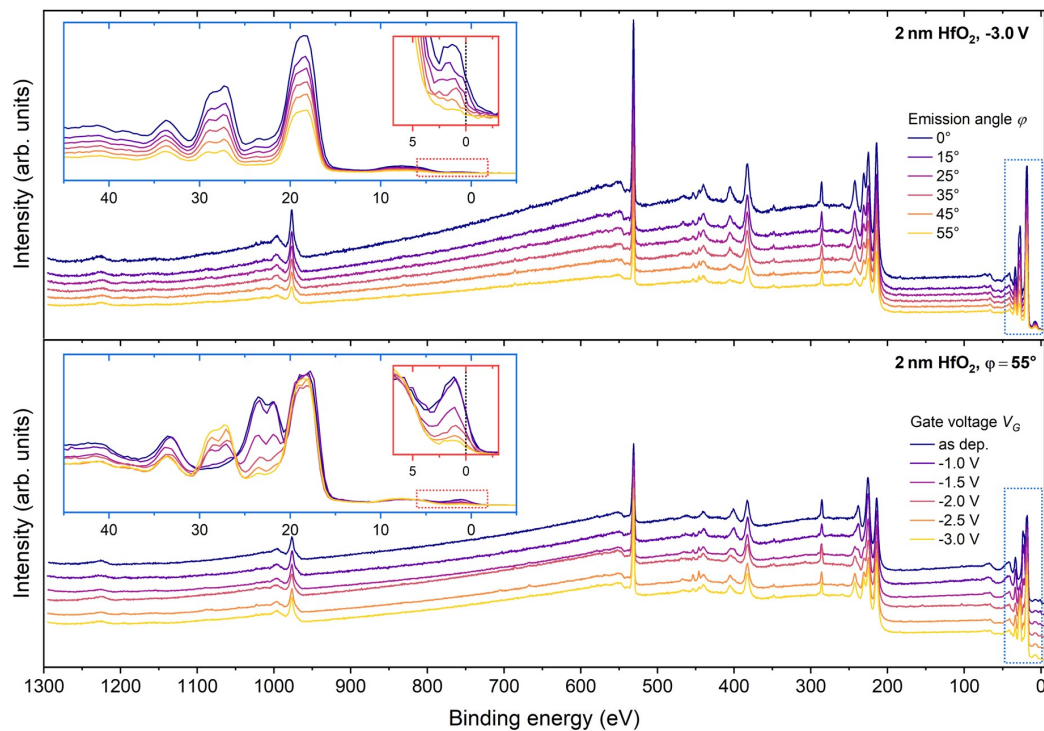


Figure B.2: Survey spectra of the samples with 2 nm HfO₂. Referencing of the binding energy scale was performed by aligning the Fermi cutoff in the valence band to a binding energy of 0 eV, as shown in the inset framed in red. The spectra in the bottom panel (2 nm HfO₂, $\Phi=55^\circ$) were normalized and shifted vertically on the intensity scale for clarity.

B.8 Overview over the XPS fits for all peak regions at all angles and gate voltages

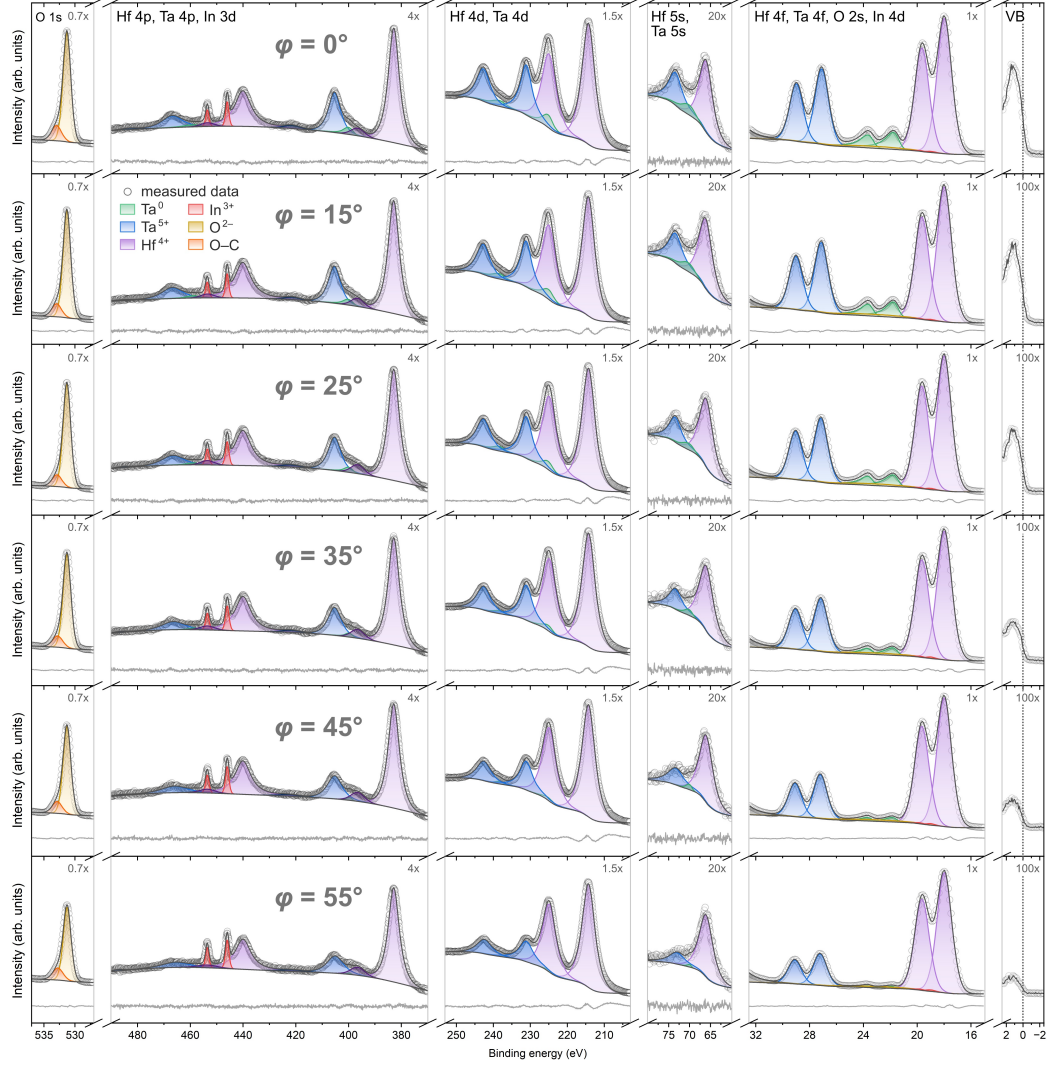


Figure B.3: Overview of the XPS spectra for the sample with 2 nm HfO₂ after -3 V gating for all analyzed peak regions at all angles.

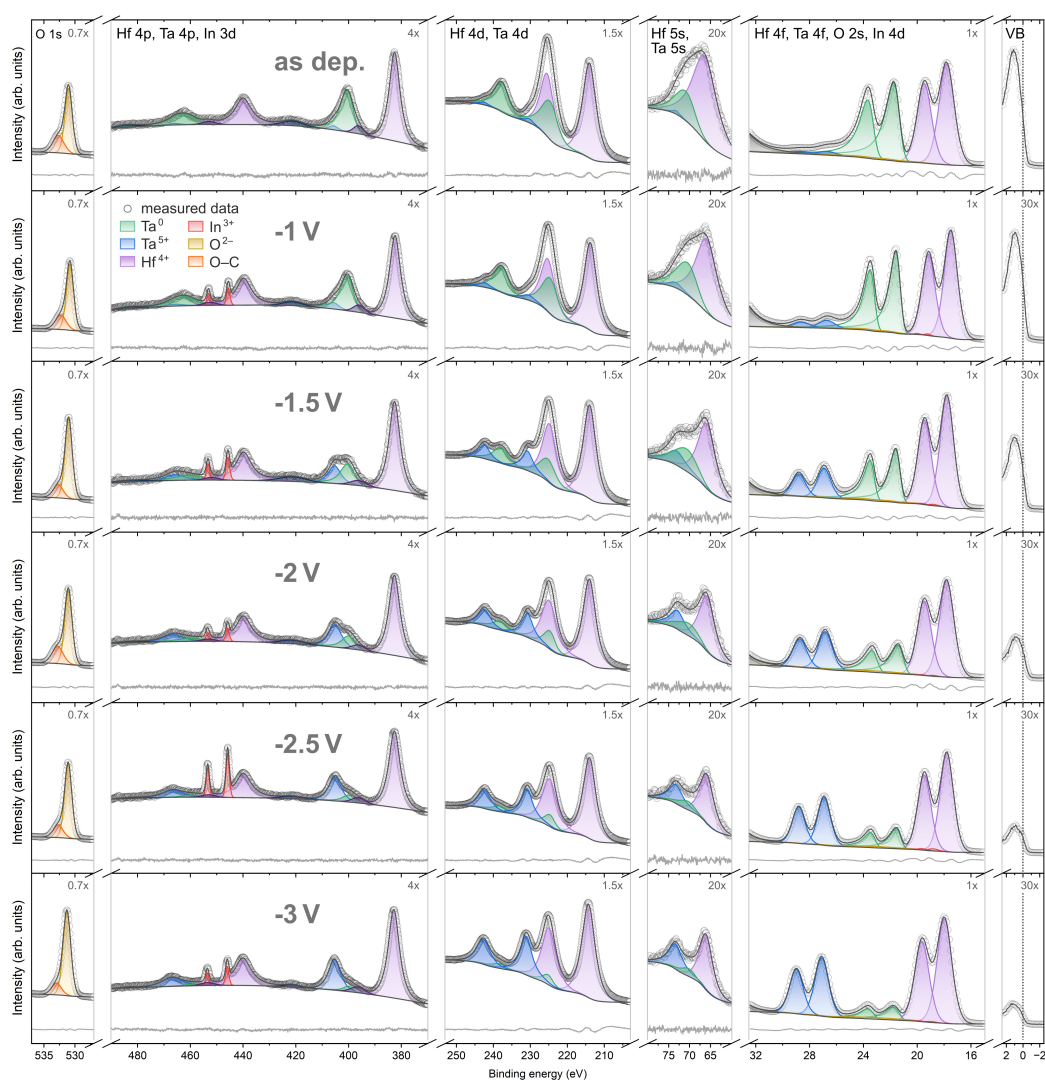


Figure B.4: Overview of the XPS spectra for the sample with 2 nm HfO₂ at 0° emission angle for all analyzed peak regions at all gating steps.

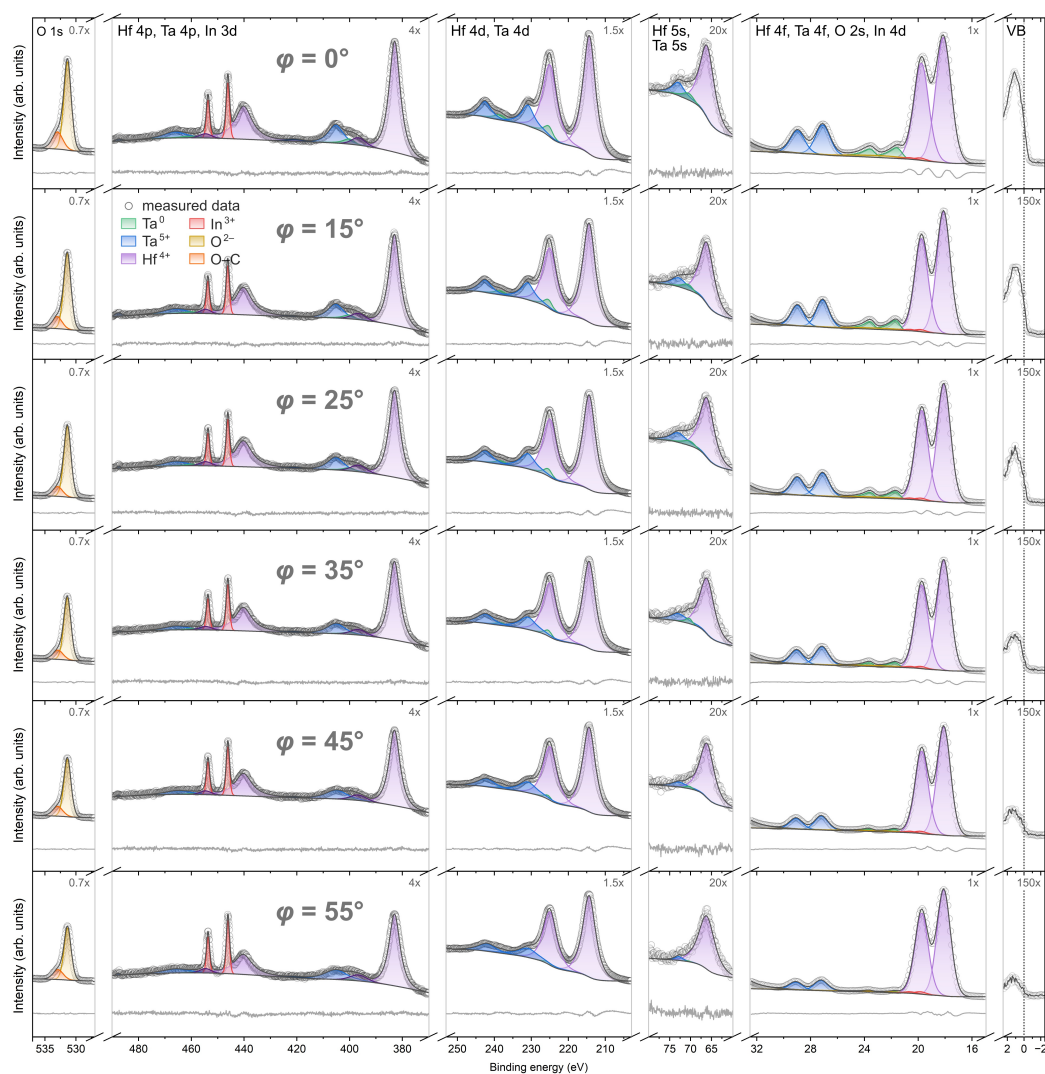


Figure B.5: Overview of the XPS spectra for the sample with 3 nm HfO₂ after -3V gating for all analyzed peak regions at all angles.

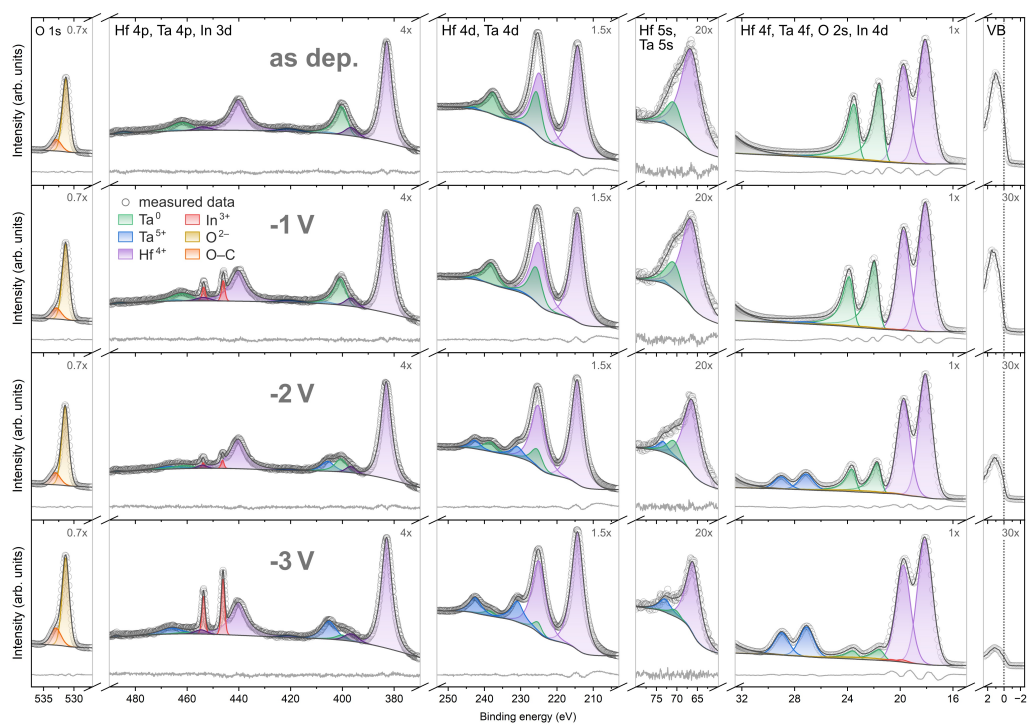


Figure B.6: Overview of the XPS spectra for the sample with 3 nm HfO₂ at 0° emission angle for all analyzed peak regions at all gating steps.

B.9 Calculation of the scattering length density (SLD)

In Figure 6.7c of the manuscript, we show an SLD profile calculated from the XPS results for a direct comparison to the SLD obtained from XRR experiments. The SLD, as given in XRR, is the measure of how strongly a material scatters incoming X-rays. It is given by the electron density ρ_e multiplied by the electron radius r_e . To calculate the electron density, the scattering factors f_0 (atomic form factor, approximately equal to the atomic number Z for small angles θ toward the sample surface) and f' (dispersion correction) have to be considered for each element. The sum of the two $f_1(E) = (f_0 + f')(E)$ as a function of the energy of the incoming X-rays is tabulated on the website ‘The atomic scattering factors’ provided by the Berkeley lab [172]. The first column gives the energy in eV, the second column gives the scattering factors $f_1 = (f_0 + f')$ and the third column gives the anomalous dispersion factor f'' which takes absorption into account and is not required here.

The electron density can be calculated from the product of the scattering factors $(f_0 + f')$ and the number density N of the respective element. For compounds with several elements, the SLD is a function of the energy E and is therefore given as

$$\text{SLD}(E) = r_e N_{\text{FU}} \sum_{i \in \text{FU}} (f_0 + f')_i(E) \cdot m_i \quad (\text{B.5})$$

with the number density N_{FU} of the formula unit and the stoichiometry coefficients m_i of each element in the formula unit.

To calculate the SLD from the XPS depth profiles, the number densities N_{Ta^0} and $N_{\text{Ta}^{5+}}$ obtained from XPS as a function of the z -position were used (see table B.6). The number density of Ta_2O_5 is obtained from $N_{\text{Ta}_2\text{O}_5} = N_{\text{Ta}^{5+}}/2$. Table B.9 provides the parameters for the calculation of the SLDs of pure Ta and Ta_2O_5 . The SLD profile at the $\text{Ta}_2\text{O}_5/\text{Ta}$ interface is obtained by including the z -dependence of the number densities and including both Ta and Ta_2O_5 in the sum defined by Equation B.5.

Table B.9: Parameters for the calculation of the SLDs of pure Ta and Ta_2O_5 at the energy of Cu $K\alpha$ radiation (8.05 keV) as used in XRR. The values of $(f_0 + f')_i$ were obtained from the Berkeley Lab tables at 8047.42 eV for Ta and 8048.79 eV for O.

	$N_{\text{FU}} (10^{22} \text{ cm}^{-3})$	m_{Ta}	$(f_0 + f')_{\text{Ta}}$	m_{O}	$(f_0 + f')_{\text{O}}$	$\text{SLD} (r_e/\text{\AA}^3)$
Ta	5.54	1	67.51	0	8.05	3.74
Ta_2O_5	1.12	2	67.51	5	8.05	1.96

B.10 Investigation of intermixing between Hf and Ta

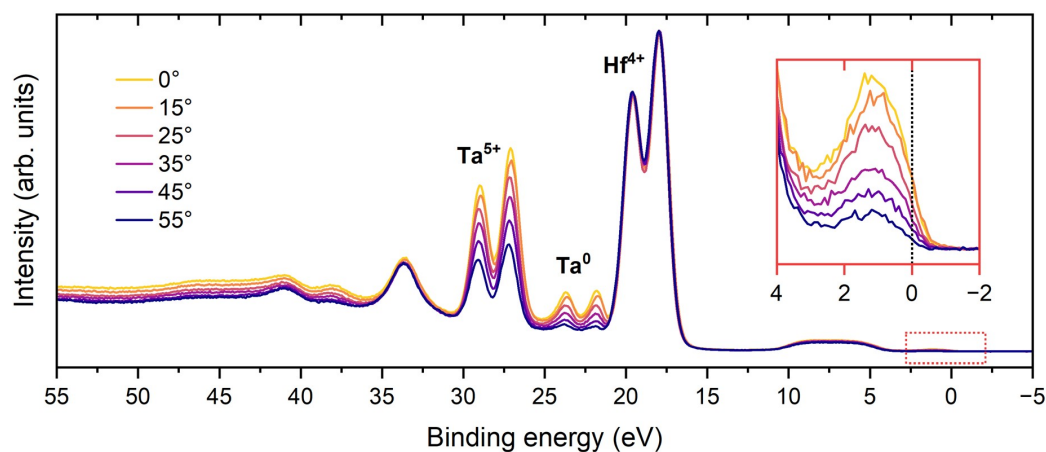


Figure B.7: Comparison between the Ta 4f and Hf 4f XPS peaks at all angles for the sample with 2 nm HfO₂. The data was normalized to the Hf⁴⁺ peaks. Like the Ta⁰ peaks, the Ta⁵⁺ peaks show a clear reduction of the signal for increasing incidence angles. This reveals that the Ta⁵⁺ signal comes from a lower thickness compared to the Hf⁴⁺ signal. This leads to the conclusion that the Ta₂O₅ layer forms at the interface between Ta and HfO₂ and there is no significant penetration of Ta cations into the HfO₂ layer. The inset shows the Fermi edge, which was used for referencing of the binding energy scale.



Use of AI Tools

Table C.1: Use of AI tools in the context of this thesis.

AI tool	Used for	Reason	Where or when
ChatGPT	Checking grammar and spelling, improving phrasing	Better readability	Individual sentences throughout the thesis except for the theory chapter
	Literature research	To find the most relevant literature	For the introduction and to ensure that no important literature was overlooked during the preparation of my papers
	Suggesting L ^A T _E X source code	For mouse-overs and formatting	L ^A T _E X source code
	Python programming support	Minor additions to the code and fixing errors	My self-written Python code for data analysis
Consensus	Literature research	To find the most relevant literature	Introduction and literature research throughout my PhD
Connected Papers	Literature research	To find the most relevant literature	Introduction and literature research throughout my PhD

D

Acknowledgments

Removed due to data privacy

Curriculum Vitae

Removed due to data privacy