ABSTRACT

GRIMLEY, EVERETT DEAN. Quantification of Atomic-Scale Structuring and Polar Phenomena in Oxides and Nitrides. (Under the direction of Dr. James M. LeBeau.)

Recent efforts in the growth and characterization of new complex oxides has yielded a tremendous wealth of material composition-space for use in next-generation electronics. This has happened largely in parallel with the advent of wide bandgap semiconductor technologies which offer new opportunities for high power electronic devices. Both developments necessitate significant work to achieve both integration and suitable material response for a given application or device. Towards this end, this work develops and utilizes advanced electron microscopy techniques and analyses to study new materials with novel functionality. In particular, the structure, properties, and growth qualities of several vogue material systems are explored including ferroelectric hafnia (HfO$_2$) polycrystalline thin films, cadmium oxide (CdO) thin films, and multiple rock-salt oxide and nitride films.

Ferroelectric HfO$_2$ thin films are poised to enable revolutionary new functionality in complementary metal oxide semiconductor (CMOS) technologies. In spite of this, knowledge of the influence of its structure on its properties is still being revealed in many areas, and is necessary to fully harness its potential. Comprehensive scanning transmission electron microscopy (STEM) experiments shed light on many aspects of field-cycling driven changes in microstructure of polycrystalline atomic layer deposition (ALD) grown films as they age. Field-cycling from pristine to wake-up is accompanied by a large increase in remanent polarization. Structurally, cycling is found to drive a bulk phase change that converts some of the non-polar monoclinic phase into the polar orthorhombic phase. Simultaneously, 90° orthorhombic domains are re-oriented and defect-rich tetragonal interfacial layers diminish, also contributing to the wake-up effect. Non-polar/polar monoclinic/orthorhombic interphase boundaries are revealed and show preference for formation across certain orientations. These are discussed in the context of phase transformation and phase stability. Finally, epitaxial relationships between the electrodes and film are investigated to inform a means by which growth
and strain may be controlled.

Functional rock-salt materials are also considered. The integration of CdO thin films on multiple substrates is investigated. This material, which is of interest for mid-infrared plasmonic devices and for use as a transparent conductive layer, is typically grown on highly lattice or symmetry mis-matched substrates. Interface and bulk structures are interrogated for CdO films on MgO-(001) and Al$_2$O$_3$-(00.1) substrates, and the misfit accommodation mechanisms are compared. Rotational variants and threading dislocations are discussed in terms of their influence on carrier mobility in CdO on Al$_2$O$_3$. Furthermore, the structures of HfN, MgO, Mg$_x$Ca$_{1-x}$O, and MnO thin films integrated on GaN-(00.1) substrates are explored. Optimized preparation and imaging conditions are presented for the oxide systems which are of interest to study polar interface compensation mechanisms and to enable integration of oxides onto nitrides. Preliminary evidence finds that Mn(II) and Mn(III) can coexist within MnO thin films which leads to formation of rock-salt and spinel phases in the bulk and surface regions, respectively. MnO lamella preparation is shown to be critical to prevent artificial sample oxidation, as the presence of spinel at the surface is found to relate to film heating during STEM lamella preparation. Further work is proposed to prepare lamellas without oxidizing them to further investigate whether pure films accommodate the polar $\{111\}$-MnO$\parallel$(00.1)-GaN interface through local Mn valence changes. In terms of the $\{111\}$-MgO$\parallel$(00.1)-GaN system, sample baking, low beam currents, and low accelerating voltages enable prolonged ability to image and perform spectroscopy on these materials. Preliminary EELS studies show shifts of the N and O K-edges at the MgO$\parallel$GaN interface which may indicate polar compensation at the interface. Further work is suggested to verify these results.
Quantification of Atomic-Scale Structuring and Polar Phenomena in Oxides and Nitrides

by
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DEDICATION

To God the Father be all glory and honor, forever, Amen. To my wife, Carolyn, to my mom and my dad, to my siblings and in-laws, to my friends and colleagues, and to everyone who has nurtured me into the person and scientist that I am today.
BIOGRAPHY

The author grew up in Texas where he started attending a classical Christian school in fifth grade. He went on to attend Centenary College of Louisiana in Shreveport where he graduated *Summa Cum Laude* with dual B.S. degrees in Biophysics and in Chemistry. He began scientific research in his second semester of freshman year with his adviser and mentor, Prof. Juan Rodriguez, to which he attributes the decision to pursue graduate school and a career in research science.
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Chapter 1

Towards Next-Generation Functional Oxides

Complex oxides provide a wide range of properties and functionalities to the materials toolbox. Many efforts, including like the Materials Genome Initiative [1] are seeking to develop new materials, characterize their properties, understand the physics and chemistry that underpins their behavior, and provide an expanded library of materials for production of next generation technologies. Broadly speaking, oxides are poised to possess a fair market share in the technological advances that await the next few decades. Many of their intrinsic properties, such as dielectric permittivity and ferroic behavior, do not have direct analogues among typical semiconducting materials. For this reason, oxides will continue to provide these functions to electronic devices.

The contents of this dissertation on a Chapter-by-Chapter basis are:

- Chapter 3 begins a series of three Chapters that present some of the first in-depth studies into the structure of ferroelectric HfO_2 thin films. Ferroelectricity in thin film HfO_2 (or hafnia) was recently discovered in 2011 by Böscke and coworkers in 2011 [2], and many aspects of its ferroelectric behavior are still being revealed. In this section, the structure of HfO_2 films are investigated to assist in modeling performance instabilities of the polarization hysteresis. Because the remanent polarization of a ferroelectric is the basis on which ferroelectric memo-
ries work, stability is essential. The results of this Chapter provided insight into underlying changes in film structure with field-cycling, aiding the development of models of wake-up and fatigue, and suggesting routes to further improve the performance of HfO$_2$. These are specifically bulk and interfacial-layer changes that are driven by field-cycling. The results of Chapter 3 are published in Ref.[3], and text and figures from that article are reproduced here with permission from the article copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

• Chapter 4 continues on the subject of ferroelectric HfO$_2$ films, which typically contain multiple phases and must contain domains on the basis of being ferroelectric. In Chapter 4, the grain sub-structure is explored in detail. This involves a discussion of 90° domains in the polar orthorhombic phase, the presence of twin boundaries in the non-polar monoclinic phase, and the existence of coherent interphase boundaries between the two phases. These are discussed in the context of phase stability, phase transformation, and influence on electrical behavior during field-cycling. The results of Chapter 4 are published in Ref.[4], and text and figures from that article are reproduced here with permission from the article copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

• Chapter 5 serves as the final section dealing directly with investigation of ferroelectric HfO$_2$ thin films. Efforts have begun growing orientation controlled [5, 6] and even epitaxial [7, 8] films of ferroelectric HfO$_2$ and ZrO$_2$. This begs the question whether orientation control is occurring in the polycrystalline atomic layer deposition (ALD) samples and whether existing texture might be controlled. In Chapter 5, evidence is presented for certain innate orientation interactions between the polycrystalline TiN and the polycrystalline thin HfO$_2$ films grown with atomic layer deposition. The observed interactions are used to derive models for orientation control on TiN, and other substrates are suggested for strain tuning and possible epitaxy.

• Chapter 6 discusses interface and film structures of CdO thin films grown on MgO and sapphire,
which of are of interest for use as transparent conductive oxide films and for uses in mid-infrared plasmonic devices. The interface structures of CdO thin films are considered and compared between MgO-(001) and Al₂O₃-(00.1) substrates, which both can support growth of high mobility CdO in spite of different types of structural misfit in each case. The interface, strain, and defect structures are considered for the films on the different substrates. In both instances, growth is facilitated adaptations of the interface structures.

• Chapter 7 involves growth of a variety of rock-salt materials on a variety of substrates, though chiefly on (00.1)-GaN∥(00.1)-Al₂O₃. This section is concerned with the desire to engineer polar interfaces between rock-salt oxide materials and wurtzite nitrides. Such interfaces are polar and might compensate the polar catastrophe by generating high-mobility carrier gases at the interface, which are be desirable for forming high-mobility transistors in high-power GaN devices. Towards this end, results from MnO, MgO, and MgₓCa₁₋ₓO films are presented. Sample preparation proves critically important and very challenging for these samples, but optimized preparation and imaging methods are presented. Preliminary electron energy-loss spectroscopy (EELS) suggests that some changes in bonding may be occurring at \{111\}-MgO∥(00.1)-GaN interfaces which require further study to validate and understand. The structures of \{111\}-MgO and \{111\}-MgₓCa₁₋ₓO on (00.1)-GaN are found to be consistent with prior reports. Preliminary results with the newly-developed \{111\}-MnO∥(00.1)-GaN system suggest it may be suitable for spectroscopic studies of polar interface compensation because of the ability of Mn cations to adopt multiple oxidation states that are readily distinguishable within single films. Moreover, MnO possesses low misfit to GaN and thus has largely defect-free interfaces. Films of metal-like rock-salt HfN on different substrates are compared.

• Chapter 8 presents a brief summary of the conclusions of the individual Chapters and provides suggestions for further work to validate, explain, and build upon the conclusions of this work.

Both the development of new materials and the better interfacing of materials with semiconducting platforms will be needed to continue pushing the envelope of possibility in electronic devices.
These efforts motivate the present work. In particular, this dissertation seeks to characterize some of the new generation of oxide and nitride materials to understand how their properties arise and how they can be integrated into various electronic systems. Scanning transmission electron microscopy (STEM) is heavily utilized to this end. It enables direct visualization of the crystal structures, defects, and internal structuring that drives various materials to perform as they do. Moreover, this technique enables visualization of the orientation relationships and macroscopic features that controls the growth and final quality of a film.

An additional common theme is that many of the studies in this work are seeking to understand phenomena resulting from polar structuring within a material. This may be present on the basis of a non-centrosymmetric crystal space group that may be pyroelectric or ferroelectric. Polar phenomena may also be present on the basis of the design of the material system. Polar interfaces within materials have been previously been shown to possess unique properties as will be discussed, and this work seeks to characterize new polar interface systems in an attempt to discern if polar phenomena are occurring.

1.1 A Brief Introduction to Ferroelectrics

Chapters 3-5 are concerned with ferroelectric materials. Following the example of Lines and Glass [9], ferroelectrics can be well described on the basis of a crystal class hierarchy. Of 32 total crystal classes existing on the basis of crystal systems and point symmetries, 21 lack a center of symmetry and are termed “non-centrosymmetric.” 20 of these are “piezoelectric,” which describes the phenomenon by which a material responds to a mechanical stress by polarizing which leads to a measurable voltage. An inverse piezoelectric effect is also possible and technologically useful, where an applied voltage to a piezoelectric material leads to an expansion or contraction of the crystal lattice. 10 of the 20 piezoelectric crystal classes are polar and exhibit a spontaneous polarization. A “pyroelectric” material exhibits a spontaneous polarization and adopts one of these 10 crystal classes when cooled beneath the Curie temperature $T_c$. If this stable spontaneous polarization can be switched between two orientation states using an applied electric field, the material is considered a “ferroelectric.” In
Figure 1.1 Polarization versus voltage hysteresis curve (red trace) with two remanent polarization $\pm P_r$ states indicated by black circles on the red trace at 0 V bias. Coercive fields ($\pm E_c$) and near-saturation $\pm P_{r,\text{max}}$ values are similarly listed. The schematics show the two separate polarization states for HfO$_2$ with the red oxygen atoms showing the atoms that move to render two polarization states. Arrows indicate direction in which polarization sweeps with field. The hysteresis curve is with data of woken-up HfO$_2$ from Ref. [3].

many ways, a ferroelectric is the electrical analog of a re-orientable magnet. Common ferroelectric materials include BaTiO$_3$ and PbTiO$_3$. All ferroelectric materials are pyroelectric. Not all pyroelectric materials are ferroelectric because not all pyroelectric materials have switchable polar moments, i.e. some cannot be reconfigured. Pyroelectric materials that are not ferroelectric include the wurtzites AlN, GaN, and ZnO. Phase transformations from high temperature, high symmetry phases into pyroelectric/ferroelectric phases are complex and are largely outside the scope of the present work. More information on descriptions of such phase transformations, as well as a mathematical description of ferroelectricity, is available in Lines and Glass [9].

One common figure of merit for ferroelectric materials is the remanent polarization $P_r$, which is the polarization that remains in a material in absence of an applied electric field. These states are manifest in the material’s polarization response versus applied voltage. For example, Figure 1.1 shows the polarization-voltage characteristics for a ferroelectric capacitor of HfO$_2$. The loop contains a standard hysteresis-like behavior of a ferroelectric (and analogous to a magnet’s magnetic hysteresis), where two different stable polarization states ($\pm P_r$) are available to the material at 0 V.
bias. The state a ferroelectric adopts at 0 V bias is history dependent. A material will typically have a remanent polarization of nearly 0 as processed and must be poled or conditioned into an initial state (not shown). After this, a ferroelectric can be switched between states, and will traverse its hysteresis curve in a counter-clockwise manner (see arrows). Switching occurs rapidly at applied electric fields that are near the material’s coercive field \( (E_c) \), and the \( \pm E_c \) values are shown in Figure 1.1. With continued application of higher bias fields, a material reaches a saturated instantaneous polarization \( \pm P_{r,max} \), but this value is not maintained in the absence of a field and the material relaxes towards the zero-field \( \pm P_r \) states as bias is decreased to 0. Figure 1.1 shows \( \pm P_{r,max} \) values that are approaching saturation, but to prevent dielectric breakdown the field was not taken to that point. The model schematics show how the HfO\(_2\) structure changes between the \( \pm P_r \) states: the oxygen positions move to change the polar moment of the material. Many useful aspects of material structure and physics can be deduced from the shape of, features in, and evolution of polarization hystereses [10]. Additionally, these curves can be asymmetric and the positive and negative states of the \( E_c, P_r, \) and \( P_{r,max} \) need not be symmetric (i.e. equal in amplitude). Asymmetry of these values can occur for a variety of reasons [10] and can actually be invaluable for some devices [11].

Non-volatile memories utilizing ferroelectrics have been an attractive prospect for computing for several decades. These technologies are expected to enable rapid read/write speeds approximately on the order of standard random-access memories with the capability of safely retaining information for 10 years or longer. Technologies based on the use of ferroelectrics in non-volatile memories have been proposed [12] and fabricated [13] for many decades. Though multiple architectures have been proposed and demonstrated in concept, large scale implementation of these technologies has been hindered by the lack of a material system that retains reliable ferroelectric hysteresis for competitively-scaled film thicknesses (i.e. on the order of 10 nm) [14] and possesses desirable electrical characteristics for retention purposes [15]. For these reasons, ferroelectric memory technology has been stymied compared to that of conventional hard-disk drives and especially recent flash memories. Further details on ferroelectric memories can be found in Ref. [16]. This section (Chapter 1.1) contains introductory material that is relevant to Chapters 3, 4, and 5.
1.1.1 Ferroelectric HfO$_2$

In 2011, Böscke and coworkers published results on ferroelectric behavior in 10 nm thick films of a common material that was not a known ferroelectric: Si doped HfO$_2$ [2]. It immediately sparked interest for use in ferroelectric field effect transistors (FeFETs) and ferroelectric-based non-volatile memory devices [17–19]. First and foremost, the demonstration of ferroelectricity seemed remarkable because HfO$_2$ was already present and utilized in fabrication facilities across the world as a gate dielectric, and had been studied rather intensely as such. Already being present in fabs, it was directly compatible with silicon-based complementary metal-oxide-semiconductor (CMOS) technology. The initial discovery has since inspired a rush of studies, validating the potential for ferroelectric hafnia with/without various dopants/alloys [2, 20–28] grown by multiple deposition techniques [2, 7, 23, 29] and being studied and validated by various groups around the world [2, 5, 8, 29–43].

Naturally, the ferroelectric behavior of HfO$_2$ was not well understood in the years following the first publication. To begin, it possesses a pseudo-fluorite structure rather than the perovskite structure of conventional ferroelectrics. Studies by the structural ceramics communities had established that heating of undoped HfO$_2$ and the related ZrO$_2$ structures introduced phase changes in the sequence from monoclinic to tetragonal to cubic [44, 45]. These polymorphs adopt space groups $P2_1/c$ no. 14, $P4_2/nmc$ no. 137, and $Fm\bar{3}m$ no. 225 [44].

Hafnia had also been studied in the gate dielectrics community for CMOS applications. As device scaling rendered SiO$_2$ leaky, HfO$_2$ became a heavily researched alternative material that was eventually adopted by the electronics industry. The dielectric permittivity was shown to vary considerably between the various different hafnia polymorphs, and doping studies were carried out to control the phase presence to achieve targeted permittivity values [46, 47]. Structural studies were also conducted to understand film structure [48], formation of interfacial layers [49], and stability/formation of secondary phases [50, 51].

The possible stabilization of other phases beyond the monoclinic/tetragonal/cubic polymorphs had also been established. Metastable orthorhombic phases had been reported in both HfO$_2$ and
ZrO$_2$ well before the discovery of ferroelectricity [44, 52–58]. In many of these studies, the orthorhombic phases were considered high pressure phases. Furthermore, these studies did not form a consensus on the space group of the orthorhombic phase, many of them achieving satisfactory refinements of scattering data with multiple space groups. Among these were the $Pbc2_1$ no. 29, $Pbcm$ no. 57, and $Pbca$ no. 61 space groups. Note that $Pbc2_1$ is a non-standard setting of the identical space group $Pca2_1$, with the only difference being a reversal of the assignment of the $a$- and $b$-axes. Since the ferroelectric hafnia community presently utilizes the $Pca2_1$ phase assignment in most occasions, it will be utilized here throughout.

The three “candidate” orthorhombic phases derived from the structural ceramics community are worthy of discussion in a bit more detail due to their unique similarities and differences. This has also been discussed in detail by Trolliard and coworkers for zirconia along with its structure and phase transformations [59], and recently in the context of ferroelectric HfO$_2$ by Barabash and coworkers in a first principles study [60]. First and foremost, the three phases possess effectively identical Hf atom sub-lattices. The phases differ in regard to the ordering of their oxygen atoms. The $Pca2_1$ phase is the only non-centrosymmetric one of the three, and was refined in partially stabilized zirconia by Kisi and coworkers [44] (see Figure 1.2d). It is polar on the basis of its oxygen atoms which can arrange such that the structure is polarized in two states [36] similar to those shown in Figure 1.2b,c. Kudoh and coworkers also obtained satisfactory fits with the $Pca2_1$ phase, but ultimately chose the $Pbcm$ structure for the orthorhombic phase due to better agreement with Raman experiments [52] (see Figure 1.2a).

The $Pbca$ phase is twice the size of the other two phases (it contains eight Hf and sixteen oxygen atoms, compared to four and eight respectively for $Pbcm/Pca2_1$). The $Pbca$ phase is equivalent to an anti-ferroelectric doubling of the $Pca2_1$ phase, i.e. the $Pbca$ cell contains two stacked $Pca2_1$ unit-cells such that their polarizations cancel. For this reason, the $Pbca$ phase is non-polar and is considered an anti-ferroelectric phase. The final phase is the $Pbcm$ phase which is the size of the $Pca2_1$. The $Pbcm$ phase is non-polar on the basis of having eight oxygen sites (of twelve total) that are partially occupied by four atoms such that the the structure has no polarity (see Figure
Figure 1.2 The “prototype” Pbcm orthorhombic phase, showing how different oxygen atom occupancies lead to “Pca2₁-like” and “P2₁/c-like” oxygen orderings. Work by Barabash and coworkers suggests relaxations of these orderings in the Pbcm orthorhombic lead to the Pca2₁-like or P2₁/c cells [60]. Pbcm cell from Ref. [57], P2₁/c from Ref. [54], and Pca2₁ from Ref. [44]. The orthorhombic phases are tilted slightly off the [010]-zone-axis//[100]-upward (using Pca2₁-like axes), whereas the monoclinic is slightly off the [010]-zone-axis//[001]-upward. Large gray are Hf and small black are O (half-filled are half occupancy).
These sites that are randomly occupied correspond to the sites that can order to generate the polar $Pca2_1$ phase (see Figure 1.2b,c) or the anti-ferroelectric, non-polar $Pbca$ phase by forming cell-doubled and anti-aligned $Pca2_1$ unit-cells.

Because the differences in these phases primarily lie in the oxygen sublattice, differentiating between them with scattering experiments poses a tremendous challenge that has yet to be fully addressed even for bulk ceramics using synchrotron and neutron sources. The situation is even worse for the thin film ferroelectrics, where differentiating between the tetragonal/cubic/orthorhombic phases is challenging and requires examining peak ratios and changes in peak positions with doping [61]. In view of this understanding in 2011, signatures of a(n) unrefined high-symmetry phase(s) in grazing incidence X-Ray diffraction (GI-XRD) of the Si doped HfO$_2$ films showing polarization hysteresis led Böscke and coworkers [2] to hypothesize that the same $Pca2_1$ phase refined by Kisi and coworkers [44] was present in their samples, leading to the ferroelectric behavior.

The orthorhombic phase was first identified directly in the ferroelectric films by Sang and coworkers [37] who used HAADF STEM to identify the phases and structures present within them. Their results provided conclusive evidence that (1) an orthorhombic phase existed in the films, (2) that the orthorhombic phase was non-centrosymmetric on the basis of broken mirror symmetry in the position-averaged convergent beam electron diffraction pattern (PACBED, as discussed in Refs. [62, 63]), and (3) that the Hf sublattice was consistent with the “$Pca2_1$-like” family of orthorhombic phases. From this, Sang and coworkers [37] explained the ferroelectricity in HfO$_2$-based ferroelectrics on the basis of a ferroelectric orthorhombic phase of space group $Pca2_1$. Thereafter, Shimizu and coworkers [7] grew epitaxial Y doped HfO$_2$ films and performed annular bright-field imaging which revealed an oxygen sub-lattice more consistent with the $Pca2_1$ phase than the others.

The question naturally arises whether all of the orthorhombic grains are of the polar $Pca2_1$ phase, or whether the $Pbca$ or $Pbcm$ phases might also exist? Based on first principles simulations, the $Pbca$ (anti-ferroelectric) phase is predicted to be stable under certain circumstances [60, 64]. Presence of $Pbca$ has been evidenced experimentally using microscopy of zirconia particles containing metastable orthorhombic phases [65] and coexisting with the $Pca2_1$ phase in islands of zirconia on
sapphire substrates [66].

In terms of the Pbcm phase, a question arises to whether a random occupancy of four oxygen atoms amongst the eight partially-occupied sites is truly physical (see Figure 1.2a)? In the an early work discussed above, Kudoh and coworkers [52] suggested that the Pbcm refinement in their data was likely caused by diffraction from multiple larger domains with opposite oxygen configurations (i.e. domains of regions adopting the structures of Figure 1.2b,c) rather than from a truly “random” configuration of oxygen atoms amongst the fractionally occupied sites. Recent evidence also suggests that certain configurations of oxygen atoms amongst these fractionally occupied sites are much more energetically favorable than other configurations, with the favorable configurations leading to the Pca2₁, Pba, and even to the P2₁/c phase (see Figure 1.2e,f) after structural relaxation using first principles methods [60]. In many regards, these findings of the Pca2₁, Pba, and Pbcm phases suggest that at least functionally, the entire orthorhombic phase can be considered as being comprised of “Pca2₁-like” units that cluster and order to varying degrees. Barabash and coworkers’ [60] findings are highly suggestive that considerable short range ordering of the oxygen sublattices is energetically favorable for hafnia, which leads to the formation of Pca2₁ phase domains, or into the “Pba” ordering of Pca2₁ unit cells.

Much of the current dissertation research was conducted with the goal of bridging present gaps that remain between an understanding of HfO₂ properties and their direct relation to HfO₂ structure. This work places considerable emphasis on comparing the structure of HfO₂ in pristine samples to that of cycled devices in an attempt to structurally explain the evolution of hafnia's electrical properties with field-cycling. The structure/property relationships relating to field-cycling endurance will be discussed in greater detail in Chapter 3. Chapter 4 then progresses to more broadly discuss the native grain and domain structure in samples and the influence of these structures on field-cycling and phase stability. Finally, Chapter 5 explores evidences of natural texturing between HfO₂ and TiN. Through observation, models of preferred texturing are developed which may inform further avenues to improve ferroelectric properties by altering the texture of the substrates.

Finally, it is worth calling attention to several reviews and an article that are very helpful for
learning more about HfO$_2$-based materials and technologies. These include a 1992 review of hafnia as a structural material by Wang and coworkers [45], a comprehensive article on phase transformations and phase relations in zirconia by Trolliard and coworkers from 2011 [59], and a review of ferroelectric hafnia written in 2015 by Park and coworkers [67]. Ferroelectric hafnia is also an old enough discipline that it now has been the topic of several Ph.D. dissertations. At the time of this work, some of these include those of Stefan Mueller [68], Ekaterina Yurchuk [69], Tony Schenk [70], and Milan Pešić [71] from NaMLab gGmbH; Min Hyuk Park [72] from Seoul National University; and Weston Straka [73] from North Carolina State University. All of these are sources of additional information. This section (Chapter 1.1.1) functions as the introduction to Chapters 3, 4, and 5.

1.2 Functional Rock-Salt Systems

Simple binary rock-salt oxides and nitrides are a fairly diverse class of materials that can be utilized in various technologies. They occupy a cubic lattice with space group $Fm\bar{3}m$ no. 225. A select few oxide and nitride rock-salt systems are considered in this work for their advanced properties that allow their use as conductive refractory layers, transparent conductors/tunable plasmonic layers, and as layers to allow oxide growth on nitrides and to form polar interfaces with nitrides.

1.2.1 HfN and TiN: Conductive Metal Nitrides

In terms of the nitrides, rock-salt nitrides are frequently metal-like conductors with very high melting temperatures [74, 75]. Due to their conductivity and heat resistance, they commonly are applied in situations that take advantage of their conductivity and refractory properties [74]. Many different rock-salt nitrides exist including TiN, TaN, NbN, VN, and HfN. TiN has commonly been used in CMOS applications as a diffusion barrier and as a metal contact [74]. For instance, HfO$_2$ ferroelectrics grown with atomic layer deposition (ALD) are commonly grown on polycrystalline TiN electrodes [2, 76]. Superlattices of multiple metal nitrides with lattice and elastic mismatch have been incorporated into coatings for machining and tool coatings as they exhibit significantly enhanced strength [77]. Often, rock-salt nitrides can deviate significantly from perfect 1:1 cation/anion stoichiometry which
can prove frustrating or advantageous to the film grower depending on the circumstances [74]. Recently, HfN film growth was optimized to yield high quality high temperature transducers for time domain thermoreflectance [78]. Chapter 5 discusses local epitaxy and orientation relation between TiN and polycrystalline HfO$_2$ ferroelectric films. Chapter 7 possesses a section considering the structure and interface quality of HfN films grown on various substrates. These HfN films are also considered as a possible electrode layers for textured/epitaxial HfO$_2$ growth and to enable integration of HfO$_2$ ferroelectrics onto different substrates.

1.2.2 CdO: A New Conductive Oxide with Plasmonic Potential

Transparent conductive oxide materials are desirable for applications where a material possesses good conductivity while being transparent to certain wavelengths of light [79]. Commonly, it is desirable for these materials to be transparent to visible radiation for applications like displays, window coatings, and solar panel technologies [79]. This can permit visible light to pass unimpeded while still enabling conduction of current for displays and photovoltaics. On the other hand, for windows, it is desirable that visible light be transmitted while infrared light be reflected to minimize heat exchange [79].

Many transparent conducting oxides have lower free electron concentrations ($\sim$10$^{20}$-10$^{22}$ cm$^{-3}$) than metals (10$^{23}$ cm$^{-3}$) yet higher free electron concentrations than semiconductors ($\sim$10$^{19}$ cm$^{-3}$) [80]. This is not necessarily a problem, and in fact it can be beneficial to be able to tune the conductivity of a material for various applications. The $n$-type conductivity of a semiconductor or conductive oxide is the product of the free electron concentration times the mobility, i.e. $\sigma_e = n\mu_e$. For this reason, tuning of the conductivity of a transparent conductive oxide material depends not only on the carrier concentration, but also on the carrier mobility.

Carrier mobility is also important for a material’s plasmonic properties. Decreased carrier mobility leads to increased dielectric loss which hinders plasmonic performance [81, 82]. In plasmonic devices, certain frequencies of light are absorbed by a material and initiate resonance of a surface plasmon out of the free carriers in the material [80–84]. Since these are surface plasmons rather than
bulk plasmons, they are sensitive to interactions at the surface of the material and thus can be useful for sensors [81, 83–85]. Surface plasmon resonance is highly tunable in transparent conductive oxides where doping can have a strong influence on the quantity of conduction electrons, and moreover, the resonances occur in the mid-infrared which is a useful portion of the optical spectrum for sensing [81, 84].

This section provides some background information for the research presented in Chapter 6, which discusses the film and interface structure of CdO films grown on various substrates for conductive oxide layers and for plasmonic properties. The mechanisms CdO film growth are discussed for two separate cases where large lattice or symmetry misfits are overcome to lead to surprisingly high-quality interfaces and films. The mechanisms of lattice accommodation and the film quality including defects are discussed.

1.2.3 Polar Oxide Interfaces by Design: {111}-Rock-Salt Oxides on GaN-(00.1)

Polar surfaces are by nature thermodynamically unstable [86–88]. By theory of electrostatics, an infinite polar surface with a dipole moment oriented normal to it will possess an infinite surface energy. Real, finite surfaces do not entirely escape the energy cost of an “infinite” polar surface, and finitely-sized polar surfaces still yield surface energies that rapidly diverge with increasing area [89]. Since polar surfaces are so high in energy, materials tend to facet such that non-polar surfaces are exposed. In the event that a polar surface or facet is exposed or grown, the energy of the surface is commonly diminished by passivation by a foreign species, surface rumpling or restructuring, change in surface stoichiometry, or though change in charge distribution at the surface. This is shown by Xu and coworkers [90] for the polar (110) surface of SrTiO$_3$, where heating with *in situ* electron microscopy leads to the formation of a thin TiO$_x$ surface reconstruction to lower the energy of the polar surface. Similarly, Dycus and coworkers demonstrate the formation of surface oxides on GaN-(00.1) and AlN-(00.1) materials which diminish the polarity at the surface [91]. Broadly speaking, different compensation mechanisms can be grouped under the larger umbrellas of polarity mitigation by structural means or by electronic means.
Similarly, a polar dipole moment originating at an interface within a material is also unstable. Interface polarity can arise when a polar material is grown on a non-polar substrate, or by heteroepitaxy of a polar material on another material. Polar interfaces are almost inevitably stabilized by structural or electronic compensation [92, 93]. Polarity at the interface can be accommodated structurally by reconstruction of the interface, changes in interface stoichiometry, and generation of charge compensating defects at the interface including misfit dislocations and stacking faults. By contrast, electronic compensation involves redistribution of electron or hole density to the interface. Two-dimensional electron gases are of particular technological interest for use in functional devices.

Different material systems have exhibited compensation of polar interfaces by forming two-dimensional electron gases. Especially of note are GaN∥Al\textsubscript{x}Ga\textsubscript{1−x}N [94–97] and different perovskite-(001)∥perovskite-(001) systems [93, 98–105]. Different theories exist to explain the source of the free carriers at the interfaces of these materials. For both GaN∥Al\textsubscript{x}Ga\textsubscript{1−x}N [95] and perovskite∥perovskite systems [93, 100, 104, 106], layer thickness proves important for two-dimensional electron gas formation. In the case of GaN∥Al\textsubscript{x}Ga\textsubscript{1−x}N interface, unintentional donor doping (i.e. oxygen vacancies) has been suggested as an origin of the gas [96], and surface states as another possible source [97]. In the case of the perovskite systems, most theories of the origin of the interface metallization involve either electronic compensation by cation valence changes which are accessible in some of the systems [98, 99, 105, 106] or by unintentional doping by off-stoichiometry of oxygen [102, 103]. Other studies suggest oxygen vacancies can only be partially responsible for interface metallization of perovskite∥perovskite systems [93, 100, 106].

Broadly speaking, the structure and bonding/chemical similarity between film and substrate in these two classic systems increases the challenge in interrogating the origins of their respective interface metallization. Systems with increased structural and chemical incompatibility of film and substrate would ease the identification of the origin of interface metallization. In theory, a \{111\}-rock-salt∥(00.1)-GaN interface should be polar [107]. GaN adopts the non-centrosymmetric hexagonal wurtzite structure [108]. For each tetrahedral center in GaN, one nearest neighbor has a slightly smaller bond length from which the [00.1] and [00.\bar{1}] directions are derived, and this
bond length represents the free space between repeating dipole units [109]. On the other hand, the rock-salt structure is cubic and centrosymmetric. In spite of this, the \{111\} planes of a rock-salt contains either pure anions or pure cations, and it thus forms a polar surface. For this reason, the GaN-(00.1)||rock-salt-{111} interface would be polar. Moreover, general structural discontinuity of the (HCP-wurtzite versus a FCC-rock-salt) symmetries, bonding discontinuity of the more covalent GaN versus the more ionic MgO, and general chemical incompatibility of the two species should help minimize various means by which polarity could be compensated by several mechanisms.

Recent technological advancements in thin film growth have greatly improved the ability to fabricate both nitride wide bandgap semiconductors and oxide thin films. As such, the growth of rock-salts and other oxides on nitride substrates has a rather recent history. Initial growth of the polar \{111\}-oriented rock-salt face onto (00.1)-GaN resulted in granular films, indicating a rough, 3D-growth mechanism [110–112]. Layer-by-layer growth was shown to be achieveable with molecular beam epitaxy (MBE) of CaO \{111\} on GaN (00.1) by introducing a water surfactant into the chamber during growth, which served to transiently stabilize the polar surface before dissociating during the formation of a subsequent layer [107]. This method of surfactant enabled epitaxy was then extended to layer-by-layer growth of MgO on GaN, though water vapor was insufficient to oxidize Mg adatoms and growth of MgO ceased after Mg reacted with residual surface oxide on the GaN [113]. Instead, use of pulsed laser deposition (PLD) generated a plasma out of the water vapor, producing species capable of both oxidizing the Mg adatoms and pacifying the polar surface as it grew. Lattice matching of rock-salts on GaN has also been accomplished with layer-by-layer growth of an Mg$_x$Ca$_{1-x}$O solid solution [114]. As Al$_2$O$_3$ templates the GaN, the steps and threading dislocations native to the substrate are preserved in the GaN surface and thus can cause defects in the rock-salt hetero-layers [114]. Work is ongoing to grow step-free and dislocation-free mesas to minimize defect density [115]. The role of defects on properties in rock-salt||wurtzite systems, especially on the mechanisms that mitigate the polar interface, remains to be fully revealed.

This section provides background and introductory information for the research presented in Chapter 7. Chapter 7 discusses new results of the interface structures of \{111\}-oriented MnO, MgO,
and Mg$_{x}$Ca$_{1-x}$O films grown on GaN-(00.1). These layers seek to generate interface metallization states. Optimized sample preparation and imaging methods are presented for the MgO films on GaN, and preliminary evidence finds results that may indicate some polarity compensation is occurring at the interface. Further results are needed to validate these preliminary findings and to explain the origin of what is occurring. The structures of the interface between MgO and Mg$_{x}$Ca$_{1-x}$O on GaN are found to be consistent with prior reports [114]. {111}-MnO||(00.1)-GaN films are grown for the first time and are shown to have a good quality interface. Moreover, evidence suggests that the Mn oxidation state can readily change within the films. Further work is needed to prepare high quality STEM lamella to examine polar compensation at the interface, and routes to achieve this are discussed.
Chapter 2

General Methods and Associated Background

2.1 STEM Imaging

Scanning transmission electron microscopy (STEM), transmission electron microscopy (TEM), selected area electron diffraction (SAED), and convergent beam electron diffraction (CBED) have been discussed extensively over the past few years and are the subjects of several different volumes [116–120]. STEM and TEM are related through the theorem of reciprocity [118]. The complex mechanisms of scattering physics, microscope operation, and contrast generation are well described in these texts. A short summary of STEM is presented here relevant to this work.

STEM operates with a convergent electron beam that is rastered across the sample akin to scanning electron microscopy (SEM), yet the electrons are transmitted through the sample as in TEM. Because the beam is rastered across the sample area and data is collected at each pixel, the image is collected serially over a matter of seconds (typically > 8 seconds). The beam convergence is frequently on the order of 10 to 30 mrad (i.e. 0.57° to 1.72°) in probe-corrected microscopes, and the electrons are relativistic (60-300 keV). Figure 2.1 shows a schematic of a STEM with several components indicated. Electrons are emitted in the electron gun using a thermal source or a field-
emission source. These electrons are then rapidly accelerated to the desired operating voltage. The spectral purity of the electrons (i.e. their energy) can be increased using a monochromator. Without excitation of the monochromator, the electrons are typically within \( \sim 1 \text{ eV} \) of each other. A series of condenser lenses with apertures are used to shape the electron probe, and may be used in conjunction with an aberration corrector to remove aberrations. This beam is then transmitted through the objective lens which focuses the convergent probe on the sample. Beam scan coils (not shown) are utilized to raster the beam over the sample.

A probe-corrected STEM commonly possesses a probe size of 0.8-1.2 Å measured at the full width at half maximum (FWHM). The profile is well modelled by a combination of Gaussian and Lorentzian functions [121], though it can be approximated as a Gaussian for some purposes [122]. This probe is positioned on an electron transparent sample which is inserted into the microscope on a sample rod (see Figure 2.1). Samples are commonly prepared by focused ion beam, by dispersing onto a thin lacy carbon grid in particulate form, or by polishing to transparency using mechanical methods and sometimes Ar ion milling. Best results are often achieved when samples are very thin (below \( \sim 50 \text{ nm} \), and ideally thinner than \( \sim 10-15 \text{ nm} \)). Interaction of the high energy incident beam (blue rays in Figure 2.1) with atoms in the sample leads to generation of X-Rays (purple rays in Figure 2.1) which can be collected by one-or-more energy-dispersive X-Ray spectroscopy (EDS) detectors. Different atoms emit different characteristic X-Rays when illuminated with high energy electrons, as will be discussed later.

Provided that the sample is sufficiently thin, the electrons will transmit through the sample (see red rays in Figure 2.1) and can be detected afterwards by several means. Electrons can be captured on a bright-field detector, a CCD detector, or one (or more) annular dark-field (ADF) detectors. These can be utilized simultaneously in certain instances. Bright-field and annular detectors in the STEM typically act as “bucket” detectors that effectively count electrons that scatter onto them during the time a pixel “dwells” at each sample position, illuminating it with incident electrons. Dwell times per pixel can be on the order of 6-20\( \mu \text{s} \)/pix, and images are commonly 512 x 512, 1024 x 1024, or 2048 x 2048 pix.
A diffraction pattern is formed post-specimen at the plane of the ADF detector (see the Bragg spots in Figure 2.1). Diffracted electrons form discs due to the finite beam convergence of the STEM probe, and thus the Bragg peaks are larger than in conventional electron diffraction. These diffraction patterns are known as convergent beam electron diffraction (CBED) pattern. If the beam is being rastered over the sample, the CBED pattern is a position-averaged CBED (PACBED) pattern that is equivalent to the mean CBED pattern acquired from a sample region [62]. The PACBED pattern gives information about sample symmetry, orientation, and thickness [62, 63]. Note that the ADF detector is typically capable of being rapidly inserted and removed so that PACBED/CBED patterns can be projected onto the CCD (which itself is able to inserted and retracted) for acquisition.

The electrons in the diffracted discs that fall onto the ADF detector generate signal (i.e. “counts”) during imaging which the detector integrates into an intensity for a given probe position. Thus, the quantity of electrons falling onto the ADF detector at a given probe-position correlates to the
intensity of a pixel in a STEM image. One consequence of this is that STEM is an incoherent imaging technique [123]. The inner semi-angle of the ADF detector annulus strongly influences the types of information an image provides about the sample because it includes and excludes certain diffracted beams from falling on the detector. For example, Figure 2.1 shows the entire unscattered beam (i.e. the direct beam) passing through the center of the annulus, so it is not contributing to any counts generated in the ADF signal. The effective “camera length” of the ADF detector can be changed electronically such that the inner semi-angle can be altered to influence the effective inner-angle. This enables including or excluding beams diffracted out to a certain angular range. For example, the camera length could be tuned such that the first diffracted beam on either side of the detector might pass through the center of the annulus without falling on the detector. The type of ADF STEM image is typically referred by the effective inner semi-angle of the detector as low- or high-angle ADF.

High-angle ADF (HAADF) is typically referred to as “Z-contrast” STEM because the contrast scales approximately as $Z^2$, with $Z$ being equivalent to the atomic number of the atoms at which the probe is positioned in the sample [123, 124]. Thus, intensity increases in HAADF STEM as either (or both) atomic number and atom density increases. Lighter elements (i.e. C, N, O, Mg, etc.) generate small signals which can easily be masked in the background of the sample in the presence of much heavier atoms (i.e. Hf, Cd, Ga, etc.). This happens because lighter elements scatter many fewer electrons out to higher angles, and thus the detector counts many fewer electrons at probe locations where only light elements are present. A typical HAADF detector inner angle can be within the range of approximately 50 to 80 mrad.

Decreasing the inner angle to ~30 mrad results in low-angle ADF (LAADF) imaging. In LAADF STEM, coherence effects that de-channel the electron probe play a more prominent role in governing image intensity than in HAADF conditions [125, 126]. As such, distortions due to strain and defects play a more influential role in impacting contrast [125, 126]. Decreasing the inner-angle even further allows annular bright-field (ABF) imaging which allows visualization of light elements like O which scatter electrons weakly out to small angles [127, 128]. Likewise, STEM instruments also can
capture the direct beam using a bright-field (BF) detector, which can provide information about light elements and may be preferable to ABF in certain instances [129]. All of these imaging modalities regardless of the detector configuration, are serially acquired pixel-by-pixel as the beam scans.

The pixel-by-pixel acquisition is one of the chief benefits of STEM, because structural and chemical information can be acquired with local sensitivity [130, 131]. STEM and TEM instruments are frequently equipped with detectors for energy-dispersive X-Ray spectroscopy (EDS) and electron energy-loss spectroscopy (EELS). In EDS, the 60-300 keV incident electron beam excites electrons out of core states and an X-Ray is emitted when another electron falls into this core state. These X-Ray emissions are characteristic of the element. One or more detectors can measure the energy of emitted X-Rays which can be correlated to different atoms present at a site in the sample (see purple rays and EDS detectors in Figure 2.1). Efforts are seeking to understand EDS at the atomic scale and to achieve quantitative agreement with simulation [132–134]. Light elements typically possess poor EDS signals. As such, EELS complements EDS for analysis of light elements [135].

As mentioned, the 60-300 keV electrons emitted by the STEM/TEM electron gun are equivalent in energy to within ~1 eV in energy (measured by the FWHM). This variation in incident electron energy can be decreased substantially with different tiers of monochromators [136]. As electrons are transmitted through the sample, they can excite plasmons (collective oscillations of electrons within the sample) or even excite electrons into unbonded states. These excitations require energy transfer from the incident electrons to the sample which leads to a loss of energy of the incident electrons within the realm of 0.01-2000 eV. Using an EELS spectrometer, the electrons transmitted through the sample can be analyzed in terms of their energy “losses.” This is shown in the schematic as a separation of the individual rays by their energy (i.e. color) in the spectrometer in Figure 2.1. Various losses are characteristic of plasmons in certain materials and of different valence states of the various elements [135]. Variations in the loss-energies and of the fine structure near a loss can correspond to changes in atom valence or bonding environment[135]. In this work, EELS analysis is performed using Gatan DigitalMicrograph. Spectra backgrounds are fit to power laws and are removed for core-loss analysis. Open source analysis tools are also available for this analysis [137].
Further details on STEM and TEM image can be found in Refs. [116–120], EDS in Refs. [116, 138], and EELS in Refs. [116, 135].

2.2 STEM Image and Diffraction Simulations

STEM image simulations enable easy comparison of measured image features to simulated images acquired from known structures. Simulations can be performed on structures where atom positions can be displaced or where species can be vacant or substituted as desired. Because of this control, STEM simulation is a powerful tool for analyzing what contrast would be expected in an image containing a certain image feature. Moreover, quantitative agreement is achievable for atom column intensity between STEM imaging and STEM simulations using either direct [122, 139–141] or statistical methods [142, 143].

STEM and TEM image simulations are typically performed using the multislice algorithm which has been comprehensively discussed by E.J. Kirkland [118]. Briefly summarizing here, this algorithm divides the potential of a large crystal slab of dimensions x,y,z into slices on the order of 1 to 2 Å thick along the beam direction (z). Atoms in each slice are co-planar or nearly co-planar in terms of their z position. Scattering at each slice is considered an independent event (i.e. the probe only interacts with the potential of each slice in sequence and independently of the potential of the other slices), and thus the beam/sample interactions are truncated and more computationally tractable. In this manner, the incident probe wavefunction diffracts from the first slice of the crystal potential, and the resulting probe wavefunction is propagated to the next slice of the crystal potential to diffract, and so-on. This is conducted through the whole thickness of the sample with each new layer modifying the probe that propagated from the previous layer. The entire probe wavefunction interacts with the entire crystal potential of a given slice.

STEM images are composites of the beam positioned at different initial points on the crystal surface. Likewise, STEM simulations must include different initial probe wavefunctions positioned at different initial positions on the sample surface. Because the crystal potential of each slice is unrelated to the initial probe position, the potentials of the crystal slices are typically stored in
computer memory for the duration of the calculation to prevent the need to recalculate them (i.e. for computational efficiency). All of the slice potentials can thus be re-used for the simulation of each probe position. Importantly, atoms are not static in positions within a crystal but are commonly displaced from their mean position. The motion of atoms during STEM acquisition results in thermal diffuse scattering which alters their measured atom column intensities. To incorporate thermal diffuse scattering effects into simulations (which is necessary to match measured intensities to those simulated [139, 144]), it is necessary to perform the entire simulation for several configurations of randomly displaced atoms based on their measured or estimated atomic displacement parameters [118]. The physics and rationale behind all components of this algorithm are discussed extensively elsewhere [118]. The results of this algorithm are reliable and agree quantitatively with experimental images [122, 139].

In multislice image simulations, it is important to match simulation conditions to those of experimental images [145]. This will almost always include matching the probe semi-convergence angle, the microscope accelerating voltage, and the detector inner and outer semi-angles [118]. Likewise, aberration coefficients can be utilized if known. The sampling size of the probe and crystal potential wavefunctions can be chosen, and is always a power of 2 for fast Fourier transform (FFT) efficiency. The Nyquist frequency must be achieved in STEM for the number of simulated probe positions so that outputs possess sufficient spatial frequencies for Fourier interpolation to increase the resolution of simulated images which typically contain many fewer pixels than experiment to increase computation speed [146]. The Nyquist frequency is maintained when \((4a) \times (4b) \times a^2 \lambda^{-2} = x \times y\), where \(a\) and \(b\) are the real-space dimensions of the region the probe is sampling, \(a\) is the probe semi-convergence angle (in radian, i.e. 0.0196 rad for 19.6 mrad), \(\lambda\) is the relativistic wavelength of the electron (i.e. 2.508 and 1.969 pm at 200 keV and 300 keV), and with \(x\) and \(y\) yielding the necessary number of probe positions to meet the Nyquist frequency along \(a\) and \(b\) respectively (details on the Nyquist frequency from Ref. [146] and personal communications with the author). Note that the units should cancel, and thus care must be taken that the units of \(a\), \(b\), and \(\lambda\) are compatible and that \(a\) is in radian. The total crystal potential (which is not necessarily equivalent to
the region sampled by the probe) should ideally be as close to square as possible so that sampling
is equivalently spaced in each direction. Depending on aspect ratio of the region sampled by the
probe, the Nyquist frequency can be solved for the long dimension and then scaled appropriately for
the shorter dimension. Best results are achieved when the pixel values can be reasonably rounded
to the nearest integer. Afterwards, simulation outputs can be expanded using Fourier interpolation
and can be blurred with a Gaussian function with full width at half-maximum of ~0.7-1.0 Å to
incorporate effects of the finite size of the STEM probe which deviates from a perfect point source
[139].

Many software packages are available for STEM simulation using different methods (i.e. not
all with the multislice algorithm) and different computing architectures. Some of these include
QSTEM [147], COMPUTEM [118], Dr. Probe [148], Prismatic [149, 150], and µSTEM [151]. In this work,
an in-house GPU accelerated code for mac OS is utilized using the multislice algorithm. PACBED
patterns can be simulated using COMPUTEM [118] or MBFIT (“Many-Beam dynamical-simulations
and least-squares FITting”) package by K. Tsuda at Tohoku University [152]. In this work, MBFIT
is utilized, which is a Bloch wave approach to determining convergent beam electron diffraction
patterns.

2.3 STEM Lamella Preparation

Many methods can generate a thin lamella for microscopy. The knowledge base of our group
has focused on mechanical wedge polishing [153, 154] using an Allied Multiprep polishing unit
(Allied High Tech Products, Inc, Rancho Dominguez, CA, USA) followed by argon ion milling with a
Fischione Model 1050 (E.A. Fischione Instruments, Inc, Export, PA, USA). In uncommon scenarios
where mechanical polishing may be changing sample microstructure, or where samples do not
argon ion mill well, a normal liftout procedure was utilized using an FEI Quanta focused ion beam
system with 2 kV final polishing capability.

In this section, the general guidelines of wedge polishing and Ar ion milling are given. Many
of these protocols are influenced or derivative of training by former group members J. Houston

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Dycus [134] and Adedapo A. Oni [155], and from Prof. James M. LeBeau. In principle, any method for preparation can be used that generates a relatively undamaged lamella with intact microstructure. For this reason, nothing here should be taken as “hard-and-fast” rules.

1. Section samples into ∼2-2.5 mm squares for cross sectioning or into 2 mm x 1 mm pieces for planview samples. Orient the sample appropriately with the final zone axis in mind. Substrate backs can be scribed lightly to assist sample orientation during cross sectioning.

2. If cross sectioning, glue together the two pieces with the films facing inward (rotate 90° if multiple zone axes are needed using scribe marks as guides) using M-Bond 610 (Micro Measurements, Wendell, NC, USA) or EpoxyBond 110 (Allied High Tech Products, Inc, Rancho Dominguez, CA, USA). Binder or alligator clips can be used to secure samples as they cure.

3. If cross sectioning, cut the ∼2 mm square samples in half after curing to yield two ∼1 mm x 2 mm pieces.

4. Planarize pyrex sample mounts using a worn film with grit size ∼9 µm (diamond or SiC lapping films can be used from a vendor like Allied High Tech Products or Ted Pella Inc), “Full” load, 200 RPM, and with arm oscillation.

5. Use a wax like Crystalbond 509 (Ted Pella, Inc) to fasten two samples onto each stub. The “glue-line” formed by cross sectioning should be mounted as vertically as possible.

6. Polish the first side of the samples using lapping films, arm oscillation, and a load of 3-5 (lower load for more brittle samples). A standard film progression is 15 to 9 to 6 to 3 to 1 to 0.1 (µm grit size) with an RPM progression of 100 to 100 to 100 to 80 to 25 to 30 RPM. Use GreenLube (Allied High Tech Products) with the 1 and 0.1 µm films. A loose rule-of-thumb for material removal for a given film is ∼three times the prior grit size.

7. After polishing the first side with a 0.1 µm film, both samples on each stub should be (nearly) scratch free. For each sample, examine the glue line under an optical microscope and determine if one side of the sample has a narrower glue line. Target this side for wedging, as a thin
glue line is preferable for wedge polishing and ion milling. If both edges are nearly equivalent, choose the side which has better alignment of the two substrate halves. Remove the samples, dab the polished side into a wax bead, and set aside for later. Do not lose the edge with the “better” glue line.

8. Planarize all pyrex stubs with a worn \( \sim 3 \, \mu m \) film at “Full” load and 200 RPM for a few minutes each.

9. Take samples out of the wax bead. Set each one onto a glass microscope slide three-to-four times to minimize the wax on the sample, and set onto a planarized stub. Place one sample on each stub with the “good” edge of the sample slightly (\( \sim < 0.1 \, \text{mm} \)) overhanging the front edge of the pyrex stub. This will cleave off when a wedge is polished into the sample. After a minute or two, move the sample around to distribute wax onto the stub which further decreases the wax layer and prevents gluing of the grid to the stub in later steps. Re-center the sample with the edge overhanging the front of the pyrex as described earlier. Allow the samples to sit on the hot plate for 5 to 10 minutes to settle in the wax.

10. Repeat step 6 for the film/RPM progression through the 3 \( \mu m \) film, using it to achieve a final sample thickness of \( \sim 30 \, \mu m \).

11. For wedging, set the angle to 2-4°. This corresponds 2 to 4 complete turns (corresponding to 1 to 2 mm) of the front left micrometer on the Multiprep. Lower angles yield more thin area, while higher wedge angles are easier to achieve with brittle samples. Begin wedging slowly with 25 RPM, a 1 \( \mu m \) film, and GreenLube, setting the front Multiprep detection micrometer to no more than a few (to perhaps 10) \( \mu m \). Check periodically. Often, the pyrex will begin polishing at the front edge. Ideally thickness fringes will appear in the sample. The front edge will ideally be somewhat smooth in softer substrates, and the glue line will be neat and with good structural integrity (i.e. no broken pieces). Judging by thickness fringes and the smoothness of the edge, the sample can be considered “finished.” Brittle samples can go directly to the ion mill (Step 13). Softer substrates can be polished further with the 0.1 \( \mu m \) film.
with GreenLube and 30 RPM to improve thinness and improve the quality of the edge before proceeding to an optional colloidal silica polish (Step 12).

12. Clean the felt-coated Multiprep platan. With the platan spinning at 150 RPM, coat the felt platan with a thin layer of colloidal silica suspension (such as from Allied High Tech Products, Inc). Lower the sample gently into the felt until the sample is wicking suspension from the felt as visible through the transparent portion of the pyrex touching the felt. Reapply small amounts of suspension when needed as the platan dries (perhaps every 1.5 minutes). Polish for 3 to 10 minutes. When finished, allow water to wash the sample for a few minutes on the spinning platan to clean away any residual silica from the sample.

13. Use M-Bond 610 to affix a grid to the sample using a TEM grid like a Mo 3 mm slot grid (slot dimensions are typically 2 mm x 1 mm in this work). After curing, scribe off any substrate that overhangs the outside of the grid

14. If ion milling is necessary, examine the edge of the sample and visually gauge the thickness. Herein, the Fischione Model 1050 is typically operated with liquid nitrogen cooling. The sample is inserted such that the guns fire directly at the thin wedged edge while the posts are as removed from the beam trajectory as fully as possible. This is accomplished by loading the sample between the mount elevator posts such that the sample is clamped within one of them, and faces towards the other with the thin wedged edge stranded in the center of the slot between them. Loading like this requires a ±90° rotation offset in each recipe step of the Model 1050 software. There is a “handedness” to this: the sign depends on whether the sample faces left-to-right or right-to-left within the elevator clamps, and trial-and-error can show which sign to use. The sample is set to rock between 25-30° during all operation steps, with the proper 90° rotation, and gun angles of ±5°. For a thick sample, iterative 20 minute steps are typically performed with both guns operating at 2.0 kV and with one firing from +5° and one firing from -5°. In the case of a thick sample with iterative premilling at 2.0 kV, once the edge is smooth and full of fringes, the author typically then operates the guns at 1.0 kV for
15 to 30 minutes, and then at 0.5 kV for 20 to 40 minutes. Softer materials typically have recipe steps of 15 minutes, 20 minutes, and 30 minutes at 2.0 kV, 1.0 kV, and 0.5 kV. On the other hand, harder substrates typically need longer mill times at each step, such as 30 minutes at 2.0 kV, 30 minutes at 1.0 kV, and 40 minutes at 0.5 kV. The total 2.0 kV step can be longer (40 minutes to over an hour) if needed. Angles can be experimented with, but there is typically a trade-off between thin samples and redeposition at lower angles.

2.4 RevSTEM, Atom Column Indexing, and Image Analysis

Since STEM images are acquired serially on a pixel-by-pixel basis, any motion of the sample during acquisition can result in shear related distortions. This commonly occurs due to thermal drift. To overcome this, different methods of image acquisition and post-processing can be employed to reduce jitter and distortion in images [156–159]. One method is to use non-rigid registration of atom columns in large series of images to align different frames for frame averaging [158]. In this work, the revolving STEM (RevSTEM) is utilized as developed by Sang and LeBeau [157].

In the RevSTEM method [157], a series of 20 to 40 STEM images are acquired with a small dwell time (2 µs/pix which yields a 1024 x 1024 pix frame time of 2.1 s) and with a 90° rotation of the scan direction between successive frames. As such, each image frame is acquired much more rapidly than standard STEM images which can require several times longer for a frame (8.4 s for 8 µs/pix or 12.6 s for 12 µs/pix). This speed decreases the signal-to-noise ratio of each image frame, but it yields images with less inherent shear distortion. Rotation of the scan direction by 90° between sequential frames effectively “rotates” the drift direction between them. This leads to different shear distortions in each successive image. These shears can be measured and utilized to correct the images using the RevSTEM technique [157].

The shear of each image frame is quantifiable by measuring the variation of the position of the lattice vectors in the image. This can be performed without any knowledge of the sample structure [157]. Figure 2.2a shows an atomic resolution STEM image to demonstrate this process, representing a hypothetical “single image frame” of a RevSTEM series. For post-processing removal of drift
Figure 2.2 (a) STEM image as an example of an image frame (sample courtesy of Craig Eaton and Prof. Roman Engel-Herbert). (b) Normalized radon transformation of subregion indicated in (a). (c) Projective standard deviation of (b). (d) The PSDs of the 40 frames of the low-drift RevSTEM series used to form the image in (a).
distortion, all of the images in the series are rotated to a single reference frame. The normalized radon transformation is acquired from each image (typically using an image subsection rather than the entire image). The radon transformation is a construction commonly used in computer assisted tomographic reconstructions where a two-dimensional projection is projected at a given angle to form a single intensity profile [157]. Figure 2.2b shows the normalized radon transformation spanning $200^\circ$ for the indicated subregion in Figure 2.2a. The arrows indicate radon transformation projection angles where strong oscillations run vertically. These occur at projection angles that are parallel to lattice vectors within the crystal lattice of the image. The strong oscillations in intensity occur because of the strong contrast difference between atom columns and the vacant space between them [157].

Sang and LeBeau [157] recognized that the standard deviation of the normalized radon transformation would be the largest for the projection angles that were along lattice vectors. This can be seen understood by comparing the angles with oscillating intensity (arrows) to the angles between them that possess relatively uniform contrast. The angle-dependent standard deviation will be much higher in the regions with oscillating intensity. Thus, they developed the projective standard deviation (PSD) to locate lattice vectors by taking the angle-dependent standard deviation of the normalized radon transformation [157]. Such a PSD plot is shown in Figure 2.2c for the radon transformation in Figure 2.2b. A comparison of the white arrows in Figures 2.2b and 2.2c shows that the peaks are falling in the same angle location. The position of peaks in the PSD can be readily fit to obtain the angular position of the lattice vectors in the image. On a frame-by-frame basis, these peak locations may shift a few degrees due to drift related image shear. By rotating the scan coordinates a known quantity between successive frames and assuming the sample is drifting linearly, the dilation and shearing of these peaks will change for the different rotation angles. From this, the drift rate and drift direction can be calculated.

Figure 2.2d shows a 2D plot of PSDs for a RevSTEM series (the one used to generate image shown Figure 2.2a in fact). In this instance, there is little to no shifting of the lattice vectors from frame to frame, indicating the sample drift was minimal during acquisition. In more highly drifting samples,
regular oscillations in these peak positions are visible [157]. By fitting these peaks, measurements of drift can be made to remove the influence of drift. Assuming that drift is linear or nearly linear on a frame-by-frame basis (an approximation that is validated in multiple instances [157, 160, 161]), affine transformation matrices can be generated to remove drift distortion from each frame individually. After each frame is transformed to correct for drift shearing, the frames can be averaged together to yield an image with high signal-to-noise ratios and reliable crystallographic features [157, 160–162].

RevSTEM images can provide reliable information regarding the crystallography and chemistry of a sample. This first requires identification of atom column positions in the lattice from which this information can be extracted. This is performed using Gaussian peak fitting of the atom columns and by indexing them into a matrix for analysis [163]. As an example, consider the RevSTEM image in Figure 2.3a of a (052)-oriented CdO thin film on a (00.1)-Al₂O₃ (i.e. c-Al₂O₃). In this example, a question may be asked as to the uniformity of the CdO lattice and if the interface between the CdO∥c-Al₂O₃ alters the lattice strain several nanometers into the sample. In this example, an image subregion is selected for peak-fitting (see Figure 2.3b). Image pixel intensities outside of this are set to zero to preserve the image aspect ratio and to prevent the fitting algorithm from looking for peaks in the c-Al₂O₃ (breaks in symmetry can prevent reliable matrix indexing). The mass centers within this image subregion are then determined and thresholded before Gaussian peak fitting. Note that the fitting protocol and code is available elsewhere [163].

After the peaks are identified, the PSD [157] is performed on the subregion being fit (see Figure 2.3c). In this case, the two ⟨110⟩ lattice vectors contained by the CdO image yield small peaks, while the [010] and [001] lattice vectors yield large peaks. These large peaks are selected for matrix indexing. The lattice vectors here are orthonormal, but this is not a requirement [163]. Figure 2.3d shows the indices of the ~400 atom columns as indexed into a matrix, where the rows are the first index $i$ and the columns are the second index $j$. Note that some of the atoms at the boundary have not been fit (see small arrow), which can relate to the thresholding values, large amounts of distortion, and/or on the subregion choice (atoms near the boundary are often excluded). Figure 2.3e shows a zoomed-in view of the sectioned edge between CdO∥c-Al₂O₃, where some atoms are not indexed.
Figure 2.3 Indexing protocol for image analysis as described in the text. (a) A STEM image from which a cropped image subregion is chosen (b) with other pixel intensities set to 0 to maintain an identical image size. (c) The projective standard deviation from a subregion of (b). (d) Fitted matrix of atom column indices. (e) Index notation plotted onto some atom columns near the cropped boundary. (f) Near-neighbor atom column distances plotted onto the original image.
but the remaining are well fit. The missing atoms could likely become a portion of the indexing if
the image segmentation (see Figure 2.3b) had proceeded slightly further into the Al₂O₃. The indices
shown on the atom columns correspond to \((i, j)\), and the indices increase as shown by the arrows
(compare to Figure 2.3d).

After the atoms are indexed in this manner, quantitative measurement of features in the image is
readily achievable. For example, Figure 2.3f shows colored lines plotted between neighboring atom
columns that indicate the distance (in pixels) between columns. The initial question of whether
strain is penetrating deeply into the sample due to the interface can now begin to be addressed.
Some of the near-neighbor atom distances nearest the interface show expansion and contraction to
the extrema of the colorscale (note the colorscale is set manually). As such, there are some expanded
and contracted near-neighbor atom column distances near the interface, but they do not persist
deeply into the film and are effectively confined to the first layer or two of CdO. Some change in the
CdO lattice occurs locally near the interface, but it does not change the lattice appreciably beyond
perhaps 0.25 nm. Fitting of all CdO atom columns at the interface would enable improvement upon
this understanding slightly.

In Figure 2.3f, the (020)- and (002)-CdO spacings are plotted, but larger distances can also be
plotted as well. Using the matrix of fitted positions, the mean (010)- and (001)- spacings can be
measured. They are revealed to be \(58.45 \pm 0.03\) pixel \((n = 350)\) and \(57.05 \pm 0.02\) pixel \((n = 362)\) (mean
\(\pm\) standard error of the mean). The two lattice spacings appear to be different by \(~2.4\%\). This is
likely due to global residual distortion in the image, which can be linked to scan coil calibration and
other microscope-dependent factors \([161]\). In effect, global residual distortion can result in different
pixel dilations in the \(x\) and \(y\) directions. Global residual distortion is found to be rather constant
within the period of a microscope session and even over the course of a few days or weeks \([161]\).
The impact of global residual distortion can be compensated chiefly by two methods.

Global residual distortion can be measured by acquiring an image of a standard sample with
known structure (such as Si or SrTiO₃) with RevSTEM. These calibration series can be processed,
the atoms fit, and the known lattice vectors measured. From this, an affine transformation can be
developed that shears this standard image to yield the ideal lattice parameters and lattice vector angles. Likewise, a true scalebar for the given magnification can also be extracted from that image. This affine transformation can then be used to correct residual distortion of microscope images acquired the same day or within a few days of acquisition. Correction of residual distortion by this method has allowed precise measurement of Bi$_2$Te$_3$/Bi$_2$Se$_3$ alloy lattice parameters with less than 0.1% error even though the unit cell is quite large [161]. The second method is by measuring the lattice parameters using an internal standard within the image if the lattice vectors are aligned (i.e. for an epitaxial film). In the absence of these methods, the image can only be interpreted in terms of local variations within the image (i.e. only in terms of relative strain). In the present case where the lattice vectors of the film and substrate are not coincident, and without an external reference, leaving them in terms of the strain and comparing the image to itself locally is the best achievable. In this work, the quantitative image analysis is most frequently performed using scripting in Mathworks Matlab.

2.5 Geometric Phase Analysis and Bragg Filtering

Geometric phase analysis [164–166] and Bragg filtering [167] are two additional means used to interrogate and quantify image features in this work. In the case of Bragg filtering, the fast Fourier transform (FFT) of an image is taken. Select $g$ and $-g$ Bragg spots are bandpass filtered with remaining spatial frequencies set to zero. The inverse FFT of this bandpass filtered FFT yields planes in the image corresponding to these filtered Bragg peaks. Disruptions of these Bragg peaks are frequently more readily apparent in images of these sorts [168]. As such, they can be useful for defect analysis and identification.

Geometric phase analysis (GPA) is chiefly used for strain analysis [164–166]. In this method, two or more non-colinear Bragg peaks are selected in the FFT of a “reference” subregion of the sample. Deviation of Bragg reflections from these positions in the reference are measured for FFTs recorded from local regions across the image. Any local deviations in Bragg peaks correspond to local lattice strains. As such, GPA is capable of mapping strain in atomic resolution images and has
demonstrated accuracy of \(\sim 3\) pm for dislocation displacement fields [165]. The resolution of GPA is limited the size of the FFT needed to reliably measure Bragg peaks. GPA can be prone to some artifacts especially when image contrast reversals are present, so care should be taken to check the consistency of results with several sets of Bragg peaks [166]. In some instances, the results can also be compared to strain measurements measured directly from STEM images [162].

In this work, Bragg filtering is accomplished with scripting in Matlab or using the built-in procedures of ImageJ (i.e. crop, FFT, IFFT). Furthermore, this work performs GPA using a script in Gatan DigitalMicrograph called FRWRtools that is developed and distributed by Christoph T. Koch [147]. Different implementations of GPA are available, including one from HREM Research Inc. More details on Bragg filtering can be found in Chapters 6 and 7, and on GPA in Chapter 6.
In this chapter, we begin our discussion of ferroelectric hafnia (HfO$_2$). This study in particular deals with an investigation into the origin of “wake-up” and “fatigue” behavior. Wake-up and fatigue is a common phenomenon in ferroelectrics that describes changes in the polarization hysteresis of a material over time as a ferroelectric is cycled between states. Ferroelectric HfO$_2$ exhibits these behaviors, which is undesirable for memory applications. This section explains experiments that sought to identify the structural underpinnings that might aid the development of models to explain wake-up and fatigue in HfO$_2$ with the ultimate aim of assisting methods to overcome these shortcomings. Background information on ferroelectrics (Chapter 1.1) and on ferroelectric HfO$_2$ in particular (Chapter 1.1.1) is available in the introduction.

The vast majority of the content of this chapter was initially reported in the main article and online supporting information of the publication Ref. [3]:

3.1 Introduction

Research on ferroelectric thin film HfO₂ [2] continues to mature with details of its rich science and functionality beginning to emerge. Though many recent studies have sought to examine general principles of ferroelectricity and stability of various HfO₂ phases [36, 169], perhaps preeminent among the current research efforts of HfO₂ thin films is the investigation of the “wake-up” and “fatigue” effects [29, 31, 170–175], as both phenomena are of crucial relevance for the performance of ferroelectric memories [16, 176]. The phenomenon of wake-up refers to the transition from a pinched hysteresis with a low remanent polarization $P_r$ to an open (depinched) hysteresis during a certain amount of initial switching cycles. Internal bias fields [176] have recently been shown to account for this behavior and have been speculated to be caused by charged oxygen vacancies at top and bottom electrodes [31, 172]. The phenomenon of polarization fatigue is characterized by a gradual decrease of $P_r$ with continued application of switching cycles beyond wake-up [177, 178].

Despite the importance of these phenomena, they have yet to be thoroughly explained for this
rather new type of ferroelectric. To address this lack of understanding, we chose a combined approach of sophisticated electrical and structural analysis. We report the first impedance spectroscopy measurements of ferroelectric doped HfO$_2$ thin films using TiN-Gd:HfO$_2$-TiN metal-ferroelectric-metal (MFM) capacitors at different stages of cycling lifetime. These findings are then correlated to aberration corrected atomic resolution scanning transmission electron microscopy (STEM) measurements. Direct evidence for the evolution of multiple aspects of film structure during field cycling is shown to underlie the observed electrical behavior.

3.2 Results

The electrical response of the Gd:HfO$_2$ MFM capacitors exhibits typical behavior of HfO$_2$ ferroelectrics. Figure 3.1a shows the manifestation of both wake-up and fatigue in the polarization hysteresis whereas Figure 3.1b depicts the evolution of $P_r$ throughout the course of continuous field cycling. Besides the aforementioned changes in the polarization-voltage ($P-V$) hysteresis (loop opening and $P_r$ increase followed by a decrease in $P_r$), the slopes of the saturated hysteresis branches hint at changes in relative permittivity of the film. These changes become even more apparent when measuring the small signal capacitance as a function of applied bias voltage. As expected from the $P-V$ hysteresis, the peaks in the butterfly like hysteresis in relative permittivity $\varepsilon_r$ that result from additional domain wall capacitance during polarization switching [179] first increase during wake-up before decreasing upon further cycling. Interestingly, the minimal relative permittivity $\varepsilon_{r,\text{min}}$ outside these regions, which represents only the dielectric contributions (no domain walls present), exhibits a steady decline from around 33 to 27. Since this value is coupled to the phases present in the polycrystalline film (Figure 3.1c), the question arises whether phase fractions in the bulk and/or at the electrode interfaces are subject to a continuous change during field cycling. For comparison with the data in Figure 3.1a,b, different hafnia phases with their corresponding relative permittivities are shown in Figure 3.1d. From the change in these values, the trend in relative permittivity seems to suggest a change from predominantly tetragonal/cubic phases toward predominantly orthorhombic/monoclinic phases. It should be noted, however, that a signif-
significant polarization is still present in the film even after the $\epsilon_{r,\text{min}}$ dropped to 27. Moreover, judging solely from published X-Ray diffractograms of this sample [37, 169], a predominantly monoclinic to orthorhombic character can be inferred for the pristine case. This seems to partially contradict the electrical results and mandates clarification.

To elucidate the origin of these changes in permittivity, impedance spectroscopy was performed. Impedance spectroscopy provides the potential to identify structural inhomogeneities and their evolution via frequency dependent small signal measurements of the complex impedance $Z$ ($Z = Z' - Z''$) [182]. Bulk ceramics, for which this technique is frequently used, are often represented by parallel arrangements of a capacitance $C$ and a resistance $R$ (an $RC$ element) to account for the dielectric properties and finite conductivity (i.e., nonideal insulating capabilities), respectively. In series with this $RC$ element, an additional resistance contribution is usually included to represent uneliminated resistances of the electrodes, the electrode interfaces, the cables/contacts, and corollary parasitic elements of the measurement setup. In the Supporting Information S1 in the full article (Ref. [3]), a more exhaustive description of this very basic equivalent circuit and its reflection in the frequency dependent behavior of the measured impedance is provided.

In contrast to mm thick ceramics [182], grain boundaries are not expected to necessitate a second $RC$ element in series to the first one. As Figure 3.1c shows, grains span the whole film thickness and should, from a physical point of view, give rise to an $RC$ element in parallel to the $RC$ element of the grains. However, from a mathematical point of view, the two parallel resistances and two capacitances could be condensed into one $R$ and one $C$, respectively. A unique best fit for the two $R$ and two $C$ elements is impossible as it is an underdetermined system. Thus, also for thin films, the modelling strategy does not change and series arrangements of $RC$ elements are primarily used and then later on assigned a physical meaning in all conscience. Differences in interface and bulk properties, for example, can explain the necessity of two or more $RC$ elements in series. The sample studied in this work requires an equivalent circuit of three $RC$-like elements and one series resistance $R_4$ to adequately fit the measured impedance results shown in Figure 3.2a,b (for a mathematical description, see the Supporting Information S2 of the full article in Ref.[3]).
Figure 3.1 a) Hystereses of polarization $P$ (dotted lines) and relative permittivity $\varepsilon_r$ (solid lines) for the three different regimes: pristine (0 cycles), during wake-up (1000 cycles), and during fatigue (215,000 cycles); b) the evolution of remanent polarization $P_r$ and minimum relative permittivity $\varepsilon_{r,min}$ versus number of switching cycles; c) a bright-field STEM image of the complete film stack; and d) literature values of $\varepsilon_r$ for the ferroelectric (FE) orthorhombic (O) $Pca2_1$ and the paraelectric monoclinic (M) $P2_1/c$, tetragonal (T) $P4_2/nmc$, and cubic (C) $Fm3m$ phases. The corresponding $\varepsilon_r$ spans derived from the data in (d) are marked in (a) for comparison. The citations [2] and [48-51] in the table in d) refer in order to Refs. [36], [180], [181], [46], and [47]. From Ref.[3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
Figure 3.2 Results of impedance spectroscopy: a) logarithmic Bode plots of impedance $Z$ with arrows indicating the dominant $RC$ elements in the respective $f$ range and admittance $Y$ (inset); b) Nyquist plots of impedance as well as admittance in both full scale and magnified sections to demonstrate the high quality of the fit throughout the whole frequency spectrum. From Ref. [3], and reproduced with permission from the copyright holder, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
These RC elements and the parts of the film stack they represent are derived in the following. The first RC element consists of an ideal capacitance $C_1$ and a resistance $R_1$, with the latter being orders of magnitude too large to be properly fit within the accessible frequency range. The second RC-like element consists of a finite resistance $R_2$ and a constant phase element (CPE) $Q_2$, which can be considered as a nonideal capacitance. A wealth of potential sources for such nonideal capacitance behavior have been found previously including film roughness [182] as well as inhomogeneities in resistivity and/or permittivity (distributed inplane and/or normal to it) [183–188], which are all possible explanations for the present sample. Finally, the third RC element is given by another ideal capacitance $C_3$ and a resistance $R_3$ on the order of 100 $\Omega$, which is similar to the series resistance $R_4$. Thus, it is likely that this third RC element is more reflective of a nonideal electrode than of a real capacitance, and it therefore likely stems from the interface of TiN to HfO$_2$ or imperfect electrode behavior of the TiN itself. It can be explained by a TiO$_x$N$_y$ interfacial layer formed during the deposition and subsequent annealing process [189–191] or a partial oxidation of the Ti adhesion layer below the Pt pad. Despite the high ratio of roughness to thickness anticipated for an interfacial TiO$_x$N$_y$, this electrode-like layer does not require a CPE for a proper fit. Existence of an interfacial TiO$_x$N$_y$ electrode interfacial layer of $\approx$ 1 nm thickness would result in $\varepsilon_r \approx 6$ for all three stages of field cycling. The scenario of an interfacial layer with such a low permittivity combined with a high uniformity in dielectric and resistive properties is, thus, unlikely. Instead, assuming a layer thickness of $\approx$ 10 nm as would be the case for a partially but uniformly oxidized TiN or Ti layer, the permittivity would be around 60, which is in the range of what has been reported for TiO$_2$ [192].

Comparing the remaining parameters to the actual film, we see that the high resistance $R_1$ together with a capacitance $C_1 \approx 1$ nF (resulting $\varepsilon_r \approx 30$) is exactly expected from the capacitor geometry and the bulk of the thin film. Thus, the second RC-like element has also to be in a thickness range of an interfacial-like layer, but still possesses notable insulating properties with $R_2 \approx 10^5 - 10^7$ $\Omega$. Assuming $\approx$ 1 nm interface thickness, $Q_2$ results in a relative permittivity on the order of that of the bulk dielectric layer for a frequency of 10 kHz. Figure 3.3 summarizes the equivalent circuit with extracted fit parameters at different stages of field cycling and the concluded counterparts for each
Figure 3.3 Film stack with corresponding equivalent circuit and model parameters used to fit the impedance spectra presented in Figure 3.2. Relative standard deviations of all fit parameters are $10^4$ or below. From Ref.[3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
element in the physical film stack. From this overview, some trends can be identified:

1. The resistance of the electrode-like layer \((R_3, C_3, R_4)\) does not change substantially. A drop of the capacitance occurs during the wake-up stage. No CPE was needed to fit the data.

2. The capacitance \(C_1\) of the bulk layer remains nearly constant during wake-up, but drops by 20\% during fatigue. A look at Figure 3.1a reveals the problem with arguing with these values: At 0 V, they are superimposed by domain wall contributions (peaks of the butterfly like curve). Moreover, impedance spectroscopy is not able to account for the evolution of the exceedingly large \(R_1\). However, the static leakage current measurements (see Supporting Information S4 of the full article in Ref.[3]) suggest a resistance degradation of this thickest layer by at least one order of magnitude for the fatigued sample.

3. The dielectric interfacial layer is subject to notable changes of both resistance and permittivity. Its resistance (both the \(R_2\) and the real \(Q_2\) contribution) increases during wake-up, which hints at a reduction in the number of defects, but it then drops by two orders of magnitude during fatigue. Interestingly, \(n\) (exponent of the constant phase element) increases continuously from about 0.87 via 0.91 to 0.93, which represents a decrease in inhomogeneity.

These results also highlight the importance of checking a broad frequency spectrum when arguing with permittivity data, i.e., for temperature dependent measurements to investigate phase transitions. In the present case, the frequency of 10 kHz falls in a range which does not predominantly reflect the dielectric properties of the ferroelectric bulk.

To help explain the impedance spectroscopy and electrical measurements, aberration corrected STEM was conducted on Gd:HfO\(_2\) capacitors in pristine (0 cycles), woken-up (1000 cycles), and fatigued (after onset of fatigue, see Figure 3.1b; 215,000 cycles) states to gain insight into any changes in structure that occur with field cycling. These numbers of cycles were chosen in compromise between a best possibly saturated hysteresis (amount of domains taking part in the switching) and low enough field to avoid an early dielectric breakdown of the lab-scale capacitor stack. The incoherent imaging afforded by high-angle annular dark-field (HAADF) STEM enables direct visualization of
atomic arrangements, which is sufficient to distinguish crystal structures. While STEM is limited in its sampling capabilities, it is uniquely situated over conventional techniques such as X-Ray diffraction (XRD) to address changes in HfO₂ structure with field cycling. Since the target regions in the present sample are cycled HfO₂ areas beneath top electrode pad of a few hundred µm width, they are spatially too small for common XRD without special microspot optics. The use of pad diameters in the millimeter or centimeter range is hampered by the increased probability of including defects that result in dielectric breakdown after only a few cycles or a short of the capacitor from the start. Furthermore, the spatial resolution of STEM enables direct interrogation of the interfacial structure, which is critical to help interpret the impedance spectroscopy results.

Through observation of multiple regions in each sample, all three samples are found to be polycrystalline containing orthorhombic and monoclinic grains of various sizes, including many grains that span the entire film thickness in the direction of growth (such as in Figure 3.1c). Phase fractions are determined by identifying phases in a region with high magnification images and measuring the grain areas from lower magnification images. Further description of this process as well as a practical example of this process is included in the Methods section of this chapter and in Figure 3.10.

Nine regions in both the pristine and woken-up samples and eight for the fatigued are suitable for phase fraction measurement. From pristine to woken-up to fatigued stages of field cycling, the presence of the monoclinic phase decreases from roughly 90% to 20% and finally to 10%, respectively. The remaining regions are all orthorhombic. The STEM phase measurements have estimated error of ±10% to the reported phase fractions (limited by STEM sampling and challenges in measuring area due to grain overlap, localized tilting, etc.). Hence, the phase fractions of the woken-up and fatigued samples are within error of each other. Measurement of phase fraction using a histogram “counting” method by tallying the zone-axis/phase combinations from the different regions yields phase fractions which are in good agreement with the values and trends of the area measurements. Further information on this alternative measurement is presented in the Methods section of this chapter.
Figure 3.4 Tabulated monoclinic (M) and orthorhombic (O) phase fractions measured from the pristine, woken-up, and fatigued samples together with corresponding remanent/maximum polarization $P_r / P_{r,max}$ values. HAADF-STEM images show that the interfacial HfO$_2$ layer undergoes complex changes in interfacial strain and phase presence with field cycling, including some reduction of the presence of the tetragonal phase in the cycled (woken-up and fatigued) samples compared to the pristine. Lattice parameter maps from these regions further highlight the complex interface environments and assist in visualizing strain and phase presence (color-scale ranges set manually to better visualize details). From Ref.[3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
Though the above phase fraction assessments approach the limits of what STEM can provide in terms of statistics, it remains a competitive and realistic approach especially without an easy alternative at hand. Furthermore, the reliability of the phase fraction results is augmented by its good agreement with the findings of the global technique impedance spectroscopy as will be described later. Lastly, it is worth noting that while the polarity of each orthorhombic grain was not sampled individually in this work, it is a safe inference that many of the orthorhombic grains generated by field cycling here are polar. The \( P_r \) increased with cycling suggesting generation of polar grains, and polar orthorhombic grains have been previously isolated in these films [37].

In addition to changes in bulk structure, complex changes particular to the interfacial HfO\(_2\) layers occur with field cycling. For the pristine Gd:HfO\(_2\), some grains exhibit a noticeable transition into tetragonal phase directly adjacent to TiN electrodes (Figure 3.4a). These regions are regularly between half a unit cell to several unit cells thick and they abruptly relax into the bulk monoclinic or orthorhombic phase. These regions are expected to be stabilized by and relate to the defect concentration and strain environment at the interfaces as will be further considered in the discussion. In contrast to the pristine samples, woken-up (Figure 3.4b) and fatigued (Figure 3.4c) Gd:HfO\(_2\) samples exhibit changed and possibly diminished interfacial tetragonal regions, and their presence is often more subtle as they commonly retain some of the symmetry and spacing of the bulk grains. Changes in this interface structure with cycling is likely driven by defect redistribution and phase change/orientation change of grains which both alter the strain environment and occur with field cycling [175].

Both monoclinic and orthorhombic grains were found to undergo relaxation towards tetragonal. The extent of the tetragonal phase shows dependence on many factors including phase of the bulk grain, bulk grain orientation, local strain (which likely depends on the defect concentration in addition to the phase/orientation), and cycling history. Generally, the tetragonal phase appears increasingly present and clear in the pristine samples, and less present and more subtle in the cycled samples. Mapping of local lattice parameters (which can be performed with atom column indexing as discussed previously [163]) enables better visualization of the complex interface environment.
Figure 3.5 HAADF-STEM (above) with accompanying lattice parameter maps (below) for two additional pristine sample regions showing relaxation to tetragonal phase at the interfaces. Films are oriented such that growth direction is the same as presented in Figure 3.4 of the main text. From Ref.[3], and reproduced with permission from the copyright holder, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
Figure 3.6 HAADF-STEM (above) with accompanying lattice parameter maps (below) for two additional sample regions from the woken-up sample. Images exhibit bulk orthorhombic structure which relaxes towards the interface while maintaining the symmetry of the orthorhombic phase. The relaxed orthorhombic further relaxes to the tetragonal phase very near the interface. Arrows guide the reader in the direction where zig-zagging lines have nominally the same spacing. Note the difference in colorscale here compared to Figure 3.5. From Ref. [3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

including the strain gradient and the extent to which the interface layer retains the symmetry of the bulk grain. Images from two different monoclinic grains in the pristine sample demonstrate that relaxation can occur at both top and bottom electrode interfaces and that the symmetry change towards tetragonal is easily recognized along the principal zone axes (see Figure 3.5). Note that the images are oriented such that the growth direction is consistent with that of Figure 3.4.

Additional images are also included from two different grains from each of the woken-up (Figure 3.6) and fatigued (Figure 3.7) samples. The projection of Hf atoms in the \{110\}-type zone axes are more closely spaced than in the \{100\}-type and thus require a smaller colorscale range to accentuate
details in Figures 3.6 and 3.7 compared to Figure 3.5. While both sets of lattice maps might appear to contain pseudo-random distributions of spacings between projected atom positions, the samples are in fact ordered and possess the symmetry of the space group along the given zone-axis. Overlaid arrows in the lattice maps in Figures 3.6 and 3.7 guide the reader to this ordering: zig-zagging lines formed by nominally equivalent spacings in projected atom positions run in the direction parallel to the arrows, and zig-zagging lines normal to the in-plane direction of the arrow alternate between large and small spacings. For the woken-up sample (Figure 3.6), both zones have standard orthorhombic structure in the grain bulk which relaxes into a “relaxed orthorhombic” towards the interface. This relaxed orthorhombic region further relaxes towards tetragonal near the interface. This is especially evident in the O-[101] zone-axis in Figure 3.6. Here, the orthorhombic symmetry is still present in the relaxed region until the HfO$_2$ just borders the electrode, at which point it is nearly tetragonal. For the woken-up sample, relaxation is also evident in the HAADF-STEM images, though it is more readily evident in the lattice maps. By contrast, the fatigued sample in Figure 3.7 does not possess substantial strain at the interface and possesses little tetragonal phase directly at the interface.

The woken-up images highlight how interfacial relaxation and strain are associated with the tetragonal phase at the interface, and shows to some extent how the two phenomena are inter-connected. Changes in interfacial strain and tetragonal-phase symmetry are occurring with cycling. However, it is challenging to quantify the extent to which the tetragonal phase is diminishing with cycling because strain and the tetragonal phase are inter-related. This is compounded by difficulties in comparing relaxation among monoclinic and orthorhombic phases along different orientations with each other. Nonetheless, the comprehensive findings indicate that the tetragonal phase is present in the pristine sample. In the woken-up sample, the tetragonal phase is still present with some evidence of diminishment in its extent. Moreover, it is often directly adjacent to relaxed orthorhombic phase. The fatigued sample exhibits the least tetragonal phase, though there is still evidence for its existence in thin layers directly adjacent to the interface.
Figure 3.7 HAADF-STEM (above) with accompanying lattice parameter maps (below) for two additional sample regions from the fatigued sample. Some tetragonal phase exists at the interface, but it is slight in extent and subtle in symmetry. From Ref. [3], and reproduced with permission from the copyright holder, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
3.3 Discussion

Combining the electrical and structural findings, the following pictures of interfacial effects and bulk effects that change with field cycling can be identified. Beginning with the electrode-like layer (circuit elements $R_3$, $C_3$, and $R_4$), existence of an interfacial TiO$_{x}$N$_{y}$ layer with a high ratio of surface to roughness would necessitate inclusion of a CPE element to properly fit the impedance data. This, however, is not needed for the current fit, which suggests the absence of such a layer. Furthermore, electron energy loss spectroscopy (EELS) found oxygen in the $\approx$ 10 nm thick Ti adhesion layer beneath the Pt electrode (see Figure 3.8), suggesting partial but uniform oxidation of the Ti into TiO$_x$. Integrated spectra from multiple regions within the Ti adhesion layer in the pristine, woken-up, and fatigued samples show uniform presence of oxygen. This oxygen presence within all three samples indicates that the Ti adhesion layer layer oxidizes into TiO$_x$. A characteristic EEL spectrum image from the woken-up sample is shown in Figure 3.8. The spectra integrated from the three separate regions in the adhesion layer are almost identical in oxygen signal, indicating relatively uniform oxygen content within the adhesion layer. Thus, impedance spectroscopy suggests that the equivalent circuit elements $R_3$, $C_3$ do not stem from a thin interfacial TiO$_{x}$N$_{y}$ layer and EELS shows oxidation of the Ti adhesion layer into TiO$_x$.

More importantly, interfacial changes do occur in the thin dielectric layer comprising circuit elements $R_2$ and $Q_2$, and these changes originate from a strained and defective dielectric interfacial layer of tetragonal HfO$_2$. The tetragonal phase and the related strained region appears to change and diminish during field cycling. Impedance spectroscopy reveals that the resistance of this layer increases during wake-up (both in $R_2$ and $Q_2$ contribution), although the thickness decreases. This hints at a reducing number of defects in the layer counteracting and surpassing the effect of physical thickness reduction. Defects can enhance both the charge carrier transport through and the injection of carriers into the dielectric film [193–195]. This was shown in earlier studies for similar films [175]. Adjacent to an oxidized electrode, these defects are likely to be charged oxygen vacancies (O ions scavenged from the HfO$_2$ film). The non-uniform lateral distribution of this tetragonal, defect rich
interface layer in the pristine sample explains the observed constricted hysteresis, which is known to result from internal bias fields (for a detailed illustration, see Supporting Information S8 of the full article in Ref.[3]) [176]. A uniform charge accumulation at one electrode can result in a so called imprint [10, 16, 196], as was observed by Lomenzo et al. [172] for a pristine Si:HfO$_2$ sample with TaN electrodes. Since oxygen vacancies stabilize the tetragonal compared to the monoclinic bulk phase [169], the result of tetragonal regions being defect rich and thus, charged regions, is plausible. A recent simulation approach [175] and other studies on hafnia [197, 198] also support a redistribution of interfacial oxygen vacancies during field cycling in similar films.

Moreover, a templating effect by the pre-deposited crystalline TiN electrode on the anneal of amorphously deposited Gd:HfO$_2$ films should be considered. During the subsequent anneal, the HfO$_2$ likely starts crystallizing beginning at the electrode interfaces with a structure more compatible to the cubic TiN lattice which then relaxes after the strain relaxes away from the interface. Evidence of an orientation relationship was found in STEM, and can even be seen in the pristine sample in Figure 3.4. Moreover, first principles studies have explored the nuances of formation of higher symmetry phases (i.e., orthorhombic, ferroelectric orthorhombic, and or tetragonal), finding that
strain and surface energy effects play a crucial role in stabilizing them over the monoclinic phase. [34, 36, 199] The presence of an interfacial layer that is involved in the wake-up process is consistent with recent electrical work on Hf$_{1-x}$Zr$_x$O$_2$.[173, 174, 200]

Finally, for the bulk of the films (circuit elements $C_1$ and $R_1$) a transformation from monoclinic to orthorhombic phase HfO$_2$ is found. Only 10% of the grains were orthorhombic in the pristine sample, but remanent and maximum polarization are found to be 40% and 70% of the value after 1000 cycles, respectively (see Figure 3.4). This strongly suggests that part of the transformation already took place during the very first $P-V$ measurement (see Supporting Information S7 of the full article in Ref.[3] for further insights into the evolution of the first $P-V$ hysteresis loops and XRD data). The similar amount of orthorhombic phase found during wake-up and fatigue is consistent with Figure 3.1b indicating that the present domains get stuck after the maximum $P_r$ was reached around 5000 cycles. Of course, besides the mentioned limitation of sampling of the STEM approach, texture might serve to hamper quantitative statements. Texture also needs to be considered when interpreting former results of microspot XRD in Bragg Brentano geometry, which did not give strong indications of a structural change during wake-up in a similar sample. [169] The tetragonal $P4_2/nmc$ to the orthorhombic $Pca2_1$ phase transformation barrier has been calculated to be $\approx 30$ meV per ZrO$_2$ formula unit (f.u.) [33, 36]. From a (orthogonalized) monoclinic $P2_1/c$ phase to the FE phase, several 100 meV (per HfO$_2$ f.u.) are anticipated [201]. Materlik et al. [36] reported that 1 MV cm$^{-1}$ reduces the ground state energy (not the barrier) of the FE phase by around 10 meV. The effect on the barrier can, thus, be expected to be in the same order of magnitude. The redistribution of oxygen vacancies from the interface into the bulk is expected to result in an additional leverage to surmount the energy barrier. Leakage current measurements indicate an increasing amount of bulk defects in the layer with field cycling. With the applied methods, it cannot be explicitly determined if these defects act as pinning centers for the domains and consequently induce fatigue, but there is a correlation of the onset of fatigue and the leakage current increase similar to what has been demonstrated for Sr:HfO$_2$.[175]

As a final note, this work further stresses the importance of optimizing processing conditions.
to yield interfacial layers that contribute minimally to wake-up and fatigue effects. Previously, Hoffmann et al. [169] pointed out the structural (certain extent of orientation relationship, lateral grain size confinement, nucleation sites during crystallization of HfO$_2$, maybe strain) and chemical role (oxygen is scavenged from HfO$_2$ and resulting vacancies destabilizing the monoclinic phase) of the electrode for the stabilization of the ferroelectric phase. Schenk et al. [176] examined internal bias fields similar to what was found in conventional ferroelectrics and concluded that similar routes could be used to prevent their formation, which include:

- finding proper annealing conditions;
- carefully adjusting the stoichiometry of HfO$_2$ regarding O and dopant content;
- use of inert electrodes.

Our results confirm and provide a structural understanding of these phenomena and serve to further emphasize the importance of engineering high quality interfaces between HfO$_2$ and electrodes. First attempts at devices with Pt [29, 30], Ir [32, 35, 202], and RuO$_2$ [191] electrodes exist, but none of them yielded a dramatic improvement of the endurance performance. In fact, in some cases $P_r$ seemed compromised compared to TiN. Other studies showed the impact of annealing conditions [203, 204] and Hf$_{1-x}$Zr$_x$O$_2$ stoichiometries [200] on the wake-up behavior, which proves that the interplay between ferroelectric and electrodes is more complex. Simply exchanging the electrode material is not expedient and a careful adjustment of other process parameters is additionally mandated to make HfO$_2$ fully competitive for memory applications. The present work, thus, provides helpful instruments for the route forward.

### 3.4 Conclusion

To summarize, we present work that synergizes the global impedance spectroscopy technique with the site specific and in-depth structure analysis afforded by HAADF STEM. Combined, the two provide insight into the evolution of structure that underlies wake-up and fatigue in FE-HfO$_2$. 
thin films. This evolution was separated into bulk and interface changes. The wake-up regime is governed by (1) a phase transformation from monoclinic to orthorhombic grains (bulk effect) as well as (2) changes in and diminishment of a nonuniform, defect rich, tetragonal HfO\textsubscript{2} layer near the electrodes (interface effect). These findings explain the increase in $P_r$ and the opening of the initially constricted $P - V$ hysteresis. The fatigue regime is characterized by an increase in the bulk defect concentration, which is proposed to give rise to domain wall pinning.

3.5 Experimental Section

3.5.1 Growth and Electrical Characterization

Gd-doped HfO\textsubscript{2} thin films capacitors between TiN electrodes were deposited and processed by methods previously outlined \cite{169}. A 650°C anneal in N\textsubscript{2} ambient for 20 s was used after top electrode deposition. Polarization and small-signal capacitance measurements were performed at different stages of field cycling using a TF Analyzer 3000 (aixACCTSystems). Polarization hystereses were recorded at a frequency of 1 kHz. A triangular large-signal voltage excitation was used with a modulated 10 kHz small signal of 150 mV amplitude to record the capacitance-voltage characteristics. Impedance spectroscopy was conducted with an HP 4294A (Agilent Technologies). Small-signal amplitude was the same as for the $C - V$ measurements and a point averaging factor of 25 was applied. Details about the choice of the equivalent circuit as well as about the fitting procedure can be found in the Supporting Information S2 and S3 of the full article in Ref. \cite{3}.

3.5.2 STEM Sample Preparation and STEM/EELS Acquisition Parameters

Cross-section samples for STEM were prepared using either an FEI Quanta Focused Ion Beam or an FEI Helios nanolab 600i. STEM images were recorded with a probe-corrected FEI Titan G2 60-300 kV operated at 200 kV with a beam current of \sim 80 pA, a probe semi-convergence angle of either 13.5 or 19.6 mrad, and an HAADF detector inner semi-angle of 77 mrad. STEM images were acquired and processed with the RevSTEM technique including 20-40 1024 x 1024 pixel frames with a 2 $\mu$s
pixel\(^{-1}\) dwell time and a 90° rotation between each successive frame [157].

EEL spectrum imaging was performed on a probe-corrected FEI Titan G2 60-300 kV equipped with an X-FEG source and a Gatan Efinium EELS Spectrometer. The microscope was operated at 200 kV with a probe semi-convergence angle 19.6 mrad. The EELS entrance aperture semi-angle was approximately 39 mrad, the energy resolution was approximately 1 eV, and the dispersion was set to 0.25 eV/channel.

3.5.3 HfO\(_2\) Phase Determination and Image Simulations

HAADF-STEM simulations were conducted for monoclinic (M) and orthorhombic (O) phases oriented along various zone axes to assist in phase identification (see Figure 3.9). Distinguishing the monoclinic and orthorhombic phases can be done rapidly for some zone axes, but it can be a non-trivial problem for other zone axes, especially for images from experiment. For instance, the monoclinic [001] and the orthorhombic [001] zones are nearly identical, and lattice parameter measurements must be used to distinguish one from the other. Additionally, the monoclinic and orthorhombic \(\langle 110 \rangle\) family of directions can also be challenging to distinguish from one another. Thus, correct phase identification often depends upon plane spacing and angle measurement, nearest-neighbor distance measurement, visualization of slight periodic displacements or zig-zagging of atom columns, and by use of the fast Fourier transform. The RevSTEM technique [157] used to acquire the images in this work has demonstrated ability to measure lattice parameters from STEM images with accuracy and precision [161]. For this reason, it is well suited for measuring structure features in HfO\(_2\). This is especially the case when measurements can be compared to similar measurements acquired from simulated STEM images.

Simulations were performed using an in-house, GPU-accelerated implementation of the multislice simulation algorithm. Simulation by the multislice method has been extensively covered elsewhere [118]. Supercells with lateral dimensions of approximately 2 nm by 2 nm and thicknesses of approximately 10 nm were simulated for the various phases and zone-axes. The simulated conditions matched those from experiment (200 kV accelerating voltage, -6 micron \(C_{(3,0)}\), 2.5 mm \(C_{(5,0)}\),
Figure 3.9 Simulated HAADF-STEM images for orthorhombic, monoclinic, and tetragonal phases viewed along the given zone axes. From Ref. [3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

19.6 mrad probe semi-convergence angle, and detector inner and outer semi-angles of 77 and 260 mrad respectively). The crystal and probe wave functions were sampled approximately every 2 pm. The simulated images were expanded using Fourier interpolation and were convolved with a 0.1 nm full-width at half-maximum Gaussian function to approximately account for the finite size of the electron source.

3.5.4 STEM Measurement of Phase Fractions

Two methods of phase fraction measurements were used. For the phase fractions presented in the main text, measurements of phase fraction for the three samples are made by identifying the phases in high magnification atomic resolution images, and then coarsely measuring the area of those regions in lower magnification images. Practically, this is accomplished by importing a low-magnification image into Matlab. The ROIPOLY function is used to 1) generate a binary matrix corresponding to the grain area from the parent image, 2) summing the binary matrix to calculate the binary area, and 3) multiplying by the pixel area. The process of identifying a grain from a high-magnification image and measuring its area from a low magnification image is presented in Figure 3.10. Errors in these measurements arise due to difficulty in properly assigning the boundaries for the grain area, which are obscured by grain overlap. Additionally, tilting, poor contrast, and grains extending beyond the acquisition frame hamper the procedure. These contributions to error can be
For area based phase fraction measurement, grains are a) identified from high-magnification images (here the grain is [111]-oriented monoclinic) and b) their area is measured from lower magnification images. In b), the white “polygon” mask overlaid on the STEM image shows the complex polygon measuring the extent of the grain. A given sample region may contain multiple phases and zone axes, and must be binned accordingly into monoclinic or orthorhombic. From Ref. [3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

In the current work, measurement of areas from eight to nine regions in each sample is expected to be sufficient sampling for several reasons. First, and foremost, the values given make qualitative sense – as deposited pristine films are found to contain significant amounts of monoclinic phase (compare also GIXRD results of section S7 in the full article in Ref. [3]), which is the thermodynamically stable phase of hafnia [36]. With cycling, the films change to primarily orthorhombic, which explains an increase in remanent polarization. Secondly, the phase fractions of the woken-up and fatigue samples are found to be within error of each other which is expected since phase conversion is anticipated to be complete or nearly complete by wake-up. As such, the measured phase fractions are in good agreement with the electrical measurements in this regard.

Although the area measurements are reliably self-consistent, it is possible to consider measurement of phase fractions in a purely counting fashion. Thus, as a second method to crosscheck the area method, a histogram was constructed of phase presence based on unique, spatially separated phase and zone-axis combinations spanning all the observed regions. In this method, the extent of substantial, which limits the precision of area based phase measurements.
Table 3.1 Phase fractions based on the HAADF-STEM results for the pristine, woken-up, and fatigued samples using the area method (most reliable) and the histogram method. From Ref.[3], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

<table>
<thead>
<tr>
<th>Cycling Stage</th>
<th>Counting Method</th>
<th>Monoclinic Phase</th>
<th>Orthorhombic Phase</th>
<th>No. of Regions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>Area</td>
<td>90% +/- 10%</td>
<td>10% +/- 10%</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Histogram</td>
<td>67%</td>
<td>33%</td>
<td>10</td>
</tr>
<tr>
<td>Woken-Up</td>
<td>Area</td>
<td>20% +/- 10%</td>
<td>80% +/- 10%</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>Histogram</td>
<td>30%</td>
<td>70%</td>
<td>9</td>
</tr>
<tr>
<td>Fatigued</td>
<td>Area</td>
<td>10% +/- 10%</td>
<td>90% +/- 10%</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Histogram</td>
<td>12.5%</td>
<td>87.5%</td>
<td>8</td>
</tr>
</tbody>
</table>

A phase (i.e. the area) is disregarded, and instead each unique spatially separated phase/zone-axis combination in a given sample region can be tallied and given equal weight when calculating the film phase fractions. This approach is considered inferior to the area measurement of phase fraction as grain size can vary considerably which gives unfair weight to the size of some grains. However, the histogram method does present a means to confirm the area measurement in the absence of another technique.

Within the estimated uncertainty (10%) of the area measurement, the histogram approach reproduces phase fractions obtained by the area measurement for both the woken-up and fatigued samples (see Table 3.1). The histogram method found a greater orthorhombic phase fraction in the pristine sample than did the area measurement by about 20% (without including the 10% uncertainty), though the films were still found to be majority monoclinic by this measure, and as such the agreement for the pristine sample is considered good. The histogram method reproduces the trend of phase evolution from monoclinic to orthorhombic with field-cycling. As such, in all respects we find that the histogram method confirms the findings of the more reliable area measurement.
3.5.5 Comparison to the Ferroelectric Rhombohedral Phase

After publication of the article described in this chapter (Ref. [3]), several later publications have described additional hafnia polymorphs that are worth comparing to the results of this Chapter and the following two. Beyond the standard ferroelectric orthorhombic phase, Barabash in Ref. [205] predicted several new metastable polymorphs of pure HfO$_2$ including the rhombohedral $R3$ phase (no. 146) which is non-centrosymmetric. This prediction was timely, as shortly thereafter Wei and coworkers reported that epitaxial ferroelectric Hf$_{0.5}$Zr$_{0.5}$O$_2$ thin films grown on La$_x$Sr$_{1-x}$MnO$_3$ buffered SrTiO$_3$ contain a rhombohedral-like ferroelectric phase based on imaging and diffraction [8]. In searching for a polar rhombohedral phase using DFT, Wei and coworkers identify that ZrO$_2$ and HfO$_2$ can form the weakly polar rhombohedral $R3m$ phase (for HfO$_2$, 158 meV per formula unit (f.u.) is the energy difference between the monoclinic and $R3m$ phases). Additionally, they calculate that pure HfO$_2$ can form a highly polar rhombohedral $R3$ phase at 195 meV/f.u. above the monoclinic (similarly, Barabash found it to be 216 meV/f.u. above the monoclinic). Schematics of this $R3$ rhombohedral phase are shown down several projections in Figure 3.11. Importantly, Wei and coworkers showed that substitution of Zr for Hf in the HfO$_2$ cell destabilized the $R3$ phase. Furthermore, they demonstrate that the weakly polar $R3m$ phase increases in polarity considerably when under compressive strain conditions. The strained $R3m$ phase is also displayed in Figure 3.11 down several projections. Wei and coworkers [8] and Materlik and coworkers [36] find that the orthorhombic $Pca2_1$ phase is 64 meV/f.u. and 62 meV/f.u. above the monoclinic, respectively, and the $Pca2_1$ is thus several times lower in energy than that of the rhombohedral phases.

A comparison of the proposed structures for the ferroelectric rhombohedral phases and the ferroelectric orthorhombic phase reveals that the structure of the Hf atom sublattices are quite different and distinct from each other, especially down low-order zone axes (see Figure 3.11). There is some similarity between the $R3$-[10.0]/-[01.0] zone axes and the [110]-O-, [101]-O-, and the [011]-O-$Pca2_1$ axes. Thus, distinguishing rhombohedral from orthorhombic phases in these samples may be challenging by visualizing these sets of zones alone. However, no zone axes in the $R3$ and (strained) $R3m$ phases have yet been found that resemble the low order $Pca2_1$ zones, i.e. the [100],
Figure 3.11 Low-order zone axes of the $R3m$ (strained) and $R3$ phases identified and refined by Wei and coworkers [8], compared to the orthorhombic $Pca2_1$ unit cell of Kisi and coworkers [44] using lattice constants from Sang and coworkers [37].
Thus, epitaxial films may be able to access strained metastable phases that have yet to be identified in polycrystalline films.

Polycrystalline Si doped, Gd doped, and Hf$_{0.5}$Zr$_{0.5}$O$_2$ samples grown with ALD and examined during the course of this work have exhibited the following zone axes consistent with the orthorhombic $Pca2_1$ phase (compare to schematics in Figure 3.11 and simulations in Figure 3.9): the [010] (Figures 3.4, 4.2, and 4.7), the [010] (Figure 4.2 and Figure 2f. in Ref. [175]), the [001] (Figure 3.4 and Figure 4 in Ref.[206]), the [110] (Figures 3.6, 3.7, 4.1c, and Figure 2 in Ref.[207]), the [101] (Figures 3.6, 3.7, 4.1b, 5.2c, and Figure 2 in Ref.[207]), and the [111] in the forthcoming Ref.[208]. As such, phase assignments in the samples observed by this work have strong evidence pointing to the polar orthorhombic phase presence in these samples rather than the polar rhombohedral phase described elsewhere [8, 205].
Chapter 4

Domain and Interphase Boundary Structures in Polycrystalline HfO$_2$ Thin Films

In spite of new strides in understanding the phase composition of ferroelectric hafnia thin films and their evolution with field-cycling as presented in Chapter 3, the domain structuring and mechanisms of phase coexistence in these materials were not fully understood or reported. This section explains experiments performed to fill this gap in knowledge by studying presence of 90° domains in the polar orthorhombic phase, defects in the monoclinic phase, and phase coexistence across coherent interphase boundaries between the monoclinic and orthorhombic phase. Assessment of these features provided further insights into the impact field-cycling has on the domain state of as-grown HfO$_2$ films. Furthermore, the assessment of interphase boundaries yielded important insights into the preferential formation of certain boundaries between the orthorhombic and monoclinic phases. These boundaries act as sources of epitaxial strain within the grains, which has implications for phase stability. Moreover, variation in the structure of similar interphase boundaries suggests the possibility of boundary mobility, which is compared to previous studies of mobile interphase boundaries in freestanding particles. Background information on ferroelectrics (Chapter 1.1) and
on ferroelectric HfO$_2$ in particular (Chapter 1.1.1) is available in the introduction.

The content of this chapter was initially reported in the main article and online supporting information of the publication Ref. [4]:


Text and figures from this article and its supporting information are reproduced here with permission from the article copyright holder, WileyVCH Verlag GmbH & Co. KGaA, Weinheim. Christoph Adelmann from Imec, Belgium is gratefully acknowledged for depositing the TiN-Gd:HfO$_2$-TiN stacks. The authors thank Jacob L. Jones for helpful feedback and discussions. E.D.G. and J.M.L. gratefully acknowledge support from the National Science Foundation (DMR-1350273). E.D.G. acknowledges support for this work through a National Science Foundation Graduate Research Fellowship (DGE-1252376). T.S. gratefully acknowledges the German Research Foundation (Deutsche Forschungsgemeinschaft) for funding part of this research in the frame of the “Infero” project (MI 1247/11-2). This work was performed in part at the Analytical Instrumentation Facility (AIF) at North Carolina State University, which is supported by the State of North Carolina and the National Science Foundation (ECCS-1542015). The AIF is a member of the North Carolina Research Triangle Nanotechnology Network (RTNN), a site in the National Nanotechnology Coordinated Infrastructure (NNCI).

4.1 Introduction

Following the first report of ferroelectricity in HfO$_2$ [2], significant interest and research has been spurred on by its robust ferroelectric properties that are maintained even in films thinner than 10 nm. Because of its silicon compatibility and wide processing space, the material shows promise for use in future memories [11, 21], energy efficient logic transistors [209, 210], and devices that exploit a tunable dielectric [211] or pyroelectric [42, 212, 213].
As understanding of ferroelectricity in HfO$_2$ develops, grain sub-structure is proving increasingly important for controlling film properties. While bulk HfO$_2$ is known to adopt the $P2_1/c$ monoclinic phase (M) at room temperature and pressure [54], “metastable” high symmetry fluorite-like phases including $P4_2/nmc$ tetragonal (T) and orthorhombic (O) phases can coexist in the ferroelectric thin films [2, 21, 37, 42, 61, 206]. An orthorhombic phase Pca2$_1$ that lacks an inversion center is thought to be responsible for the ferroelectric behavior of these thin films, and has been observed with scanning transmission electron microscopy (STEM) [7, 37]. Electron microscopy has also revealed interfacial HfO$_2$ regions exhibiting tetragonal-like symmetry at electrode/bulk grain interfaces in moderately doped films [3, 175, 206], and its presence dominates at high dopant concentrations [61, 206]. Critically, the net electrical behavior is strongly governed by the fractions of each phase in a given device [61, 200, 206].

First-principles calculations suggest that various forces contribute to stabilizing the different distorted fluorite phases of HfO$_2$, enabling ferroelectric switching, and/or possibly allowing phase transformation. These include electric fields [36, 64], surface energies [36, 199], strain from different origins [33, 36, 60, 64], and alloying [36]. Experiment and theory point to an orthorhombic switching pathway through the tetragonal phase [21, 33, 34, 60], and in certain instances the tetragonal-to-orthorhombic transition might be transient during the application of an electric field [11].

Recently, studies have also highlighted the structural similarities between the orthorhombic and monoclinic phases [60, 201]. Barabash et al. report that differences in oxygen ordering in a “parent” orthorhombic phase (centrosymmetric Pbcm) can lead to stabilization of either the monoclinic or the polar orthorhombic phase. Furthermore, they speculate that a region of coherently strained HfO$_2$ lacking the monoclinic distortion might readily convert between the monoclinic and polar orthorhombic phase via a low transformation barrier [60]. Experimental evidence also suggests that some amount of phase transformation may occur during the “wake-up” effect [3, 173–175, 214]. The complexities of characterizing polycrystalline and polyphasic HfO$_2$ thin films have, however, limited current information of phase distribution, coexistence, and domain structuring in this new ferroelectric system. Domains of the orthorhombic ferroelectric phase are expected to exist based
on the polarization versus electric field response and on electrical measurements where single
domain switching is observed [76]. Direct evidence of such domains, however, remains limited [76,
214, 215].

Beyond ferroelectric domains, other internal boundaries are also crucial to consider as they
can impact a ferroelectric material’s mechanical and electrical response. This has been seen, for
example, near morphotropic phase boundaries (MPBs) in the phase diagrams of certain materials.
Pb(Zr,Ti)O$_3$ exhibits coexistence of polar rhombohedral and polar tetragonal phases, which exist
in fractions and over length scales that depend largely on the composition [216]. Domain wall
energy is an important parameter for determining the length scale of ordering and the domain sizes,
and thus has important implications for mechanical and electrical behavior [217]. Because these
systems contain multiple phases, “interphase boundaries” can form as walls between different
phases. Furthermore, mobile interphase boundaries are speculated to move during cycling in both
reversible and irreversible jumps, similar to domain walls, thereby converting between phases as
the boundary wall moves [218–220].

Despite indications that phase transformations and other defect related phenomena take place
during progressive switching of ferroelectric HfO$_2$ [3, 173–175, 214], the underlying mechanisms
remain unclear. Presence of interphase boundaries, for example, would be expected to influence
phase stability by introducing internal strains [36, 60, 64], and electrical properties if the boundaries
move during the application of an electric field [218, 220]. Identification of the phase and ferroelectric
domain structures would thus lead to approaches to further improve this lead-free ferroelectric.

In this article, interphase boundaries and single phase domains in Gd doped HfO$_2$
metal-ferroelectric-metal capacitors are studied using aberration corrected scanning transmission electron
microscopy (STEM). Monoclinic, orthorhombic, and tetragonal regions are found to coexist within
single grains. Within orthorhombic domains, 90° domain walls are found only the in pristine sam-
ples, suggesting that their presence is altered by field-cycling. Monoclinic/orthorhombic interphase
boundaries are also revealed and analyzed in the context of the structural parameters that govern
their formation. Moreover, our results highlight the similarities between the orthorhombic and
monoclinic phases. These similarities lead to challenges in distinguishing a “defect” in one phase from the “normal” structure of the other phase. These combined results suggest that the environments near interphase boundaries lead to the formation of new orthorhombic regions. Contingent on the stability/mobility of these boundaries, such boundaries are proposed to play a role in phase conversion under an electrical bias.

4.2 Results and Discussion

HfO$_2$ grains typically span the thickness of the film between the TiN electrodes, as shown by the bright grain spanning the distance between the two dark electrodes in Figure 4.1a. To simplify the referencing of regions within the various images, we sequentially number the monoclinic (M) or orthorhombic (O) regions. Using high-angle annular dark-field (HAADF) STEM, the identity and orientation of phases in HfO$_2$ films are readily determined using the atomically resolved positions of the projected Hf atom sub-lattice [3, 37]. This analysis reveals that certain grains exhibit a complex domain structure. For example, a single grain is divided into two orthorhombic (O1, O2) and one monoclinic (M1) region in Figure 4.1a. At the O1/O2 boundary in Figure 4.1c, (010)$_o$ in O1 are parallel to (001)$_o$ in O2, where \{111\}_o are continuous across the domain wall. The boundary between the two regions is sharp and possesses an abrupt change in projected symmetry at the domain wall. This symmetry change is made more visible by inspection of the atom column near neighbor distances, which are mapped in Figure 4.1d. An interphase boundary is also observed within the same grain (see Figure 4.1e), where the crystal structure abruptly transitions from O2 to M1 with (001)$_o$||[100]$_m$.

Connecting structure to polarization is essential for understanding the ferroelectric behavior of HfO$_2$ thin films. Polarization across the O1/O2 domain wall can be assessed by position-averaged convergent beam electron diffraction (PACBED), where missing mirror symmetry in the pattern corresponds to a lack of inversion symmetry in the material [37, 62]. This occurs for the $Pca2_1$ orthorhombic phase along the [001]$_o$, and is indicated by arrows in Figure 4.1b,e (note that the [001]$_o$ in Figure 4.1b is inclined with respect to the image plane, possessing a partial out-of-plane component). Figure 4.1f shows PACBED patterns acquired from regions O1 and O2. Each pattern
Figure 4.1  

a) HAADF STEM of a pristine Gd doped HfO$_2$ grain with O and M regions separated by boundaries indicated by white arrows. c) Magnified view of the O1/O2 boundary from (a), with d) displaying distances between atom columns as colored lines to emphasize changes in projected symmetry (red arrow provides a visual guide). b,e) magnified regions from (a) where planes are indicated with lines and the polar direction by arrows. f) Experiment and simulated PACBED patterns corresponding to O1 and O2 regions. The presence and lack of a mirror plane are solid and dashed lines, respectively. Arrows highlight symmetry breaking in the pattern. Brightness and contrast are adjusted to emphasize PACBED pattern asymmetry. From Ref.[4], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
Figure 4.2 (a)-(d) HAADF STEM images of various regions containing O/O domains and/or O/M interphase boundaries. Dashed lines indicate domain/interphase boundaries. White lines denote indicated Hf planes. Short, colored lines map distances between neighboring Hf sub-lattice atom columns to help guide the eye. Regions (a-c) are from an pristine sample while (d) is fatigued. This figure is shown without image overlays in Figure 4.3. From Ref.[4], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.

lacks a mirror plane across the dashed axis bisecting the pattern, which is consistent with the $Pca2_1$ polar phase simulations. In contrast, simulated patterns from the centrosymmetric $Pbcm$ phase retain mirror symmetry along both axes. These results show that the polar direction is rotated by $\sim 90^\circ$, hence forming a $90^\circ$ domain wall.

More broadly, a wide range of interphase and domain boundaries are observed throughout the samples as highlighted by Figure 4.2a-d. The images reveal several O/O domains and O/M interphase boundary structures in a variety of shapes and sizes. Changes in atom column spacing and symmetry across the boundaries are highlighted by near neighbor distance maps in the bottom panels of Figure 4.2a-d. While some boundaries are angular and difficult to precisely locate, others
Figure 4.3 Figure 4.2 without overlays. From Ref. [4], and reproduced with permission from the copyright holder, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
are flat with fractional unit-cell steps. Figure 4.2a shows a typical $90^\circ$ domain between orthorhombic regions O3 and O4. As in the case of the O1/O2 boundary in Figure 4.1c, $(010)_o$ becomes $(001)_o$ across the O3/O4 domain wall. The transition in crystal symmetry is abrupt, and like the O1/O2 boundary, occurs over a higher order crystal plane. Not all boundary transitions are sharp in the vicinity of $90^\circ$ domain walls. For example, Figure 4.2b shows a $90^\circ$ domain wall formed at the interface between regions O5 and O6. Unlike the O/O domains in Figures 4.1c and 4.2a, $(001)_o$ of this domain remain parallel across the boundary and instead rotate $90^\circ$ in-plane.

Based on the domain walls presented in Figures 4.2a-b, which are viewed down low order zone axes, some aspects of the structure of orthorhombic domain boundaries can be linked to misfit. As reported in Ref. [37], the lattice parameters of the orthorhombic structure are $a_o, b_o, c_o = 5.24, 5.06, 5.07$ Å, which results in a $\sim 0.2\%$ misfit across the O3/O4 domain wall and a rather abrupt change in rotation across the boundary. In contrast, the O5/O6 boundary exhibits high misfit of $\sim 3.5\%$, and possesses a much more diffuse transition in structure across the boundary. This likely arises due to the larger misfit and/or grain overlap. The three examples of orthorhombic domains in Figures 4.1c and 4.2a-b exemplify how local environments allow domains to form in a variety of orientations, sizes/shapes, and domain wall configurations.

The monoclinic phase is found to form twin boundaries in some grains. For example, a $(110)_m$ twin in Figure 4.2d is identified between the monoclinic regions M5 and M6. Twining also occurs on $(001)_m$ (Figure 4.4a) and $(100)_m$ (Figure 4.4b). These twin planes are in good agreement with various reports of twinning configurations identified in toughened zirconia ceramics [221], HfO$_2$ thin films grown directly on Si [48], and in Hf-rich Hf$_x$Zr$_{1-x}$O$_2$ nanocrystals [222]. Twinning is associated with the tetragonal to monoclinic martensitic phase transformation [48, 221–223]. Such a phase transformation requires a shape change to the distorted monoclinic cell, and twinning is a mechanism whereby shape change/shear strain can be minimized for the transformation of a confined grain [221].

Figure 4.2a-d also shows that many HfO$_2$ regions contain interphase boundaries. In Figure 4.2a, an interphase boundary between M2/O3 regions forms with an interface with $(100)_m\|(010)_o$. The
interphase boundary wall is discontinuous, with steps forming every few nanometers. Strain near the wall results in visible distortion of the spacing and angle between atom columns in the vicinity of the boundary, as seen in the Figure 4.2a distance map. Similarly, the structures become blurred adjacent to the boundary wall, which can indicate phase overlap or non-uniform lattice distortion near the boundary. Furthermore, the M4/O7 boundary in Figure 4.2c forms an interface with \((100)_m\parallel(001)_o\), and where lattice distortion visible in the vicinity of the interface. Visually, the M4/O7 interphase boundary resembles the M2/O3 boundary, but the orthorhombic region is rotated 90° such that \((001)_o\) forms the boundary rather than \((010)_o\).

In addition to the M/O boundaries in Figure 4.2a,c the tetragonal phase is observed near the TiN electrodes. Interfacial HfO\(_2\) layers near TiN electrodes are previously reported to relax towards tetragonal symmetry in some instances which may arise from local chemical/bonding changes, changes in local oxygen vacancy concentrations, or from local orientation relationships between the TiN/HfO\(_2\) [3, 175]. These findings suggest that the environment near interphase boundaries can help stabilize the tetragonal phase. For instance, the T regions at the M/O boundaries in Figure 4.2a,c penetrates around ~2-4 nm into the bulk grain, which is deeper than previously reported at grain/electrode boundaries [3]. Transition regions with mixed/strained symmetry like the tetragonal
interface layers reported earlier can be important for phase stabilization [224]. Due to the complex nature of this polycrystalline interface, however, further studies are needed to form a complete picture of bonding and orientation relationships for the HfO$_2$/TiN interface.

The interphase boundaries in Figures 4.2b,d have reduced step density compared to those in Figures 4.2a,c. For example at the O6/M3 interface in Figure 4.2b, an abrupt interphase boundary is formed with (001)$_o$|| (100)$_m$. The transition in crystal symmetry from orthorhombic to monoclinic is sharp in this case, having less distortion. Further, the boundary between the O8/M5 regions shows no clear steps between the (010)$_o$||(100)$_m$ planes that form the wall in Figure 4.2d. A second boundary in this region also forms between O8/M6 regions with (001)$_o$||(100)$_m$, with varied step density. Furthermore, the O6/M3 and O8/M6 interphase boundaries are equivalent, though they are viewed along different crystal projections.

Based on these observations interphase boundaries are expected to traverse complicated, three dimensional paths through the grain. The nature of the final boundary thus depends on the size and orientation of the separate phase regions that form during annealing until they merge to form a boundary wall. Furthermore, some of the distortion visible near the domain walls is likely the result of viewing a projection of the three-dimensional domain wall structure.

The library of observed interphase boundaries gives insight into how crystal chemistry may influence their formation. The examples of interphase boundaries in Figures 4.1 and 4.2 suggest that the monoclinic and orthorhombic phases tend to form coherent boundaries across low order planes in polycrystalline HfO$_2$ thin films. This is consistent with phase boundaries seen in strained epitaxial (Hf,Zr)O$_2$ thin films [215]. Additionally, the boundary step structure suggests a role of misfit in determining their periodicity. The misfit here is defined as the difference in lattice parameters divided by their average. For example, the greatest possible uniaxial misfit occurs at O/M boundaries where the $c_m$ axis of the monoclinic phase ($c_m = 5.30 \text{ Å}$) aligns to either the orthorhombic $b_o$ axis ($\sim 4.6\%$ misfit) or $c_o$ axis ($\sim 4.4\%$ misfit), where $c_o = 5.07 \text{ Å}$ and $b_o = 5.06 \text{ Å}$. These boundaries with maximum misfit still form and readily step as seen in Figure 4.2a,c. Comparatively, when O/M boundaries form such that the $a_o$ and $c_m$ axes are parallel, misfit is significantly reduced to
∼2.0% when \( b_m/c_o \) and ∼2.2% when \( b_m/b_o \), where \( b_m = 5.17 \) Å. These lower misfit boundaries subsequently contain fewer steps as seen in Figure 4.2b,d.

Figure 4.5 shows structural schematics of an interfacial plane, focusing on the Hf positions. Only a single variant of the boundary is shown here, i.e. rotating the orthorhombic lattice in-plane by 90° will change the interface orientation, strain, and alignment of the atoms. Because the \((010)_m\) is non-orthogonal (\( \beta = 99.18^\circ \)), there is relatively poor registration to all orthorhombic planes. In contrast, the set of boundaries formed with \((100)_m\) and \((001)_m\) provide reasonable registry with the low order orthorhombic planes.

Both orthorhombic and monoclinic cells possess reduced symmetry involving lateral and out-of-plane shifts in atom positions. When viewed from the side, Figure 4.5, the Hf sub-lattice remains co-planar for the \((100)_m\), \((001)_o\), and \((010)_o\), while it is rumpled out-of plane for \((010)_m\), \((001)_m\), \((001)_o\), and \((100)_o\). Based on these observations, interphase boundaries tend to form in orientations that maintain a co-planar Hf sub-lattice across the boundary, i.e. without out-of-plane rumpling. Additionally, the local Hf-O bonding configuration across the boundary may also play a role. Furthermore, this finding is in good qualitative agreement with studies that show the \((100)_m\) habit is the more favorable habit planes for related zirconia phase transformations [225]. Strain and displacements of the Hf sub-lattice needed to form certain rumpled boundaries (i.e. any boundaries with the \((001)_m\) plane) do not appear dramatically different than that of the observed boundaries. While the results suggest preference for non-rumpled boundaries involving the \((100)_m\), the existence of rumpled boundaries from this system cannot be ruled out due to the inherently limited sampling statistics of atomic resolution electron microscopy. Further investigations combined with theory are needed to provide further insight into boundary stability and preference.

Approximate configurations of the structures observed at interphase boundaries are provided in Figure 4.6. The shaded terminal Hf plane at the boundaries are those of the orthorhombic phase. Note that both phases have three-coordinate and four-coordinate oxygen atom positions. Because the oxygen sub-lattices are not observed in the STEM images, the schematics are approximate and represent one of several possible configurations. Nonetheless, the boundaries show how O/M
Figure 4.5 Schematic of a single Hf planes in monoclinic (open circles) and orthorhombic (filled circles) cells viewed from the top and side. The O sub-lattice is omitted because it is not observed in the HAADF STEM images. The structures are derived from unit-cell parameters from Ref. [54] for the monoclinic cell and Refs. [37, 44] for the orthorhombic cell. From Ref.[4], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
boundaries can form that reasonably satisfy the symmetry of both phases.

The variety of observed interphase boundaries provides insight into how they might influence phase stabilization and enable phase transformation. Immobile boundaries artificially limit the grain size and impart a coherent strain onto the lattices, which is known to play an important role in phase stabilization [36, 60, 64]. Furthermore, these boundaries can influence domain pinning. A boundary capable of moving under the influence of an electric field would alter the electrical behavior by changing the phase fractions during cycling. For example, monoclinic/orthorhombic phase transformations have been initiated during electron beam irradiation in both zirconia particles [53] and ceramics [226]. Similarly, monoclinic/tetragonal boundary propagation has been visualized during in situ heating/cooling of zirconia nanoparticles [223]. While the boundaries observed here did not move during STEM imaging, identical boundary orientations exhibit several different unique features that are not present in all instances and may suggest potential for mobility, as will now be discussed.

With respect to boundary mobility and unique boundary features, Figure 4.7b is instructive. This
Figure 4.7 (a) Schematics of the O- and M-phases with the major and minor distortion half-units indicated. (b) A complex interphase boundary in the woken-up sample with color-coded symmetry overlays (black:orthorhombic, red:monoclinic, and white:both), and important major distortion units indicated. Arrows highlight key structural figures described in the main text, and apparent symmetry of the distortion units is mapped. (c) A similar boundary dividing two pure O-phase regions in the fatigued sample. This Figure is shown without image overlays in Figure 4.8. From Ref.[4], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
Figure 4.8 Figure 4.7 without overlays. From Ref.[4], and reproduced with permission from the copyright holder, WILEYVCH Verlag GmbH & Co. KGaA, Weinheim.
boundary is oriented equivalently to ones previously shown to be mobile in particles of the related zirconia crystal structure [53]. This boundary also displays many unique features that set it apart from the similar boundary presented earlier in Figure 4.2a. Distinct orthorhombic O9 and monoclinic M7 regions are separated by a complicated interphase boundary, which is segmented into regions R1 and R2 by the dotted lines within the boundary region in Figure 4.7b. The qualitative symmetry of the Hf sub-lattice is indicated by colored overlays with black indicating pure orthorhombic symmetry, red representing pure monoclinic symmetry, and white labeling regions where the Hf sub-lattice seemingly co-satisfies the symmetry of each phase.

The monoclinic and orthorhombic unit-cells can be thought of as distorted tetragonal unit-cells [59]. Half the structure resembles, with minor distortion, the parent tetragonal phase, while the other half deviates significantly for both monoclinic and orthorhombic cells, see Figure 4.7a. The layers with minor distortions are structurally very similar between the monoclinic and orthorhombic phases. By contrast, the majority of the differences between the monoclinic and orthorhombic phase occur within the major distortion layers.

The nominal structures of the major distortion layers are labeled in Figure 4.7b. Several interesting structural features occur in this boundary. First, the bottom red arrow in R2 indicates a monoclinic-like major distortion layer that becomes an orthorhombic-like major distortion layer across the R2/R1 boundary. Next, the monoclinic major distortion layer at the same red arrow appears "twinned" with respect to the monoclinic major distortion layer indicated by the top red arrow. This twin-like feature occurs across a major distortion layer resembling the orthorhombic phase (black arrow). The monoclinic-like major distortion layer indicated by the top red arrow occurs between two major distortion units with orthorhombic-like structures. From this analysis, it becomes apparent that substitution of a monoclinic-like major distorted layer into an orthorhombic lattice results in an anti-phase-like boundary in the orthorhombic phase (see top red arrow in Figure 4.7b and red arrow in Figure 4.7c). Similarly, insertion of an orthorhombic-like major distortion layer into the monoclinic lattice results in a "twin-like" defect (see black arrow in Figure 4.7b).

The large variation in the structure at these boundaries hints at the potential for mobility during
the application of an electric field. Specifically, the “snapshot” in Figure 4.7b suggests an interphase boundary in various states of converting between the monoclinic and orthorhombic lattices, much as suggested by the “step-flow”-like motion of the same boundary orientation in Ref. [53]. Crystal chemistry suggests a double [001]_o (010)_o glide system converts the orthorhombic phase into the monoclinic phase, with the reverse occurring by a [001]_m (100)_m double glide [59]. Such glides impact the symmetry of the entire unit-cell, though a majority of the structural changes occur within the major distortion portions of the unit cells [59]. Consistent with this, the structure of the major distortion layer indicated by the bottom red arrow transitions between glide states at the boundary between regions R2 and R1. Furthermore, this glide system explains how insertion of one phase’s major distortion structure into the other phase initiates features akin to “anti-phase-like” and “twin-like” defects, as discussed above.

Consistent with the understanding that some interphase boundaries are likely immobile in ferroelectric HfO\(_2\), M/O interphase boundaries are still observed after field-cycling, of which Figure 4.7b-c is an example. Internal discontinuities and strains as encountered near interphase boundaries are important for phase stabilization as they limit grain size and exert an internal force. Domain boundaries have been suggested as stabilizing higher symmetry phases in zirconia nanoparticles [65], and interphase boundaries can play a similar role in this system. Phase stability can change in the vicinity of interphase boundaries due to differences in local epitaxial strain [36, 60, 64], or even due to a departure from the undistorted monoclinic and orthorhombic lattices [60, 201]. In these instances, application of an electric field may be insufficient to destabilize one phase with respect to one another. Such boundaries would also play a role in fatigue mechanisms in these materials. While beyond the scope here, we suggest future studies utilize a combination of in situ biasing TEM experiments and theory to elucidate the mobility and impact of these boundaries.

Unlike the M/O interphase boundaries, no clear example of 90° domain walls in the orthorhombic phase are found in the field-cycled samples. This finding is significant, as more regions were observed in the woken-up/fatigued samples than the pristine sample. Within the limits of the STEM sampling, this suggests that field-cycling results in increased domain uniformity by aligning
some of the "as-grown" 90° domains. Such an increase in domain uniformity would concomitantly increase the remanent polarization, which is observed during wake-up when field cycling [3, 175, 176]. Moreover, martensitic phase changes between high symmetry phases and the non-orthogonal monoclinic phase necessitates a shape change. This has been seen in the case of both orthorhombic zirconia particles [53] and tetragonal HfO₂-zirconia nanoparticles [222]. Twin formation in the monoclinic phase has been shown to minimize shear strain during such a transformation for both HfO₂-zirconia nanoparticles [222] and HfO₂ thin films [48]. Due to a restricted geometry, thin films have fewer degrees of freedom by which to change shape, and likely rely more on generation of accommodating defects like dislocations and twin and/or anti-phase boundaries to convert between phases. Moreover, the shear strains required for such a transformation may be inaccessible to certain regions of the sample, locking in a higher symmetry phase [48]. As such, the geometric constraints due to electrode(s), neighboring grain(s), and/or other boundaries may immobilize some of the interphase boundaries with little to no room to move around their eccentric positions.

4.3 Conclusions

This work demonstrates the rich structural chemistry accessible to ferroelectric HfO₂, which enables formation of a complex mixture of domains, planar defects, and interphase boundaries. The complex structure near interphase boundaries hints at a possible continuum between orthorhombic and monoclinic phases in the vicinity of the boundary walls. Further, the distortions present near these boundaries suggests the potential for mobility. These insights yield new perspectives for the modeling of switching and domain wall motion, and provide a basis for comparison to domain wall and interphase boundaries in conventional perovskite ferroelectrics. Overall, this work lays the groundwork for calculations aiming to explore interphase boundary energetics, where further knowledge is needed to improve stability, mobility, and their impact of field-cycling.
4.4 Methods

4.4.1 Sample Information

27 nm Gd:HfO$_2$ capacitors with 10 nm TiN electrodes were grown using atomic layer deposition as described previously [169]. Lamella were prepared for scanning transmission electron microscopy (STEM) by focused ion beam from both cycled and pristine devices using an FEI Quanta. The lamella were extracted from either pristine (0 cycles), woken-up (1.0E+03 cycles), or samples after the onset of fatigue (2.15E+05 cycles) as indicated. Cycling was performed at 1 kHz with an 8.5 V triangular voltage sweep [3].

4.4.2 Scanning Transmission Electron Microscopy

High-angle annular dark-field (HAADF) STEM was performed on an FEI Titan G2 60-300 kV equipped with a probe-corrector and an X-FEG source. The microscope was operated at 200 kV with a detector inner semi-angle of approximately 77 mrad, probe currents of around 80 pA measured with the current monitor on the screen, and probe semi-convergence angle approximately equal to 19.6 mrad. RevSTEM images [157] were acquired using 40 1024 x 1024 pixel frames with a 2 $\mu$s/pixel dwell time and a 90° rotation between each successive frame. Where necessary, scan coil distortion was removed by previously described methods [161]. The atom column positions were determined by fitting two-dimensional Gaussian distributions via MATLAB scripting [163]. PACBED patterns were simulated using the MBFIT (“Many-Beam dynamical-simulations and least-squares FITting”) package by K. Tsuda at Tohoku University [152]. Simulation parameters matched those from experiment. Structural parameters were taken from Refs. [37, 44, 55, 57]. The simulation output was rescaled using bicubic interpolation to match experiment.
Chapter 5

Towards Orientation Controlled Polycrystalline Thin Film Ferroelectric Hafnia Capacitors

Many HfO$\textsubscript{2}$ films are deposited as amorphous layers with atomic layer deposition (ALD). They then require a post-deposition rapid thermal anneal to crystallize. If the film crystallizes with randomly oriented grains, the polar axes of some of the grains end up misoriented with regards to the switching field. This decreases the achievable switchable polarization of the device. Furthermore, the polar axis may naturally be fixed at an angle with regards to the direction of the applied voltage, minimizing the useful component of the polarization. Different studies have now achieved growth of textured and even epitaxial HfO$\textsubscript{2}$ and ZrO$\textsubscript{2}$-based ferroelectrics, demonstrating the important role substrate can play in stabilizing and orienting the ferroelectric phase. This Chapter presents a study of the native orientation relationships that form between the polycrystalline HfO$\textsubscript{2}$ films and the polycrystalline electrodes on which they are grown for ALD prepared films. Various regions of hafnia are observed in orientation relation to the TiN. From these, a model of preferred epitaxy is developed for HfO$\textsubscript{2}$$\parallel$TiN, with important implications for tuning the orientation of the electrodes to influence the final alignment of the polar axis of the HfO$\textsubscript{2}$ grains. Background information on
ferroelectrics (Chapter 1.1) and on ferroelectric HfO$_2$ in particular (Chapter 1.1.1) is available in the introduction.

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5.1 Introduction

Ferroelectric HfO$_2$ thin films are impacting many technologies that have lacked a ferroelectric that retains strong switchable polarization at thicknesses below 10 nm [2, 25, 67]. At present, efforts are exploring its use in ferroelectric tunnel junctions [38], ferroelectric memories [11, 76], energy storage devices, and devices that use its negative capacitance for logic purposes [210]. In most instances, hafnia layers in these sorts of devices are deposited using atomic layer deposition (ALD) processes [2]. This method leads to an amorphous hafnia film with some small crystallites between two sputter deposited crystalline electrodes, and the amorphous HfO$_2$ layer is fully crystalized subsequently
with a post-deposition annealing process which generates a polycrystalline film [227]. Diffraction studies on these materials have yet to elucidate any prominent film or electrode texturing or any preferred orientation relationship between the two. This can be attributed to the shear complexity of refining this type of information from the polycrystalline metal-ferroelectric-metal sample geometry with a total region of interest that is commonly below 50 nm in thickness. The problem is then further complicated by the multiple polymorphs that are typically present in hafnia films including the monoclinic $P2_1/c$, the ferroelectric orthorhombic $Pca2_1$, and the tetragonal($P4_2/nmc$)/cubic($Fm\overline{3}m$) phases [2, 37, 61, 228].

Nonetheless, the importance of orientation control and strain tuning are manifest for hafnia and zirconia films. Shimizu and coworkers achieved fully epitaxial Y doped HfO$_2$ films exhibiting the polar orthorhombic phase by pulsed laser deposition on yittria stabilized zirconia substrates [7, 229]. Altering the substrate choice for epitaxial hafnia films has been shown to influence the orthorhombic domain structure of epitaxial films [230]. Epitaxial and uniaxial textured Y doped HfO$_2$ thin films have been achieved on (111) indium tin oxide layers grown on various substrates [6]. Epitaxial Hf$_{0.5}$Zr$_{0.5}$O$_2$ films have been grown as well on La$_x$Sr$_{1-x}$MnO$_3$ buffered SrTiO$_3$, and results suggest stabilization of new metastable yet polar rhombohedral Hf$_{0.5}$Zr$_{0.5}$O$_2$ phases [8]. These examples demonstrate how it is imperative to understand the local orientation relationships and texturing that are occurring for the ALD prepared capacitors on polycrystalline TiN, as orientation control and film/substrate interactions can have a large influence on the phases that form and on the properties of the layer. TiN is demonstrated to play a role in texturing HfO$_2$ and ZrO$_2$. (111)-textured ZrO$_2$ thin films were grown on (001)-TiN films on (001)-MgO [5]. The influence of substrate and orientation relationship has also been shown to extend to fully polycrystalline films [231]. Shiraishi and coworkers demonstrated that polycrystalline (Hf,Zr)O$_2$ grown on (111)-Pt coated Si, SiO$_2$, and CaF$_2$ substrates exhibited varying ferroelectric behaviors which correlated to measured mechanical stresses in the various films [232]. In the polycrystalline films on TiN, some instances of TiN||HfO$_2$ orientation relationship have been observed in scanning transmission electron microscopy images, but the exact relationships remain to be revealed [3, 233].
As evidenced by these studies [3, 5–8, 229–233], HfO$_2$ and ZrO$_2$ based ferroelectric behavior interacts with and is strongly controlled by film and substrate interactions. The thin films on nitride based metallic electrodes (i.e. TiN, TaN, etc.) are clearly polycrystalline on the basis of X-Ray diffraction [2] and transmission electron microscopy (TEM) [214]. Furthermore, the polycrystalline films do not exhibit the predicted saturated remanent polarization values expected for a fully orthorhombic, fully polar-axis oriented films [33, 201]. While some of discrepancy between predicted and observed remanent polarizations is likely due to residual monoclinic or tetragonal phase fractions within the films [3, 42, 61, 206, 228], a portion is also likely related to misorientation of the polar-axis with respect to the direction of applied electric field. The ability to better control the orientation of the grains grown on the metal nitride electrodes would enable better optimization of the remanent polarization of the films by controlling the angular distribution of the polar axes.

Towards this end, we have investigated the structure of TiN∥HfO$_2$ interfaces using scanning transmission electron microscopy (STEM). The observed boundaries indicate a strong preference for certain low order planes of the monoclinic and orthorhombic hafnia phases to align with the {111} planes of the TiN. In certain instances, the two align akin to epitaxial-like thin film growth on a substrate with a “layer-like-stacking” of the HfO$_2$ planes on flat TiN surfaces. In other instances, rough and angled (corrugated) boundaries are formed where the planes are coincident and “aligned,” though they are not stacked. We analyze the atomic structure and crystal chemistry of these boundaries and develop an understanding of the orientation relationships and their possible influence on strains near the boundaries, which in many instances were observed to pin the long axis of the monoclinic and orthorhombic phases in-plane to the TiN. This restricts the resulting geometry of the HfO$_2$ unit-cells, which has important implications for the polar-axis of the orthorhombic phase. Furthermore, the derived orientation relationships are suggestive of strain with the electrode as being one origin of tetragonal-like relaxation of the lattice near the electrode as previously observed [3]. The {111}-TiN nitrogen plane forms a rather natural growth surface for the first Hf atom plane of the low order HfO$_2$ facet, as it contains many three-coordinate sites accessible to the Hf atoms where misfit can be accommodated by site distortions and if necessary vacancies. Finally, the
bottom TiN electrode is revealed to be highly textured, while the upper electrode is revealed to be much more polycrystalline. These results inform how certain TiN textures could be implemented to improve control of the polarization of polycrystalline HfO$_2$ ferroelectrics on traditional metal nitride electrodes.

5.2 Methods

Metal-ferroelectric-metal capacitors with a 27 nm films of Gd doped HfO$_2$ were prepared using atomic layer deposition as described previously [169]. Here, the amorphous Gd doped HfO$_2$ was deposited onto an (001)-Si substrate coated with 10 nm film of polycrystalline TiN prepared with room temperature reactive sputtering [169]. After deposition of the amorphous Gd doped HfO$_2$, a 10 nm thick polycrystalline TiN top electrode was deposited with reactive sputtering at room temperature before the post-deposition anneal. The HfO$_2$ was crystallized between the two pre-crystalline electrodes using a rapid thermal anneal for 20 seconds at 650°C.

Lamella were prepared for STEM with a focused ion beam using either an FEI Helios i600 Dual Beam or an FEI Quanta Dual Beam system. Microscopy was performed on an FEI Titan G2 60-300kV equipped with a probe corrector and operated with a 13.5 mrad or 19.6 mrad probe semi-convergence angle and an accelerating voltage of 200 kV. Beam currents were typically between 60 - 100 pA as read by the Titan current monitor, and annular dark-field detector inner semi-angles were typically 77 mrad. RevSTEM imaging involved acquisition of between 20 to 40 image frames with a 90° scan rotation between subsequent frames and an $\sim$2\(\mu\)s/pix dwell [157].

The crystal chemistry graphics were prepared with CrystalMaker X by CrystalMaker Software Ltd. (Oxford, England). The TiN structure was \(Fm\bar{3}m\) (no. 225) with \(a=4.24\ \text{Å}\) [234]. The monoclinic \(P2_1/c\) cell (no. 14) uses the refinement of Adams and coworkers in Ref.[54]. The orthorhombic \(Pca2_1\) cell (no. 29) uses the refinement of Kisi and coworkers in Ref.[44] with the lattice parameters measured by Sang and coworkers in Ref.[37]. Cornell Spectrum Imager (CSI) from Ref. [137] was used to prepare the composite EMPAD image.
5.3 Results

Ferroelectric capacitors with 10 nm TiN electrodes and 27 nm thick films of Gd doped HfO$_2$ are fabricated and prepared for STEM using a focused ion beam (see methods section for more details). An example overview high-angle annular dark-field (HAADF) STEM image is shown in Figure 5.1. The overview image demonstrates that the TiN electrodes and the HfO$_2$ layers are all polycrystalline. The regions in the HfO$_2$ indicated by white arrows are brighter than the remaining portions of the film, and show lattice fringes in two of the instances. This suggests that grains in these regions are aligned close to the zone axis of the crystal. From the overview image, it is apparent that the top TiN electrode is much rougher than the bottom electrode. The top electrode is deposited onto the non-uniform amorphous HfO$_2$, while the bottom electrode is deposited directly onto the Si-(001) substrate after it is cleaned with HF to minimize surface oxide.

In HAADF “Z-contrast” STEM images, atom column intensity scales roughly as $Z^2$, and thus corresponds to the quantity and mass $Z$ of the atoms in the lattice. In Figure 5.1, both TiN electrodes appear much darker than the HfO$_2$ film due to the much smaller $Z$ (Ti = 22, N = 7 versus Hf = 72). This strong difference in contrast remains in higher magnification HAADF STEM images, and imposes an additional challenge for simultaneously imaging TiN and HfO$_2$. Provided that the crystal lattices of the TiN and HfO$_2$ are well aligned to the STEM electron probe, atomic resolution imaging is achievable. It is important to note, however, that the tolerance to crystal mistilt of STEM is lower than that of TEM, and both atomic resolution and lattice contrast (i.e. visualization of lattice planes) can be easily lost in STEM with a mistilt of even a degree or two. Figure 5.2a-d shows several examples of TiN∥HfO$_2$ interfaces where both film and electrode are visible. Broadly speaking, when the hafnia grains are tilted to zone, (1) the TiN shows neither lattice contrast nor atom contrast and is misoriented with respect to the electron beam (see Figure 5.2a), (2) the TiN is atomically resolved and in a prominent orientation relationship with the hafnia (see Figure 5.2b,c), or (3) the TiN planes are in some orientation relation to the hafnia (see Figure 5.2d). In describing these interfaces and structures, a direction or plane listing will typically be followed by the phase (M- for monoclinic,
Figure 5.1 HAADF STEM overview of the polycrystalline Gd doped HfO$_2$ capacitor stack with $\sim$10 nm thick polycrystalline top and bottom TiN electrodes. Arrows indicate bright contrast grains, two with lattice contrast, indicating the regions are aligned close to a zone axis.

O- for orthorhombic, and C- for cubic) and the material. Note that herein, we will generally use $\langle \rangle$ and $\{\}$ to indicate general lattice vector and plane types for the TiN to enable easier syntax and comparison between images.

Case (1) HfO$_2$$\parallel$TiN interfaces are most common. An example of one of these is shown in 5.2a where a monoclinic (M) grain is oriented to the [001]-M-HfO$_2$ zone axis. No clear structure is visible in the TiN, which may occur for several reasons. Since the HfO$_2$ layer is targeted for evaluation in the electron microscope, the HfO$_2$ layer rather than the TiN is typically tilted to zone-axis. As such, the exposed atom planes of the HfO$_2$ may not have any immediate orientation relation to the TiN for the given zone-axis. Nonetheless, a TiN region that appears dark may actually exist in some degree of orientation relation to the HfO$_2$ involving another set of planes and lattice vectors that are not visible. Furthermore, the grain size of the TiN is generally a few times smaller than the HfO$_2$ grain size [169], which can also be inferred from the overview image (Figure 5.1). This can potentially lead to presence of several differently oriented TiN grains within the depth-of-focus of the electron probe, leading to absence of lattice contrast or atomic resolution in the TiN. This may be especially the case for thicker regions of the lamella. Similarly, several grains of TiN for each electrode are commonly required to span the diameter of a HfO$_2$ grain. For this reason, certain TiN regions on
Figure 5.2 (a-d) HAADF STEM images of TiN\|Gd:HfO$_2$ interfaces showing varying degrees of orientation relationship. (b,c,d) exhibit visible interaction of \{111\}-C-TiN planes with low order O- or M- hafnia planes. (a) is an example of a TiN region that is not aligned to zone at the same time as the hafnia, and is the bottom interface of the same grain as in (b). (b) is an epitaxial-like interface, while (d) shows more angled orientation relationships with (c) being somewhat in between angled/epitaxial. Images are acquired with RevSTEM, and image levels are adjusted in the electrode panels due to the large intensity difference (see dark lines indicating the division in regions).

one or both electrodes may play a more influential role in texturing the crystallization of a HfO$_2$ region during the rapid thermal annealing process than other portions bounding the same grain.

In the vein of this understanding, the same HfO$_2$ grain in Figure 5.2a does actually possess clear orientation relationship with the top \{111\}-C-TiN planes of a portion of the top electrode, as shown in Figure 5.2b. The TiN in the region of the image possesses a rotation boundary where the \langle 110 \rangle-C-TiN zone-axis on the left of the boundary becomes the \langle 112 \rangle-C-TiN zone-axis on the right. In spite of this rotation, the \{111\}-C-TiN planes remain quite parallel across the boundary (see white lines in the TiN in Figure 5.2b). These \{111\}-C-TiN planes align to the \langle 200 \rangle-M-HfO$_2$ in a manner analogous to a standard epitaxial film\|substrate orientation relationship.

The rotation boundary in the TiN electrode in Figure 5.2b leads to the alignment of the \langle 001 \rangle-M-HfO$_2$ lattice vector to both the \langle 110 \rangle-C-TiN and \langle 112 \rangle-C-TiN lattice vectors in different portions of the image. In terms of the lattice structures, the monoclinic HfO$_2$ phase distorts towards the structure of the tetragonal polymorph of HfO$_2$ near the interface similarly to previous reports of interfacial layers [3, 175, 206]. The hafnia lattice nearest the interface and in the tetragonal portion is blurred, which may be occurring due to increased presence of defects or strain and distortion in its vicinity. The distortion is less present on the side of the boundary where the \langle 001 \rangle-M-HfO$_2$
aligns to the (110)-C-TiN zone, which may mean that this alignment is lower misfit than when the lattice aligns the [001]-M-HfO$_2$ to the (112)-C-TiN. This is consistent with the lengths of the TiN lattice vectors compared to those of M-phase HfO$_2$. The (200)-M-HfO$_2$ contains the [010]-M-HfO$_2$ = 5.17 Å and the [001]-M-HfO$_2$ = 5.30 Å [54] compared to the (110)-C-TiN = 6.00 Å and (112)/2-C-TiN = 5.19 Å. Thus, alignment of the [001]-M-HfO$_2$ to the (110)-C-TiN does yield a lower though still considerable misfit. Additionally, both anion atoms are rather compatible with both cation atoms, and thus some intermixing may be occurring in the vicinity of the interface leading to mottled contrast.

In the second example showing orientation relation (Figure 5.2c), the TiN environment is more complicated. The center portion of the TiN is identifiable as being the (110)-C-TiN zone axis. To the left of this portion, the {111}-C-TiN appear to continue, but atomic resolution is lost. The TiN portion in the top right corner of the image is unclear in terms of structure. The HfO$_2$ shows some orientation relation to the left/center TiN portions, with the {111}-O-HfO$_2$ and the (020)-O-HfO$_2$ respectively aligning nearly parallel to the {002}-C-TiN and {111}-C-TiN. Both sets of orientation alignments here possess slight tilting of the nearly parallel planes. This may be driven by the confinement of the TiN middle by the regions to its left and right such that the TiN and HfO$_2$ are left with slightly off-parallel plane alignments. The {111}-O-HfO$_2$||{002}-C-TiN orientation relationship observed here for polycrystalline TiN and HfO$_2$ capacitors is similar to that engineered by Fan and coworkers [5] in {111} textured ZrO$_2$ grown on (001)-TiN thin films. In the case of this work, however, the {111}-C-TiN plane is more commonly identified in texture relationships than the {002}-C-TiN based on the number of observations, which may explain the partial rotation of the TiN region here from perfect alignment with both the (020)-O-HfO$_2$ and the {111}-O-HfO$_2$.

In the case of Figure 5.2d, lattice planes are visible but individual atoms are not. The indeterminate planes of the TiN align parallel to the (002)-M-HfO$_2$ over a large region of local epitaxy without clear formation of misfit dislocations and with only slight plane bending. Since TiN adopts the rock-salt structure, its {111}-type planes alternate between cation planes and anion planes in the direction of their (111)-type plane-normal directions. If the TiN planes in the image are {111} planes,
the Ti-containing planes should be visible \((Z = 22)\) while the N-containing planes should be dark and likely invisible \((Z = 7)\), and the bright Ti-\{111\} layers should possess an interplanar spacing of 2.45 Å. In the case of the image in Figure 5.2d there is an oscillation of bright planes and dark planes and the measured mean interplanar spacing for bright planes for \(n = 8\) planes is \(2.46 \pm 0.03\) Å (mean ± standard error of the mean). The contrast oscillations and the spacing between bright planes is thus consistent with TiN-\{111\} planes and they thus are identified as such. Unlike the boundary in Figure 5.2b, the TiN and HfO\(_2\) planes associated with the orientation relation are here aligning parallel to each other across the boundary without stacking on each other like a typical film∥substrate.

Additional examples of observed epitaxial relationships are shown in **Figure 5.3a-c** and are helpful for developing a more complete model of orientation relation involving \{111\}-C-TiN planes as evidenced here. In the first example (Figure 5.3a), a large area of orientation relation is seen similar to an epitaxial film∥substrate interface. The TiN possesses several (110)-C-TiN zone axis variants that are separated by transition regions that are rich in stacking faults (see conical regions between white arrows). Nonetheless, the set of \{111\}-C-TiN planes that are parallel to the (020)-O-HfO\(_2\) and form the interface with the hafnia remain parallel across these (110)-C-TiN variants (though the other sets of \{111\}-C-TiN that are not parallel to the interface are misoriented across the variants, as evident by non-transposable white lines). In the far right, the TiN transitions to the \{112\}-C-TiN zone-axis with some bending of the \{111\}-C-TiN planes, but they are not disrupted from forming an interface with the hafnia. Similarly to Figure 5.2b, the interfacial hafnia here forms a tetragonal-like region at the electrode. Furthermore like Figure 5.2b, the interface with the \{112\}-C-TiN seems more defective than the portion aligned to the various \{110\}-C-TiN variants.

Similar orientation relationships are observed in Figure 5.3b, where the (020)-O-HfO\(_2\) align with \{111\}-C-TiN planes oriented along both [110]- and \{112\}-C-TiN directions. Here, however, the alignment is tilted across the interface because of the orientation of the HfO\(_2\) grain with respect to the interface, and thus it deviates more from the film∥substrate-like epitaxy of the interface in Figure 5.3a. This may be the origin of the several breaks in the TiN structure that are indicated by
Figure 5.3 (a-c) HAADF STEM images of TiN∥Gd:HfO₂ interfaces exhibiting clear orientation relationship. All planes (white lines) shown in TiN are \{111\}-C-TiN type. (a) White arrows indicate conical regions of rotation boundaries with stacking faults between neighboring units that are oriented along different \langle 110 \rangle-C-TiN directions, which introduces rotation between some of the \{111\}-C-TiN planes. (b) Black arrows indicate transitions in TiN structure, and all TiN regions are \sim \langle 112 \rangle-C-TiN except that in the top right. The image in (a) is courtesy of Dr. Xiahan Sang. Images are acquired with RevSTEM, and image levels are adjusted in the electrode panels due to the strong contrast difference (see dark lines indicating the division in regions).
Figure 5.4 HAADF STEM images showing orientation alignment of TiN∥HfO₂. (a) Orientation relation approximately involving [001]-C-TiN planes and [111]-O-HfO₂ planes; the arrow points to a high-angle grain boundary. (b) Orientation relation evident between TiN∥HfO₂ is visible, but symmetry and plane spacing is not unambiguously able to identify the relation. Images are acquired with RevSTEM, and image levels are adjusted in the electrode panels due to the strong contrast difference (see dark lines indicating the division in regions).

the dark arrows, where the somewhat “mosaic-like” conformity of the amorphous HfO₂ layer may have templated breaks in the [111]-C-TiN planes during deposition of the crystalline top electrode.

Only [111]-C-TiN plane-contrast is shown in Figure 5.3c. This highly corrugated interface possess alignment of the [111]-C-TiN planes to the (200)-M-HfO₂ across the boundary, but they do not possess much area of coincidence across the boundary (i.e. the planes do not possess large areas where they are actually stacking on each other). Here, the lattice spacing is measured to be 2.45 ± 0.02 Å, in good agreement with the predicted [002]-C-TiN lattice spacing.

Figure 5.4a-b shows two final orientation relationship examples. While many orientation relationships in these samples involve [111]-C-TiN planes and low order hafnia facets, not all fall within this category. Figure 5.4a shows near alignment of two sets of [002]-C-TiN type planes to two sets of [111]-O-HfO₂ planes with only slight rotation between the two sets of planes. This slight misorientation is likely driven by the lattices’ attempt to align both sets of planes. The symmetry of the TiN structure looks akin to that expected for the (100)-C-TiN zone axis. Moreover, the measured plane spacing is 2.10 ± 0.04 Å ($n = 8$), which is in close agreement to predicted [002]-C-TiN spacing.
of 2.12 Å. As such, polycrystalline ALD samples do possess some texturing and local orientation relationship that is directly akin to that shown by Fan and coworkers for \{111\} textured ZrO$_2$ on epitaxial (001)-TiN \[5\]. Likewise, the TiN in Figure 5.4b at first glance appears to adopt the symmetry of the (100)-C-TiN zone axis. However, measurement of the interplanar spacing yields a much larger value of 2.36 ± 0.06 ($n = 9$), which is much closer to the \{111\}-C-TiN spacing (2.45 Å) than the \{002\}-C-TiN spacing (2.12 Å). As such, the orientation relationship here is ambiguous and unsolved. Thus, it serves as a final example of how challenging texture information can be to extract from these sorts of materials.

### 5.4 Discussion

As demonstrated by the vast quantity of observed regions involving orientation relation of low order hafnia facets to the \{111\}-C-TiN plane, it serves as one of the important relationships to consider in terms of local epitaxy. Orientation involving \{111\}-type HfO$_2$ planes orientation to the \{002\}-C-TiN plane was also identified, but it was less common and has been discussed previously by Fan and coworkers for ZrO$_2$ grown on epitaxial (001)-C-TiN \[5\].

The atoms in the \{111\}-C-TiN plane are well resolved down the \langle 110 \rangle- and \langle 112 \rangle-C-TiN zone-axes due to fairly large in-plane separation of the atom columns (i.e. large spaces between atom columns on a given plane). In principle, atoms on \{111\}-C-TiN planes may also be resolvable down the \langle 123 \rangle-C-TiN zone-axes, however, slight crystal mistilt or presence of aberration can easily deteriorate contrast such that they are invisible. The \langle 112 \rangle-C-TiN may also be susceptible to loss of atom column visibility due to mistilt and aberration, though they are spaced slightly further apart in-plane down this projection compared to the \langle 123 \rangle-C-TiN. As such, it is unsurprising that in some instances the \{111\} planes but not the atoms are resolved due to multiple zone-axes with close in-plane spacings. Importantly, the \{111\}-C-TiN is the largest lattice spacing for TiN at 2.45 Å. Half of the mean lattice parameter of the M- and O- HfO$_2$ phases is 2.58 Å which is thus only on average ∼+5% larger than the spacing of the \{111\}-C-TiN (see Table 5.1 for a comparison of these lattice vectors).

Based on the HAADF STEM images in Figures 5.2a-d and 5.3a-c, the \{111\}-C-TiN tend to prefer-
Table 5.1 Relevant lattice vector lengths for the M-, O-, and C-TiN structures.

<table>
<thead>
<tr>
<th>Phase</th>
<th>[100] (Å)</th>
<th>[010] (Å)</th>
<th>[001] (Å)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-</td>
<td>5.12</td>
<td>5.17</td>
<td>5.30</td>
<td>Ref.[54]</td>
</tr>
<tr>
<td>O-</td>
<td>5.24</td>
<td>5.06</td>
<td>5.07</td>
<td>Ref.[37]</td>
</tr>
<tr>
<td>C-TiN</td>
<td>6.00</td>
<td>5.19</td>
<td>2.45</td>
<td>Ref.[234]</td>
</tr>
</tbody>
</table>

entially align with low order HfO$_2$ planes. For the M- phase, the (200)- and (002)-M-HfO$_2$ planes are observed to align with the {111}-C-TiN in different images and regions. The (020)-M-HfO$_2$ plane is non-orthogonal, and thus is likely much less favorable a match to the TiN than the other low order M-phase planes. On the other hand, the (020)- and (002)-O-HfO$_2$ planes are observed in different regions to align at times with the {111}-C-TiN. No clear evidence or reason excludes the possibility of (200)-O-HfO$_2$ boundaries with the {111}-C-TiN, but they have yet to be observed. This may be because this plane is corrugated and does not contain the largest lattice vector, which may make it a higher misfit surface than the (020)- and (002)-O-HfO$_2$ alternatives.

Since HAADF STEM does not typically reveal the positions of lighter elements, the exact bonding across these interfaces is unknown. Evidence for interdiffusion of both anion species suggests that both types of bonding can reasonable occur and can be compatible with formation of the clean interfaces and the more “epitaxial-like” interfaces observed. Chemical mapping of these interfaces with electron energy-loss spectroscopy (EELS) is complicated by the strong elastic and inelastic scattering by Z = 72 Hf atoms [49, 206]. Time-of-flight secondary ion mass spectrometry (TOF SIMS) [61] and EELS [3] have suggested the oxidative tendency of the TiN electrodes and of the Ti adhesion layer atop it deposited to help adhere the Pt contact layer. This may suggest that Ti-terminated surfaces in the TiN could be bonding to O-terminated surfaces in the HfO$_2$. In the case of the EELS, the O-signal persists into the TiN beyond just the interface, suggesting that O- has moved beyond the interface into the bulk of the electrode. On the other hand, nitrogen has been shown to incorporate into the films if present during sputter deposition of HfO$_2$ with its presence even promoting the formation of the ferroelectric phase in some instances [39]. Hf-N bonding has been detected at the
Figure 5.5 (a-b) Schematics depicting the nitrogen-terminated \{111\}-C-TiN surface (purple circles) with single hafnium planes of the (200)-M-, (002)-M-, (200)-O-, (020)-O-, and (002)-O-HfO\(_2\) structures (colored circles). The various HfO\(_2\) atom positions cluster in the same general vicinity, often within the natural 3-coordinate environment offered by the nitrogen \{111\}-C-TiN plane. The semi-transparent brown circles show one set of natural cation sites in the \textit{abcabc}\ FCC-type stacking of the rock-salt structure. The \{111\}-C-TiN surface is rotated under stationary HfO\(_2\) sites between (a) and (b) to show the \{\textbf{110}\}\textit{-} and \{\textbf{112}\}\textit{-C-TiN orientation variants commonly observed in experiment. The Hf atoms are displaced slightly above the Ti atoms in the side views to assist in comparison.

lower interface using X-Ray photoemission spectroscopy (XPS)\cite{172}. Furthermore, HfN is a stable metallic compound that shares the rock-salt structure with TiN, suggesting the formation of Hf-N bonds at the interface is reasonable \cite{78}.

The theoretical epitaxial relationship of HfO\(_2\) onto the nitrogen facet of the \{111\}-C-TiN can be explored on the basis of their unstrained structures. Figure 5.5a-b shows a \{111\}-surface facet of nitrogen atoms as purple circles, with the multi-colored/superimposed circles representing the positions of Hf atoms on single (200)-O-, (020)-O-, (002)-O-, (200)-M-, and (002)-M-HfO\(_2\) planes. The (020)-M-HfO\(_2\) is omitted because it contains the non-orthogonal in-plane angle which would introduce large shearing strains and a poor fit. The \{111\}-C-TiN surface is rotated between (a) and (b) so that both lattice alignments are shown (i.e. the same Hf lattices are shown aligned to
both the (110)- and (112) /2-C-TiN lattice vectors, consistent with experiment), and both top and side views are shown for each. Neighboring nitrogen atoms form octahedral sites, as shown by the lines forming the bonds. TiN being an FCC rock-salt with abcabc stacking of \{111\} planes, the upper and lower Ti \{111\} planes that would bound this N surface would fill respectively fill the two different sets of octahedral sites on top and bottom surfaces. One set of these sites is shown with the semi-transparent brown circles.

In both instances of alignment shown respectively in Figure 5.5a and b, the superposition of all of the HfO$_2$ positions at each site shows that the facets all nominally fit the surface with a similar misfit. In certain instances, the Hf atoms fall centered within the octahedral site on the N surface, and in other instances they fall off-center or even between sites. Thus, epitaxy of the Hf onto the N surface would necessarily involve distortion and possibly vacant cation sites. Nonetheless, while some strain of the HfO$_2$ lattice may be necessary to accommodate the fit of the two, completely coherent strain of the film to achieve a decent match is unnecessary. The Hf only fills 1/2 of the octahedral sites that a single abcabc-FCC Ti \{111\} plane would which can be seen by comparing the Hf atom clusters to the brown Ti octahedral sites in the top and side views of Figure 5.5b. Half occupancy could naturally give the Hf atoms more freedom to distort and possibly allow the Hf to occupy sites on a single surface that would technically fall into multiple different abcabc-FCC stacking sites (i.e. the Hf could occupy both a-plane and c-plane sites on a single ad-layer surface on a b-plane-type \{111\}-C-TiN N plane). Also of note, different distortions to the tetragonal parent fluorite HfO$_2$ structure convert 8-anion coordinate Hf atoms into 7-anion coordinate Hf atoms in the M- and O-phases. As such, both phases possess 3-coordinate and 4-coordinate oxygen atoms, so forming a surface with an octahedral nitrogen surface is not unreasonable. These considerations are most important for the stacking-type orientation relationship akin to epitaxy in regions most like those in Figure 5.2b,c and Figure 5.3a, as the surfaces are stacking such that in-plane orientation controls the majority of the misfit.

In the case of those where planes primarily align across the boundary, actual interplanar spacings of the aligned planes likely play a role in parallel to that of the lattice vectors, as the surface area
constraining the interface is much smaller leading to smaller regions where the lattice vectors are misfit. In these cases, the \{111\}-C-TiN interplanar spacing of 2.45 Å is actually quite close and only several percent smaller than many of the (200)-, (020)-, and (002)-type planes of the M- and O-phases.

In both stacking and aligning instances, one important consequence of the observed interface bears mentioning. This will likely lead to some straining of the HfO\textsubscript{2} surface as the \langle110\rangle-C-TiN is 6.00 Å which is much larger than any of the HfO\textsubscript{2} lattice vectors. Because many instances in experiment show a single HfO\textsubscript{2} zone-axis aligned to separate TiN regions with varying alignments, it is reasonable to remove the “dimensionality” of the lattice vector alignments and just consider the surface area of alignment as the product of the two lattice vectors. For the orthorhombic phase, the difference in the product ratios of the HfO\textsubscript{2} to the TiN are the (200)-O-/{\{111\}}-C = -17.6%, the (020)-O-/{\{111\}}-C = -14.7%, and (002)-O-/{\{111\}}-C = -14.9%. For the monoclinic, the (200)-O-/{\{111\}}-C = -12.0% and the (002)-O-/{\{111\}}-C = -15.0%. For both phases, a reduction in the planar strain is likely accessible for the facets that confine the long axes within the interfacial plane (i.e. the [100]-O-HfO\textsubscript{2} and the [001]-M-HfO\textsubscript{2}).

This is well highlighted in the more epitaxy-like interfaces of Figures 5.2b and 5.3a,b where the long axes are confined in-plane and other axes are approximately pointing between the two electrodes. In the case of the orthorhombic phase in Figure 5.3a, both the long [100]-O-HfO\textsubscript{2} and the polar [001]-O-HfO\textsubscript{2} axis are confined in the interfacial plane, and both run parallel to the electrodes. Since this leaves the polar axis with little-to-no component pointing between the electrodes, it is misaligned to favorably contribute to switchable polarization. In the case of Figure 5.3b, apart from some slight tilting of the grain, the long [100]-O-HfO\textsubscript{2} and the [010]-O-HfO\textsubscript{2} are confined in plane approximately parallel to the electrodes, leaving the polar [001]-O-HfO\textsubscript{2} axis pointed nearly perpendicular between the electrodes. In this instance, the polarization of the grain would contribute to switchable polarization. In the case of the grain in Figure 5.3c, even though the polar [001]-O-HfO\textsubscript{2} is confined in-plane, the actual tilt of the grain results in a partial component of orientation of the polar axis between the electrodes, enabling a reduced though present contribution to the total polarization switching of the grain.
From this, several trends can be drawn that may inform a more textured growth of HfO$_2$ polycrystalline thin films. First and foremost, the {111}-TiN surface can be a semi-natural growth plane for the first layer of many of the low order HfO$_2$ facets. In the case of TiN, this will likely lead to some amount of straining of the HfO$_2$, which can be reduced by a few percent by having the interface contain the longest axis of either the M- or the O-phase. In the case of the O-phase growing in an epitaxial layer, this can result in pinning of the polarization direction in either the in-plane or in the out-of-plane directions (with the [010]-O-HfO$_2$ adopting the opposite). A similar domain structuring has been reported for epitaxial HfO$_2$ films [230]. It is unknown whether the electric fields that cycle these films could possibly drive reorientation of the polar axis from an in-plane as-grown configuration to an out-of-plane position after cycling. Worthy of note, the [010]-O-HfO$_2$ and [001]-O-HfO$_2$ are nearly identical in length, and that field cycling fields are expected to be sufficiently strong to reorient as-grown 90° domains into uniform orthorhombic phase grains [4]. On the other hand, if a grain is tilted and the orientation relationship is angled, some amount of polarization switching would still be accessible in the native state. As such, the choice between texturing the TiN to engineer “epitaxial-like” or “aligned/corrugated” type interfaces may both have polarization-related drawbacks.

Furthermore, large strains on the HfO$_2$ by the {111}-C-TiN may be an origin of the tendency of monoclinic and orthorhombic grains to relax towards tetragonal symmetry at the electrode interfaces [3]. The epitaxial strain and symmetry of the {111}-C-TiN may drive structural distortions in the HfO$_2$ towards a tetragonally strained interface layer. The tetragonal layers are quite apparent especially in the interfaces that are epitaxial-like, though they also can be seen in the corrugated interfaces. The distortion and blurring in the lattice near some of the tetragonal layers may be the influence of more irregular structure of the atoms along the atom column, or due to increased presence of vacancies as suggested previously [3] due to their known stabilizing effect of the tetragonal phase [169] and due to wake-up related phenomena [172, 175, 176]. As mentioned earlier in the results, the blurring is more present when the HfO$_2$ long axis is not aligned to the larger of the TiN lattice vectors, which would explain a driving force for even increased distortion and need for displacements/vacancies.
More work is required to compare the standard lattice parameters of the hafnia phases near these interfaces to examine the extent to which they have strained/relaxed.

It is also important to recognize the chemical compatibility of many of the species near these interfaces. HfO$_2$ forms Hf-N bonds at the interface [172] and can incorporate N into its lattice directly [39]. TiN can oxidize and incorporate O [3]. Furthermore, HfN is a stable compound that is both metallic like TiN, and shares the rock-salt structure [78]. As such, intermixing of these species near to the interface is reasonable, but the degree to which they might is not yet fully understood.

As already shown by Fan and coworkers [5], (001)-C-TiN can texture {111}-ZrO$_2$. Here, while our findings show that this can occur in the ALD films, the {111}-C-TiN plane appears to more often be aligning to low order HfO$_2$ planes in the polycrystalline thin films. Many other rock-salt nitride films exist with metallic behavior. For example, the lattice parameters for some rock-salt transition metal nitrides have been calculated by Stampfl and coworkers [75] to be VN = 4.12 Å, TiN = 4.26 Å (compare to 4.24 Å in experiment [234]), LaN = 5.32 Å, TaN = 4.42 Å, NbN = 4.42 Å, ScN = 4.50 Å, HfN = 4.54 Å, ZrN = 4.57 Å, and YN = 4.85 Å. Electrodes could be engineered from this list based on lattice parameter to influence misfit/strain, ability to tune grain size and to texture, and based on the oxidative potential of the electrode to reduce the quantity of oxygen vacancies introduced into the HfO$_2$ which cause undesirable wake-up effects [3, 172, 175, 176]. Furthermore, additional types of electrodes could be conceived of from FCC materials that would have similar {111} planes. Au-{111}, for instance, has the ⟨110⟩ = 5.74 Å and ⟨112⟩/2 = 4.97 Å, and has a much lower potential for oxidation and misfits the (002)-O-HfO$_2$ planar area by only -7%. VN-{111}, on the other hand, would provide a lesser misfit rock-salt metal nitride via its ⟨110⟩ = 5.83 Å and ⟨112⟩/2 = 5.05 Å.

Here, the grain size and roughness of the electrode may play an important role in texturing and influencing the strain and grain size of the HfO$_2$. In the examples presented in this work, these orientation relationships are all observed at the top electrode. The bottom electrode did not as commonly reveal orientation relationships, the origin of which is not understood. The top and bottom electrodes may have different grain sizes, as they grow under very different conditions. The bottom electrode is sputtered onto an Si substrate, possessing at most a thin silica layer after HF
treatment which provides little-to-no oxygen to directly oxidize the bottom TiN during its growth. Furthermore, the (001)-Si may have a strong orienting effect on the bottom TiN electrode during its growth, which could influence its grain size and orientation. On the other hand, the top electrode is deposited onto an oxygen-rich, mostly amorphous layer which has conformed to the uniformity and structure of the surface on which it was deposited: the surface of the polycrystalline TiN bottom electrode. As such, the TiN top electrode is deposited in crystalline form on an amorphous, non-uniform layer containing high amounts of oxygen. The influence of both of these on the grain size is unknown, however, the roughness already seen in the HAADF STEM overview images lend credence to this sort of thinking (see Figure 5.1). In the event that the bottom electrode possesses more grain overlap due to thicker sample regions or due to smaller grains, less frequent atom and lattice contrast would be expected. This could also account for the infrequently observed orientation relation to the bottom electrode.

The interplay of various processes that govern the crystallization of ALD grown HfO₂ films is not entirely understood. Crystallites within the amorphous HfO₂ films are present before annealing and influence the phase formation and electrical response of the post-annealed films [227]. The interaction of these crystallites and the influence of the top and bottom electrodes on the final phase formation and orientation of the HfO₂ is unknown. In the case of these films, the bottom electrode is much smoother than the top layer as mentioned. The top electrode is crystalline as deposited onto an amorphous layer of HfO₂ that was conformally deposited on a bottom electrode. As such, the amorphous hafnia layer, possessing little crystallinity beyond the short-range ordering of perhaps a few crystallites [227] and with a non-uniform surface reflecting conformal deposition via ALD, may actually have a templating effect on the deposition of the top electrode. Thus, while the percentage of texturing of the HfO₂ that stems independently from the top electrode and from the bottom electrode is unknown, it is nonetheless reasonable to assume that the relationships derived from the top electrode are actually rather favorable and reasonable. This is further augmented by the fact that observed cases of local epitaxy fell vastly within the low-order-HfO₂∥{111}-TiN orientation category proposed.
Figure 5.6 (a) EMPAD STEM image with contrast integrated over the annular range of the 002 and 111 TiN Bragg peaks in the diffraction pattern at each pixel. (b,e) Log-scale mean diffraction patterns from the top (b, red) and bottom (e, blue) electrode regions indicated with overlays in (a). (c,f) Indexed top and bottom electrode diffraction patterns. (d) Composite image formed by the colored reflections in (f).
Some insight into the differences between the top and bottom electrode are revealed using high dynamic range pixel array detectors that are capable of recording full diffraction patterns on a pixel-by-pixel basis across an image [235]. By recording the entire diffraction pattern at each pixel, images can afterwards be constructed using any portion of the diffraction pattern, giving access to bright field, dark field, annular dark field, and diffraction analysis from a single data set which can be reconstructed after acquisition. The EMPAD detector used here acquires a 128 x 128 pixel diffraction pattern for an arbitrary number of locations across the sample area (here, 256 x 256 “probe positions”).

A dark-field STEM image acquired with the EMPAD detector is shown in Figure 5.6a. It is formed by annular integration of the signal in the diffraction pattern at each pixel over the spatial frequencies corresponding to diffraction from \{002\}- and \{111\}-C-TiN planes. Example EMPAD diffraction patterns are shown in Figure 5.6b,e, and each of them is the mean pattern integrated over the top and bottom TiN electrodes shown approximately with the red and blue insets in Figure 5.6a, respectively. The first three diffraction “rings” are indexed for each pattern in Figure 5.6c,f. First and foremost, it is immediately apparent that the bottom electrode (Figure 5.6e,f) is highly textured. Its mean diffraction pattern possesses many diffraction peaks that are quite strong, and moreover, able to be indexed. The pattern very much resembles a zone-axis diffraction pattern from TiN-\[110\] (see indexed pattern with overlay in Figure 5.7). The strong \(002\) reflection (see yellow circle) falls on the same diffraction ring as a second, weaker reflection (see small white circle), indicating that the pattern also contains at least a second (though weaker) common rotation variant. This can also be seen in the additional \{220\} reflections (white arrows) and \{002\} reflections (black arrows) in Figure 5.7. The reflections for the \(002\) and \(\bar{1}11\) planes in the average diffraction pattern are both within \(\sim25^\circ\) of the out-of-plane direction of the film, and blurring of the spots indicates presence of some variation in the rotation/alignment of these planes spatially across the image. This blurring of Bragg spots is especially noteworthy for the higher-order diffraction spots. As shown in the composite image in Figure 5.6d, constructing an image by selecting the \(002\) (yellow), \(\bar{1}11\) (red), the second \(002\) variant (white), and the \(\bar{1}1\bar{1}\) (blue) illuminates the majority of the bottom electrode.
Figure 5.7 Digitally magnified log-scale diffraction patterns averaged over the bottom TiN electrode with a TiN [110] zone axis diffraction pattern overlay (black circles). Data courtesy of James M. LeBeau, and was acquired with the 128 x 128 pixel EMPAD detector.

On the other hand, the top electrode is only partially illuminated with these same peaks. An inspection of the diffraction pattern of the top electrode in Figure 5.6b,c, which may contain a contribution from small amounts of the Ti(Ox) adhesion layer due to film roughness, shows that it is much less textured than the bottom electrode. Though not polycrystalline and randomly oriented to the degree that rings are fully formed, it is much closer to forming a traditional ring pattern than the bottom electrode. The orientations seem more random in the top electrode, while the majority of diffraction in the bottom electrode stems from (002) planes. This decreased (or even absent) texture in the top electrode can be attributed in part to its deposition onto an uneven, conformally deposited amorphous layer. Observation of electrode areas in other portions of the sample yield nearly identical types of texturing.

The bottom electrode's lack of low order planes ([111] - or {002}-C-TiN) directly perpendicular to the out-of-plane HfO₂ direction could be one reason why the ALD HfO₂ films in general are highly textured. Growth of highly epitaxial (001)-C-TiN bottom electrodes on substrates like Si [236] or
MgO [5] before conventional growth by ALD and sputtering would yield further insight into the influence of templating and orientation relation between ALD grown films of HfO$_2$ on TiN. Likewise, growth of epitaxial TiN films with different terminating surfaces would enable other orientation relationships to be probed, as well as using other metal nitrides or FCC-metals like Au to tune the strain and lattice mismatch. Nonetheless, the present orientation relationships found in the polycrystalline samples demonstrate that some amount of texturing is already occurring, and provides starting point and model for further study and engineering of HfO$_2$ and ZrO$_2$ films and devices.

5.5 Conclusions

An investigation into the interactions between ferroelectric HfO$_2$ thin films and TiN electrodes reveals many examples of regions with local epitaxy in these ferroelectric polycrystalline capacitors, where low order (002)/(020)/(200) HfO$_2$ planes align with, or stack on top of, \{111\}-C-TiN planes. Chemical compatibility of Hf and N, as well as prior spectroscopic evidence, suggests that formation of a boundary between Hf and N is feasible. The interface can be approximated as occurring between a low order Hf atom plane and a N-terminated \{111\}-C-TiN plane. In this interface, the HfO$_2$ lattice aligns to a rectangle-symmetry N lattice defined by the \langle 110 \rangle -C-TiN = 6.00 Å and \langle 112 \rangle /2-C-TiN = 5.19 Å. In some instances, a corrugated interface can also lead to the involvement of the \{111\}-C-TiN plane spacing. Hf atom columns are able to accommodate three-coordinate sites such as are on the \{111\}-C-TiN surface, and moreover, the Hf-terminated low order HfO$_2$ planes are half as dense as a typical Ti \{111\}-C-TiN plane. Thus, vacancies and local distortions are able to accommodate the misfit of these interfaces. Nonetheless, the \langle 110 \rangle -C-TiN highly misfits all HfO$_2$ lattice vectors, and the \{111\}-C-TiN repeat unit is larger and more tetragonally distorted than all of the possible HfO$_2$ primary facets. Strong tetragonal strains resulting from this are likely at least partially responsible for tetragonal distortions of HfO$_2$ lattice near the electrode interface. More work is needed to measure the mean strain at the interface to determine the extent of strain/relaxation of the hafnia. To minimize strain at the interface, the HfO$_2$ lattice commonly contains the largest low-order lattice
direction in plane. For the orthorhombic HfO$_2$ phase, confinement of the [100] in-plane can lead to two orientations of the polar [001], one of which is confined in-plane, which is an important consideration for optimizing texture. The bottom electrode is found to be highly textured, with large amounts of (002) and (111) planes lying within $\sim$25° of the out-of-plane direction of the capacitor stack. On the other hand, there is much less texture in the top electrode, which likely is driven by its deposition onto a non-uniform, amorphous film. Growth of HfO$_2$ on epitaxial layers of TiN would aid in validating the present understanding of local epitaxy in ALD grown films, though present findings appear compatible with a previous study that found a converse relationship where epitaxial (001)-oriented TiN lead to {111} texturing of ZrO$_2$ [5]. Furthermore, additional substrates like other metal nitrides, or even Au, could be utilized to further validate the present model of local orientation relationships, and to tune the strain of the interfaces to influence the ferroelectric properties.
Chapter 6

Interface Accommodation Mechanisms for Growth of CdO Thin Films on MgO and Al₂O₃ Substrates

The need for oxide-based electronics and for their integration with conventional semiconductors has led to the development of new oxide systems with enhanced properties. Recently, semiconducting CdO thin films have been grown with tunable carrier concentrations and high mobilities. These works have demonstrated that CdO can be used as a conductive oxide layer in various electronic devices. Moreover, the achievable mobilities and carrier concentrations allow preparation of tunable plasmonic properties within the mid-infrared regime that is typically unachievable with standard plasmonic materials. Here, we use scanning transmission electron microscopy to investigate how interface structure and crystal misfit impacts the structure of CdO films grown on MgO-(001) and c-Al₂O₃ (i.e. (00.1)-oriented Al₂O₃). For these systems, epitaxial growth must overcome either large lattice parameter mismatch or a strong dissimilarity between the crystal structure of the film and substrate. Nonetheless, the interface structure in both instances is able to accommodate epitaxial growth and leads to highly conductive films. Some additional introductory material to this section is found in Chapter 1.2.2.
6.1 Introduction

Recent demonstrations of extreme mobility and tunable carrier concentrations in doped CdO thin films have led to investigation of the properties of this rather new transparent conductive oxide [81, 237–244]. This material is of interest not only for its high conductivity, but also for its tunable properties within the mid-infrared optical spectrum that make it attractive for use in plasmonic devices and sensors [81, 244]. First principles work demonstrates that the naturally high $n$-type conductivity of intrinsic CdO films results from oxygen vacancies and hydrogen incorporation that are practically unavoidable under all growth conditions [240]. Extrinsic cation doping within a certain regime can increase both the carrier concentration, and perhaps counterintuitively, the carrier mobility [81, 237, 239, 243, 244]. Sachet and coworkers [81] used first principles calculations to reveal that this phenomena originates from suppression of the formation of intrinsic oxygen vacancies which act as natural scattering centers that decrease the mobility of intrinsic films. Consistent with this, films frequently possess elevated mobilities compared to intrinsic films within a certain doping
High carrier mobilities are important for semiconducting devices, as material conductivity is the product of carrier concentration and the carrier mobility.

CdO films can be grown by a variety of methods and doped with a range of cations to yield enhanced properties. Yan and coworkers [237] report carrier concentrations and Hall mobilities of $2.72 \times 10^{20}$ cm$^{-3}$ and 330 cm$^2$V$^{-1}$s$^{-1}$ for pulsed laser deposition grown CdO thin films doped with Sn on MgO-(001). Oxide molecular beam epitaxy grown CdO with Dy doping on MgO-(001) achieved mobilities approaching 500 cm$^2$V$^{-1}$s$^{-1}$ with carrier concentrations on the order of $10^{20}$ cm$^{-3}$ [81]. Kelley and coworkers [243] grew Y doped CdO on $c$-Al$_2$O$_3$ substrates using pulsed DC and RF power reactive co-sputtering, achieving intrinsic (doped) CdO films with mobilities and carrier concentrations of 330 cm$^2$V$^{-1}$s$^{-1}$ ($> 400$ cm$^2$V$^{-1}$s$^{-1}$) and $1.8 \times 10^{19}$ cm$^{-3}$ ($\sim 2 \times 10^{20}$ cm$^{-3}$).

Sol-gel methods have also been employed to create polycrystalline Al doped CdO films on glass with mobilities between 190 to 413 cm$^2$V$^{-1}$s$^{-1}$ for carrier concentrations between $0.85 - 0.34 \times 10^{19}$ cm$^{-3}$ [239].

The mobilities of these films is higher than those of many conventional transparent oxide conductors. For example, indium tin oxide thin films yield a much narrower range of accessible carrier mobilities that span $\sim 10$-50 cm$^2$V$^{-1}$s$^{-1}$ with carrier concentrations between $\sim 2 \times 10^{20}$ to $\sim 1.4 \times 10^{21}$ cm$^{-3}$ depending on film growth parameters and Sn concentration [245]. Alternatively, ZnO films grown by pulsed laser deposition can possess mobilities between $\sim 18$-20 cm$^2$V$^{-1}$s$^{-1}$ with carrier concentrations in the realm of $4 - 8 \times 10^{19}$ cm$^{-3}$ [84]. As such, CdO is well poised to offer routes to much higher mobility transparent conductive oxide layers if carrier concentrations in the realm of the $10^{19} - 10^{20}$ cm$^{-3}$ are sufficient for the application.

Initial studies looking at the optical properties of CdO films for plasmonic applications investigated Dy doped CdO grown on MgO substrates [81]. CdO and MgO share the rock-salt structure (no. 225 Fm$\bar{3}$m), though they are misfit by $\sim 11.4\%$ (MgO $a = 4.21$ Å versus CdO $a = 4.70$ Å). Alternative substrates to MgO have since been considered for a variety of reasons including issues with MgO surface quality and structural integrity. $c$-Al$_2$O$_3$ has also proven a surprisingly robust growth surface for CdO films [238, 243]. Measurement of optical/electrical properties of CdO∥$c$-Al$_2$O$_3$ finds it able to
support comparable mobilities and carrier densities to films grown on MgO [243, 244]. This finding is rather surprising, considering that cubic rock-salt CdO differs substantially in symmetry from the hexagonal-like α-alumina structure (no. 167 R̅3c). Herein, we investigate the atomic structure of these interfaces and associated defects with atomic resolution scanning transmission electron microscopy (STEM), as they can have important consequences for achievable optical/electrical properties and carrier mobility [246].

6.2 Experimental

A thickness series of undoped CdO films capped with 12 nm of MgO was grown on (001)-oriented MgO substrates with oxide molecular beam epitaxy as described previously [81]. CdO layers in the CdO∥MgO heterostructures were approximately 1, 1.7, 3, 5.5, and 9 nm thick. CdO∥MgO lamellas were prepared for STEM using a focused ion beam (FEI Quanta) with final thinning at 2 kV.

Undoped CdO films were grown on c-Al2O3 substrates with reactive DC magnetron sputtering as previously reported [243]. Lamellas from CdO films on sapphire were prepared with mechanical wedge polishing with an Allied Multiprep before Ar ion milling with a Fischione Model 1050 with liquid nitrogen cooling.

ADF STEM was performed on a probe-corrected FEI Titan G2 60-300 kV operated at 200 kV. Beam currents between 30 to 60 pA were used. Probe semi-convergence angles and detector inner semi-angles for the CdO∥MgO (CdO∥c-Al2O3) were 19.6 mrad and 34 mrad (19.6 mrad and 28 or 49 mrad) respectively. The RevSTEM method was employed to minimize drift related distortions [157], using 20-40 1024x1024 pixel frames with a 2 µs/pixel dwell time. Local strain was measured by fitting the atom column peak positions using Gaussian peak fitting followed by indexing the positions into a matrix for direct strain measurement based on the atom column positions [155, 163]. Geometric phase analysis was performed using the FRWRtools plugin developed by Christoph T. Koch [147].
6.3 Results and Discussion

6.3.1 CdO Epitaxy on MgO-(001)

Epitaxial films of CdO thinner than 10 nm are grown on MgO (001) to study how the CdO∥MgO interface accommodates such highly lattice mismatched growth. The intrinsic CdO layers are grown with oxide molecular beam epitaxy as described previously [81], before capping with a 12 nm protective layer of MgO. Annular dark-field (ADF) STEM is used to reveal the structures of the crystal lattices in the vicinity of the interfaces. A low-angle ADF (LAADF) detector inner semi-angle of 34 mrad is used to increases the sensitivity of the image contrast to sample features that de-channel the electron beam like defects and strain [125]. It additionally enables better simultaneous visualization of the heavy Cd ($Z = 48$) and lighter Mg ($Z = 12$) atoms, as well as the O atoms ($Z = 8$) in the MgO sublattice.

Images of the MgO∥CdO interface indicate that the epitaxial growth of (001)-CdO on the (001)-MgO substrate (and subsequently, the MgO-(001) capping layer on top of the (001)-CdO) is facilitated by the formation of a periodic array of misfit dislocations at both top and bottom interfaces in the confined heterostructures. These defects are indicated with black arrows in Figure 6.1a for an LAADF STEM image of a 5.5 nm thick CdO film. Misfit dislocations commonly allow epitaxial growth of films on lattice misfit substrates [247, 248]. The dislocations in this instance enable coherent registry of the $\{\bar{2}20\}$-CdO and $\{\bar{2}20\}$-MgO planes across the interface in interface regions away from the dislocation cores. Dashed lines in the digitally magnified LAADF STEM image in Figure 6.1b map the $\{\bar{2}20\}$ planes across the boundary. At the outermost edges away from the core, both MgO and CdO-$\{\bar{2}20\}$ planes are nearly co-planar due to lattice strain. As strain energy builds up due to lattice misfit, the $\{\bar{2}20\}$ alignment bends across the boundary from CdO to MgO. By mapping the registry along the interface, it is evident that two additional $\{\bar{2}20\}$-MgO planes form the dislocation core as shown in Figure 6.1.

From this analysis, the dislocation lines are identified as lying in the $\langle 110 \rangle$ directions contained in the (001) interfacial plane, i.e. the $\xi_1 = [110]$ and the $\xi_2 = [\bar{1}10]$. Each dislocation line has a
Figure 6.1 (a) LAADF STEM image of the 5.5 nm thick CdO film interface viewed down the [110] zone-axis with regularly spaced edge dislocations (indicated by black arrows) at the top and bottom CdO∥MgO interfaces. (b) Expanded view of the rectangular inset in (a) with dotted lines drawn along {220} CdO∥MgO planes, which highlights the insertion of two additional MgO {220} planes above the dislocation core.
Burgers vector of type $(110)/2$ that lies normal to it in plane, i.e. $\mathbf{b}_1 = [\bar{1}10]/2$ and $\mathbf{b}_2 = [110]/2$. The dislocations are edge dislocations which are 100% effective at relieving misfit strain since the Burgers vectors lie entirely in the plane of the interface [248]. Since the dislocation lines $\xi_1$ and $\xi_2$ intersect in the interfacial planes, the dislocations overlap and form a square-like grid.

Scanning tunneling microscopy [249] and combined X-Ray diffraction/finite element modelling [250] have studied dislocation grids of these sorts in PbTe||PbSe rock-salt systems with $\sim$7% misfit. Moreover, similar interfacial plane $(110)$-type dislocation lines with orthogonal $(110)$-type Burgers vectors have been seen in TiN-(001)||NbN-(001) metal-like rock-salt nitride systems where the misfit is only $\sim$3.6% [251]. Thus, the dislocations found for the CdO||MgO system are in good agreement with other experimentally observed heteroepitaxial rock-salt systems and with traditional understanding of dislocation structures in rock-salt materials [249–252].

Highly mismatched systems grow to minimize misfit by balancing (1) epitaxial strain absorbed by the lattice and (2) strain accommodated by the formation of misfit dislocations [247, 248]. Extending this to the present system, the greatest lattice coincidence occurs when integer numbers of $(110)$ repeat units of CdO and MgO occupy nearly identical space at the interface. Mathematically for this system, this will occur when $d_{(110)\text{CdO}} \times N_{\text{CdO}} = d_{(110)\text{MgO}} \times M_{\text{MgO}}$, where $N$ and $M$ are near integer values of CdO and MgO repeat units and $d$ are the interplanar spacings. Values of 8-10 CdO repeat units are nearly equal in distance to 9-11 MgO repeat units. From this, dislocations are expected to be spaced with a periodicity of approximately 2.7 nm to 3.3 nm to minimize strain. In these cases, the additional MgO repeat unit completes the Burgers circuit, and is thus approximately equal to the Burgers vector which is the plane spacing of the $(110)$-MgO plane.

The dislocations are readily identified in Bragg filtered images. These images are constructed by masking all spatial frequencies in the image's fast Fourier transform (FFT) except for a set of chosen $\mathbf{g}$ and $-\mathbf{g}$ reflections before taking the inverse FFT. From Bragg filtered images, the dislocation core spacings are readily measured in between regions where the lattice planes are disrupted by the dislocations. For example, a STEM image of the 5.5 nm CdO heterostructure and its FFT are shown in Figure 6.2a-b. The white regions in the FFT are the spatial frequencies that are bandpass filtered.
Figure 6.2 (a) STEM image of 5.5 nm CdO confined heterolayer. (b) Digitally magnified and cropped FFT of (a) with white circles indicating regions that are bandpass filtered. (c) Bragg filtered image (i.e. the inverse FFT of the bandpass filtered FFT in (b)).

(i.e. all frequencies outside of these are cleared). The inverse FFT of this bandpass filtered FFT is the Bragg filtered image in Figure 6.2c where the dislocation cores are readily visible as dark cores in the CdO layer. CdO film thicknesses of 1 nm and 5.5 nm possess average spacings of \( \sim 3.3 \) nm and 3.2 nm respectively. These spacings are in good agreement with the upper limit of calculated spacings based on coincidence of \{110\} repeat units. Further, they indicate that the films are fully relaxed by a CdO film thickness of 1 nm.

In the thinner films (1 nm and 1.7 nm), periodic regions of strain are evident as darker contrast running in the \( \langle 111 \rangle \)-type directions diagonally through the CdO film. These distorted regions are manifest in these LAADF images as film portions with obscured contrast as well as distortion of the atom columns and structure of the crystal lattices. Strain can be measured from the images directly on a site-by-site basis by comparing the product of the local plane spacing around each site to the mean values of that species in the image (either MgO or CdO). In other words, expansion and contraction is quantifiable at a site by measuring the distances between near-neighbor atom columns, combining these distances to generate a mean “area” of a given repeat unit, and comparing this to the global mean repeat unit size for either CdO or MgO. Figure 6.3a shows an MgO\|CdO interface for the 5.5 nm confined heterostructure viewed down the \( \langle 110 \rangle \) zone-axis. Since strain is primarily changing away from the interface, here the c-lattice parameter neighbor is chose as the
Figure 6.3 (a) LAADF STEM image of the 5.5 nm thick CdO film top interface with dislocations marked by arrows. (b) Local strain at a site relative to the mean strain across all sites of that kind for the species, the measurement of which is described in the text. Color range set manually to enhance features, as the strains at the core are much higher than the minima/maxima values in the color scale.
one in the [001] direction for the MgO and the [001] for CdO. The lateral distances (the $\langle110\rangle/2$ type) are measured as half the distance between the midpoints of the Cd or Mg atoms on either side of the site. Atom column fitting is performed as described previously [163].

The strain map measured by this method is shown in Figure 6.3b where the strain in the CdO and MgO are on the same manually-set colorscale, but are relative to the means of their particular species. At the dislocation cores, the MgO lattice is compressed and the CdO is expanded. Structural changes at each dislocation core extend approximately 0.5 nm along the interface and similar distances into the substrate and film. Strains associated with the dislocations appear to extend slightly further into the CdO film than into the MgO. The strain mapping also reveals periodic fluctuations in the epitaxial strain experienced by each species along the interface. In the regions of coherent structure, the CdO film is compressed and the MgO substrate is expanded. The periodicities of both stresses are regular, and in good agreement with the measured dislocation spacings.

Geometric phase analysis (GPA) is another method capable of accessing local strain information by analyzing shifts in the Bragg peaks of the fast Fourier transform (FFT) between an image region and a reference area within the image [164]. This must be performed with two non-colinear Bragg peaks. While the spatial resolution of GPA is more limited since it involves averaging over a larger sample area to generate a sufficient FFT, it can be performed on images where large distortions make atom column indexing very challenging like the current case.

GPA is performed here using a portion of the rather undistorted MgO substrate or capping layer as a reference. Because the focused ion beam damaged certain portions of the MgO more than others, care is taken to choose relatively undamaged MgO possessing good contrast in the lattice and atom columns. Since MgO is the reference area, the majority of the MgO substrate and capping layer appears unstrained away from the interface, which validates that the reference MgO regions are suitably chosen for each image. GPA using the $\{002\}/\{111\}$-type FFT reflections shows that the CdO films of all thicknesses are tensile strained (expanded) in the $\epsilon_{xx}$ and $\epsilon_{yy}$ directions compared to the MgO, as seen in Figure 6.4. Within the CdO layers of all thicknesses, the average in- and out-of-plane tensile strain in the CdO is very close to a $\sim10$-$12\%$ expansion of the MgO lattice, as
Figure 6.4 LAADF STEM images of ∼1, 1.7, 3, and 5.5 nm CdO∥MgO heterostructures viewed down the [110] zone axis. $\varepsilon_{xx}$ and $\varepsilon_{yy}$ derived from geometric phase analysis of the (002)/(111) spots using the MgO as a reference reveals the strains near the dislocation cores, as well as zigzagging strain fields in the thinner films that originate from overlap of dislocation stress fields. Expected based on the lattice parameter mismatch. The GPA results also reveal that the CdO and MgO at the dislocation cores experience considerable in-plane $\varepsilon_{xx}$ tensile and compressive strains, respectively, which is in good agreement with the lattice expansion and contraction that are directly measured in Figure 6.3b.

Beyond verifying the lattice expansion of the CdO relative to the MgO and the strains at the dislocation cores, GPA also reveals strain anomalies within the CdO films. The strain distributions within the thinner films (1 nm and 1.7 nm) differ from those of the thicker films (approximately > 3 nm). This non-uniformity is manifest as regions of increased CdO tension in-plane $\varepsilon_{xx}$ that are coincident with compression out-of-plane $\varepsilon_{yy}$. These regions zigzag along the same path through the thinner CdO films between the dislocation cores on opposite interfaces. The superposition of these variations in strain are in good accord with Poisson’s ratio. In contrast to the thinner films, these
strain networks are subtle and effectively absent in the 3 nm film, and have fully vanished by 5.5 nm film thicknesses. The diminishment of the strain fields with the increase in film thickness suggests that the origin of strain fields is the overlap of the dislocation strain fields between transverse dislocations on opposite interfaces. Because the regions of high lattice distortion are confined to the relatively close proximity of the dislocation cores, strain field network formation disappears when transverse dislocations are spaced such that highly strained regions no longer overlap. GPA performed with the (002)/(220) Bragg reflections shows strain field formation consistent with that seen using the set (002)/(111) reflections, validating this result.

6.3.2 CdO Epitaxy on c-Al₂O₃

The CdO thin films for this study are grown on c-Al₂O₃ using reactive DC magnetron sputtering as described in Ref. [243]. These films are previously reported to grow with the (052)-CdO||(00.1)Al₂O₃ orientation relationship with three rotation variants consistent with the three-fold symmetry of the hexagonal lattice [238]. The films here also demonstrate three-fold rotational variants [243], yet they maintain high crystallinity and comparable mobility to those grown on rock-salt MgO [81].

HAADF STEM gives insight into why the mobility of CdO grown on a substrate with such a different structure might be similar to that of CdO grown on a substrate that shares its structure. The grain size is quite large and commonly persists through the thickness of films even when they are a few hundred nanometers thick. The HAADF STEM image in Figure 6.5 shows a wide field of view of a standard grain in these films. The CdO grain is large and continuous. The interface between the c-Al₂O₃ and CdO is epitaxial and regular in the right of the image, in spite of the vastly different structures. A black arrow in the c-Al₂O₃ indicates a feature that may be a substrate step due to the change in the interface structure to the left of this feature where the interface becomes blurred and disrupted. In spite of this defect, no rotational variant is introduced, and the lattices maintain the same alignment as that to the right of the feature. In the CdO, black arrows lie on either side of a “blurring” of the lattice where the contrast of atoms on the (001) planes distort and become more “plane-like” compared to the CdO lattice outside of this area which has clearer atom contrast. This
**Figure 6.5** HAADF STEM with a wide field of view of a standard grain in CdO. Black arrows in CdO indicate distortion that threads through the CdO lattice and originates near a break in the interface, possibly due to a step, as indicated by the black arrow in the c-Al₂O₃. ADF inner semi-angle is 28 mrad.
Figure 6.6 (a) HAADF STEM image showing alignment of the (100) CdO planes to the (10.0) Al₂O₃ planes. The Al₂O₃ [12.0] has been tilted ∼3° off zone to yield atom contrast in the CdO-[013], leading to some overlap of the structures at the interface which blurs that portion of the image (horizontal white arrow). The angled arrow shows a strained portion of the lattice containing a screw dislocation. (b) A non-RevSTEM image of the same zone-axis showing a misfit dislocation indicated by the arrow. ADF inner semi-angle of 28 mrad.

may be the result of a threading dislocation's strain field that is distorting the lattice. If present, the dislocation may arise as a threading dislocation due to the step. Dislocations will be discussed in greater detail later.

The [12.0] zone-axis of the Al₂O₃ yields additional useful information about the interface structure because it is normal to the [10.0] and provides a different perspective of it. Here, CdO (100)-type planes stack vertically on the (10.0) planes exposed on the c-Al₂O₃ surface as shown in Figure 6.6a-b. The lattices align down the Al₂O₃-[12.0] zone-axis such that both phases cannot be aligned to zone axis simultaneously. In Figure 6.6a-b, the CdO has been tilted some degrees (∼3°) away from the Al₂O₃-[12.0] such that it is aligned to the [013] zone-axis. This results in a loss of atom contrast in the Al₂O₃, which results in lattice-plane contrast rather than atom column visibility. Furthermore because of the tilting, the lattices at the interface overlap which leads to a region of intermediate contrast and blurring at the interface (see horizontal arrow in Figure 6.6a). The misfit, however, is found to be rather small. The (10.0)-Al₂O₃ spacing is ∼4.76 Å compared to the CdO-(100) spacing of ∼4.70 Å. This misfit likely drives some formation of misfit dislocations as shown by the arrow in Figure 6.6b. The dislocation contrast indicated by the arrow in the left corner of the image in Figure 6.6a is likely due to a screw or mixed dislocation originating from a substrate step or other film∥substrate interaction similar to GaN∥c-Al₂O₃ threading dislocations [253], and it appears simi-
lar to the dislocation discussed earlier in Figure 6.5. It looks qualitatively different than the edge misfit dislocations observed in Figure 6.6a. Moreover, distortion of the lattice is visible in a manner consistent with variation of the structure in the depth of focus of the electron beam due to a screw dislocation [254].

As mentioned, the grain size and regions of epitaxy in these materials can be quite large. Frequently, these regions are limited by the native rotation variants, as discussed earlier. Figure 6.7a-b shows two examples of these, where the portions to the left are oriented as shown in Figure 6.5. To the right of the boundaries, only lattice planes and not atoms are visible. These are actually \{111\}-type planes of the CdO, which in the rock-salt structure alternate between anion and cation layers as mentioned in Chapter 5, and thus the Cd planes are visible as the bright lattice planes. The boundary in Figure 6.7a is more abrupt than that of b. Though the left and right portions of these images are different rotation variants, they provide the atom positions to develop models of the interface structure.

Figure 6.8 shows the orientation of a single rotational variant of the CdO||c-Al$_2$O$_3$ interface down the three key zone-axes. The model built from the experimental images has good agreement with the STEM images without straining either species. It also shows how the boundaries in Figure 6.7a-b must be between different rotational variants, because both the [100]-CdO zone-axis and the one revealing the \{111\}-planes of the CdO are simultaneously in orientation relation to the [10.0]-Al$_2$O$_3$ zone-axis. A single variant, however, has a 60° rotation of the substrate between the two “zones.” In this regard, CdO shows some differences to higher misfit rock-salts grown on c-Al$_2$O$_3$ (\(a=4.21\) Å for MgO and \(a=4.15\) Å for CrN [255]) which are reported to grow \{111\}-oriented out of plane [256, 257]. This is also found for HfN films grown on c-Al$_2$O$_3$ as will be shown in Chapter 7.

Recognizing that the [10.0]-Al$_2$O$_3 = 4.76$ Å and the [100]-CdO = 4.70 Å spacings have only moderate misfit and thus drive the lattice orientation, the CdO structure tilts to expose the (052) surface to the (00.1)-Al$_2$O$_3$, resulting in a good interfacial fit across the various directions of the c-Al$_2$O$_3$ surface. The origin of the rotation variants comes from the hexagonal symmetry of the sapphire where the [10.0]-, [11.0]-, and [01.0]-type orientations offer the identical plane spacing and symmetry that well
Figure 6.7 (a-b) Two examples of boundaries formed between different rotation variants of the CdO∥c-Al₂O₃. The boundary in (b) is less abrupt than that in (a). ADF inner semi-angle is 49 mrad.
Figure 6.8 Schematics of a single rotational variant of CdO∥c-Al₂O₃ viewed down three different axes akin to those zones observed in experimental images. Relevant zone-axes and planes are labeled.

Figure 6.9 A top down view of the last cation/anion layer of the Al₂O₃-(00.1) surface and of several layers of CdO viewed down the [052] zone-axis. The semi-transparent dashed black, white, and gray lines show the 3 rotation variants of the CdO on c-Al₂O₃.
matches the CdO-[100]. These three variants are shown as dashed, semi-transparent white, black, and gray lines overlaid onto the final anion/cation layers of the (00.1)-Al₂O₃ surface in Figure 6.9.

From the structure model, it is apparent that the rotational variants form due to the compatibility of the cubic CdO with three equivalent sets of planes in the hexagonal lattice that are separated by consecutive 60° rotations (see the hexagonal axes in Figure 6.9). Thus, the lateral grain size is likely limited by the coalescence of islands that nucleate and grow together during the growth phase. As shown in Figure 6.5, steps do not necessarily introduce rotation boundaries. Furthermore, Figure 6.7a-b shows two boundaries with different abruptness, suggesting the direction of island coalescence may play a role in the formation of a particular grain boundary. Growth methodologies or substrate preparation methods that enable control of nucleation sites and rates may enable tuning of the lateral grain size in these materials, with the potential for an increase in achievable carrier mobilities.

In terms of defects, several images presented demonstrate the presence of dislocations. Some of these are misfit dislocation akin to those seen in Figure 6.6b, and are effectively an insertion of an additional (200)-type CdO plane at the core to relieve misfit. In this way, the misfit dislocations act similar to those in the case of the (001)-CdO∥(001)-MgO epitaxy examples presented earlier. The c-Al₂O₃ substrate also leads to formation of threading dislocations in the CdO. Because of the finite depth of focus of the STEM probe and the influence of beam channeling on atom columns [258, 259], depth and focus dependent lattice distortions can be manifest in STEM images due to screw dislocations [254]. Distorted regions of the crystal lattices observed here show some consistency with the displacement fields of a screw dislocation viewed from the side, such as between the black arrows in Figure 6.5 and by the white arrow in the top left of Figure 6.6a. Steps may in some instances initiate the formation of dislocations, similar to the region suggestive of dislocation formation near the step in Figure 6.5. Defect scattering is known to decrease plasmonic performance [82]. For this reason, elimination or suppression of threading dislocations and rotational variants could lead to decreased carrier scattering which may enable increased mobility and improved plasmonic performance.
6.4 Conclusions

As revealed in individual results of CdO films grown on (001)-MgO and (00.1)-Al₂O₃, high quality crystal growth is achievable on a highly-misfit (~11.4%) MgO-(001) substrates that share its structure and on c-Al₂O₃ substrates that possess very different symmetry and structure but low misfit (~1.4%). Misfit dislocations form in both instances to relieve strain. In the case of very thin films on the highly-misfit MgO, networks of dislocations form a square lattice in the interfacial plane. As film thicknesses decrease, the strain fields of transverse dislocations at interfaces with the capping MgO layer and MgO substrate begin to overlap and to form strain field networks that zig-zag through the film. The CdO layers nearest the interface are in tension at the cores and in compression between the cores, while the MgO layers nearest the interface are in compression at the cores and in tension in between them.

For CdO on c-Al₂O₃, three rotation variants form because the [100]-CdO can align with identical misfit and structure to the [10.0]-, [11.0]-, or [01.0]- directions on the c-Al₂O₃ surface. The misfit native to the CdO∥c-Al₂O₃ results in formation of misfit dislocations to minimize strain. The (052)-CdO planes grow on the (00.1)-Al₂O₃, and the interface of the first plane adapts to the difference in symmetry of the substrate by distortion of some of the atom sites in the first plane and possible changes in site occupancy by means of vacancies. Mixed or threading dislocations are present in the films, likely originating at the interface due to steps on the sapphire surface. The lateral grain size in the CdO on c-Al₂O₃ is limited by the coalescence of islands that nucleate and grow with different orientation, which is manifest as high-angle grain boundaries formed within the film. Nonetheless, the grain size is very large, and the interface of these grains are well able to accommodate the lattice misfit and symmetry difference of the substrate, even in the vicinity of substrate steps.
Chapter 7

Towards Interfacing Rock-Salts with GaN: HfN, MgO, Mg\textsubscript{x}Ca\textsubscript{1−x}O, and MnO

This final Chapter contains structural analysis of novel rock-salt materials with particular emphasis on their structure as grown on GaN-(00.1). As discussed in Chapters 1.2.1 and 1.2.3, these new films can have various properties. In the case of HfN, it of use as a transducer for high temperature thermal conductivity measurements, and its ability to epitaxially integrate on various substrates is considered. MgO, Mg\textsubscript{x}Ca\textsubscript{1−x}O, and MnO are considered as a possible means of generating an interfacial two-dimensional electron gas (interface metallization) on GaN substrates, and as a transition layer for incorporation of other oxides onto nitrides for further functionality. As such, the structure, defects, and epitaxy of these systems are considered and interrogated. Additional introductory and background material to this section is found in Chapter 1.2.3.

The results presented in this Chapter are a product of a collaboration with Kevin Ferri (Pennsylvania State University, State College, PA, USA), Dr. Christopher T. Shelton (North Carolina State University, Raleigh, NC, USA), Dr. Xiahan Sang (Oak Ridge National Laboratory, Oak Ridge, TN, USA), Prof. Jon-Paul Maria (Pennsylvania State University, State College, PA, USA), and Prof. James M. LeBeau (North Carolina State University, Raleigh, NC, USA). HfN, MgO, Mg\textsubscript{x}Ca\textsubscript{1−x}O, and MnO films investigated in this section are grown by Kevin Ferri in the group of Prof. Jon-Paul Maria.
Kevin Ferri performed X-Ray diffraction and atomic force microscopy (AFM) measurements which are referenced but not presented here. Dr. Christopher T. Shelton is gratefully acknowledged for providing early samples of oxides grown on GaN. All authors are gratefully acknowledge for useful discussions, guidance, and suggestions in the course of this work.

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7.1 HfN Grown on GaN, c-Al2O3, and MgO

HfN films possess the rock-salt structure like MgO, CdO, MgCa1−xO, and MnO. Unlike these oxides which are insulating, it is metallic. Moreover, it is a nitride, while the others are oxides. As such, the structure of HfN films provides a complement to insulating oxide rock-salts. The HfN samples viewed in this study target application as a transducer for thermal conductivity measurements [78]. Moreover, related nitrides are often used in CMOS technology [74] which could be another application for HfN. HfN was grown as described previously [78]. Samples were prepared in cross-section for STEM using mechanical wedge polishing followed by liquid nitrogen cooled Ar ion milling. Samples were imaged using a probe corrected FEI Titan G2 60-300 kV operated at 200 kV. Images were acquired with RevSTEM [157] using 20 to 40 image frames with a 2 μs dwell time and a
Figure 7.1 (a-b) HAADF STEM images of \{111\}-HfN∥(00.1)GaN epitaxy. In regions without steps as in (a), the structures are regular on either side of the interface. The region in (b) contains a step in the GaN (see white arrow) introducing a fault into the HfN, where the FCC-abcabc HfN stacking is different on either side of the step with a “V-shaped” transition region forming between the two variants, where the \{111\}-type planes (white and black lines) cannot be transposed between the regions. (b) also shows an integrated line profile of the first HfN layer indicated by the black arrow, with the white arrows in the plot and image corresponding to the approximate region of the step, and the dashed gray line showing the mean value of the line profile.

HfN films are grown on (00.1)-GaN∥c-Al2O3, c-Al2O3, and MgO-(001) for comparison of growth orientation, film quality, and defects. On the basis of HfN being both a nitride and a low misfit system to GaN (HfN a=4.52 Å [75] with \(a\sqrt{2}/2 = (110)/2 = 3.19 \text{ Å}\) compared to GaN \(a=3.19 \text{ Å}\) [108]), it is expected to grow with highest quality when GaN is the substrate. As shown in Figure 7.1a, HfN films do grow epitaxially on GaN and form high quality interfaces and film structures. As previously demonstrated by Paisley and co-workers [114], rock-salts commonly grow \{111\}-oriented on the GaN (00.1), and Figure 7.1a shows this to be the case of HfN.

GaN-(00.1) substrates typically contain high densities of threading dislocations which result in many steps on the substrate surface [253]. Since GaN and Al2O3 are both hexagonal-close-packed (HCP) structures and since both possess surface steps, they alternate ababab plane stacking in the [00.1] direction such that threading dislocations/substrate steps result in \(a\)-plane and \(b\)-plane terminations on either side of the step. On the other hand and as previously mentioned [114], rock-salts adopt abcabc-type face-centered-cubic (FCC) stacking along the \{111\}-type directions. Growth
Figure 7.2 HAADF STEM images of (a) (001)-HfN∥(001)-MgO and (b) ~{111}-HfN∥c-Al₂O₃. Relevant planes and directions are marked. Both interfaces and regions are defective due to misfit.

of {111}-HfN planes on either side of a substrate step thus leads to a breaking in the FCC stacking sequence. An example of this is shown in the STEM image of HfN on GaN in Figure 7.1b. The set of {111}-HfN planes (white lines) to the left of the step cannot be transposed to the region on the right of the step, and neither can the {111}-HfN planes (black lines) on the right be transposed onto the region on the left. This arises because of the variation in stacking, which leads to different rotational variants of the structure. Between these variants and originating at the step, a “V-like” structural features forms and propagates out through the thickness of the film, filling the region between the two variants. Defects of these sorts have previously been identified in rock-salt-{111} films on GaN-(00.1) [114]. This defective region is crystalline though highly faulted. An integrated line profile of the first HfN-{111} plane shows the intensities of atom column peaks and troughs moving left to right (see the graph at the right of Figure 7.1b). Visually, the substrate step appears to occur at the region marked with a white arrow in the image, which corresponds to the marked intensity peak shown in the graph at the right. Shortly after this peak in the graph, the intensity of the atom column peaks falls below the mean intensity of the spectrum (dashed gray line), indicating that the atom columns contain more Ga. The variation in the intensity of the final GaN-(00.1) plane and the first HfN {111} plane suggests that some cation intermixing may occur on these planes.

HfN can be grown on other substrates. Figure 7.2a-b shows STEM images of HfN grown on
(001)-MgO and on c-Al$_2$O$_3$. Both cases are growth of nitrides on oxides, and the film and interface qualities in both instances are poorer than the case of HfN on GaN-(00.1) in Figure 7.1. In the case of the (001)-MgO substrate in Figure 7.2a, the HfN is (001)-oriented but is highly defective due to misfit. In certain instances, the (001) planes of the HfN rotate slightly from each other across defective regions. The misfit between MgO∥HfN is $\sim$30 pm or $+7.8\%$ ($a=4.21\text{ Å}$ for MgO versus $a=4.54\text{ Å}$ for HfN), but the epitaxy and film quality appears worse than the higher misfit CdO∥MgO system ($a=4.70\text{ Å}$ for CdO) which was discussed in Chapter 6. The poorer quality growth in this case may from the fact that the two rock-salts differ in their anion species.

Growth of HfN on c-Al$_2$O$_3$ substrates results in formation of \{111\}-HfN oriented films similarly to HfN films on GaN, but the HfN epitaxy is degraded and the films are more mosaic (see Figure 7.2b). The rock-salt \{111\}-HfN planes form with rotation boundaries similar to those seen for TiN in Chapter 5, where the \{111\} planes remain continuous across the boundaries but the zone switches from [1\bar{1}0] to [112]. An arrow also indicates a region where stacking faults are occurring on the \{111\}-HfN planes. The orientation of HfN on c-Al$_2$O$_3$ is in good agreement with reports of growth of \{111\}-oriented MgO [256] and CrN [257] on c-Al$_2$O$_3$. Comparatively, the HfN epitaxy is much poorer than the CdO epitaxy on c-Al$_2$O$_3$ presented in Chapter 6. This may perhaps relate to greater misfit of the HfN than CdO to the c-Al$_2$O$_3$ (HfN $a = 4.52\text{ Å}$, CdO $a = 4.70\text{ Å}$, and Al$_2$O$_3$ $a = 4.76\text{ Å}$), or perhaps due to the challenges with nitride growth on oxides. Moreover, the rotation of the CdO lattice to orient (052) to c-Al$_2$O$_3$ indicates it was adapting to the substrate more than the HfN is here. Nonetheless, in all three cases of observed epitaxy for HfN, it grows with relatively good orientation control and affords a good means of producing a conductive metal-like electrode or high melting temperature layer.
7.2 Towards Polar Oxide and Nitride Interfaces: MgO, Mg$_x$Ca$_{1-x}$O, and MnO on GaN

One of multiple reasons for integrating rock-salts onto GaN is to create a polar discontinuity at the interface to try to produce metallized interface states. While this cannot be accomplished with a metal rock-salt like HfN, it may be possible with an insulating rock-salt oxide. Another benefit of using an oxide film is that it can be used as a transition layer to allow growth of other oxide materials onto GaN. Rock-salt oxides thus offer the ability to function in two separate roles for high power nitride electronics. Towards these ends, understanding of interface and film quality for oxides grown on GaN is critical.

For a GaN high electron mobility transistor to take advantage of the polar discontinuity at the interface with an oxide rock-salt, the film must possess a higher bandgap than the GaN. If this is not the case and depending on the compensation mechanism, any charges redistributed to the interface to minimize the polar discontinuity may flow into the oxide epilayer rather than into the GaN. MgO is suitable, with a bandgap of $\sim$7.8 eV [260] compared to 3.45 eV of GaN [261]. Likewise, CaO possesses a suitable band alignment and can be grown on GaN [262]. For this reason, MgO [110, 113, 263, 264], CaO [112, 262], and Mg$_x$Ca$_{1-x}$O [107, 114] are some of the first material compositions that have extensively investigated for forming high quality films on GaN to port other oxides onto GaN and to create polar interfaces [265].

Rock-salts possess some natural similarities to wurtzite nitrides since both structures are close-packed. When fcc-rock-salts grow on hcp-GaN, the GaN-[00.1] aligns to the rock-salt-[111] out-of-plane (i.e. the growth direction) and in-plane the (110)/2-rock-salt aligns to the GaN-[10.0] (or equivalently, the [11.0]- or [01.0]-GaN) [110]. The GaN-[10.0] ($a = b = [11.0] = 3.19 \text{ Å} [108]$) is $\sim$6.5% larger than the MgO $a/\sqrt{2} = 2.98 \text{ Å} [266]$). This high misfit leads to the formation of dislocations at the interface which may serve as scattering centers that diminish carrier mobility or as sources for charge compensation since dislocations can bear charges [267]. For this reason, CaO (bandgap $\sim$7.1 eV [260]) has also been grown [112, 262], and it is needed for alloying with MgO to tune the lattice
Figure 7.3 (a) HAADF STEM image of \{111\}-MgO∥(00.1)-GaN and (b) Bragg filtered image of (a) with dislocations marked by white arrows. Image is acquired with an FEI Titan at 200 kV using RevSTEM.

parameter to match GaN to decrease misfit dislocations [114]. Its relevant lattice parameter is much larger than that of MgO \((a/\sqrt{2} = 3.40 \text{ Å} \text{ for CaO} [268] \text{ versus } 2.98 \text{ Å} \text{ for MgO})\) which facilitates lattice matching of GaN when alloyed. Threading dislocations originating in the GaN substrate can also disrupt the film quality, and thus considerable efforts are seeking to minimize threading dislocation densities on the GaN substrate which can even include selected area regrowth of GaN to achieve step-free mesas [115].

To better understand epitaxy and charge compensation in rock-salt systems on GaN, MgO films on GaN are revisited. Pure MgO films were grown on GaN-∥c-Al₂O₃ using pulsed laser deposition as outlined previously [114]. Samples were prepared with mechanical wedge polishing and Ar ion milling at liquid nitrogen temperatures. Sample preparation proves very important for these samples. They do not ion mill particularly well, as the rock-salt oxide films preferentially etch more rapidly than the GaN∥c-Al₂O₃ substrate and they often end up rather damaged. Use of capping layers [114] can partially protect them during sample preparation, though damaged and amorphous regions remain a problem. The samples are best imaged within a day or two of preparation, as hydroxides can form on the surface of the sample by absorption of moisture in the atmosphere. Additionally, the samples are prone to charging as they are quite insulating, and they are prone to damage in the microscope.
Figure 7.3a-b shows a HAADF STEM image (200 kV, FEI Titan with RevSTEM) of an \{111\}-MgO||\{00.1\}-GaN interface where Bragg filtering reveals two misfit dislocations at the interface due to the large $\sim 6.5\%$ misfit between MgO and GaN. The dislocation cores are indicated by the arrows in both the normal image and in the Bragg filtered image. The Bragg filtered image also shows the gradual bending and misalignment of planes near the dislocations as the misfit strain builds. The contrast in the MgO is non-uniform and shows some signs of damage either from ion milling or from the electron beam. The high signal to noise ratio of RevSTEM affords sufficient sensitivity to reveal the oxygen sublattice in the MgO. The transition from the \textit{ababab-}hcp stacking in the GaN to the \textit{abcabc-}fcc stacking in the MgO is apparent based on the alignment of consecutive (00.2)-GaN planes and consecutive \{111\}-MgO planes. In an attempt to mitigate beam damage which is evident by the non-uniform contrast in Figure 7.3a, imaging is performed rapidly at low beam currents (well below the 30 pA cutoff of the Titan screen monitor). While this helps minimize damage, it is insufficient to prevent it entirely. Some of the damage may be destruction of any surface hydroxide portions which may increase propensity for damage of regions beneath.

Imaging conditions are explored to try to minimize beam damage and increase the sustainable dose of the films for spectroscopy and prolonged imaging purposes. This includes use of the Nion
UltraSTEM 60-100 kV at CNMS at ORNL with Xiahan Sang. The MgO film seems less prone to beam-induced damage in the Nion compared to the Titan, as is evident in Figure 7.4b. Imaging on the Nion is performed at 100 kV, which alone may have served to enhance contrast and to minimize beam damage. Furthermore, the Nion U100 is an ultra-high vacuum system, and thus samples are baked in vacuum at ~160°C overnight before loading. This bake may serve to clean off some amount of surface hydroxide that may have formed between sample preparation and imaging, and it additionally may enable some recrystallization of surface-localized ion mill damage. Of note, MgO substrates typically prove more robust to the 200 kV Titan beam even with several times higher beam currents than those used to image the \{111\}-MgO films. As such, the MgO films themselves may be less stable than MgO single crystals because of forced growth along the polar orientation by the GaN substrate. The films may also contain higher point defect concentrations leading to beam sensitivity.

Following improved results at lower accelerating voltages, the \{111\}-MgO∥(00.1)-GaN sample is observed at 80 kV in the Titan following an overnight bake in vacuum at ~160°C. Figure 7.4a-b compares an 80 kV Titan RevSTEM image to a 100 kV Nion U100 STEM image. In both instances, the signal-to-noise ratio and resolution appears degraded compared to the 200 kV Titan RevSTEM image in Figure 7.3a. Nonetheless, these results suggest that baking samples in vacuum and operating at lower accelerating voltages may enable longer imaging and spectrum acquisition times. As such, these are suggested as means to improve the ability to image beam sensitive rock-salts on GaN and is suggested as standard protocol when necessary. Nonetheless, damage free MgO∥GaN samples remain to be prepared for STEM studies.

EELS experiments are performed using the Nion U100 in an attempt to detect any chemical changes in the various elements at the interface of \{111\}-MgO∥(00.1)-GaN. In particular, the K-edges of N and O are investigated as their signals are much stronger than the Ga and Mg signals. A HAADF survey image used for EELS is shown in Figure 7.5 from which a line-scan is acquired. The exact location of the line-scan is not available, but is from near the center of the image. The HAADF signal during acquisition is shown in the plot in Figure 7.5 which shows that the line-scan included a
fairly large amount of material on either side of the interface. The line scan is 40 pixels long with a step size of approximately 5.4 Å. Sub-pixel scanning during the line-scan enables visualization of oscillating intensity in the HAADF signal due to the \{111\}-MgO planes and the (00.2)-GaN planes.

The N K-edge and O K-edge are background subtracted using standard power-law fitting using Gatan DigitalMicrograph 2. Where indicated, spectra are smoothed using a moving average filter. Indicated spectra are normalized to the maximum value in the relevant energy window range.

The O K-edge EEL spectra (0.2 eV dispersion) are shown in the images in Figure 7.6. In Figure 7.6, the columns separate un-normalized from normalized EEL spectra and the rows separate spectra with different amounts of smoothing (raw, span = 5, and span = 9). The progression of the positions is akin to that in the survey image and corresponding HAADF intensity profile shown in Figure 7.5. Specifically, the position proceeds from the MgO at position = 1 to the interface at position = \(\sim 22\) to the GaN. Between positions \(~20-25\), the loss peak at \(\sim 538\) eV broadens considerably in the images, with more broadening on the lower energy side (see and compare to 1D line plots in Figure 7.8).

From the normalized images (Figure 7.6), it is evident that the true maximum of the loss is shifting
Figure 7.6 O K-edge spectra at the various positions spanning the \{111\}-MgO||(00.1)-GaN interface according to Figure 7.5. Normalization and smoothing procedures are described in the text. Acquired at the CNMS at ORNL using the Nion U100 with X. Sang, operated at 100 kV with a 0.2 eV dispersion.
Figure 7.7 N K-edge spectra at the various positions spanning the [111]-MgO∥(00.1)-GaN interface according to Figure 7.5. Normalization and smoothing procedures are described in the text. Acquired at the CNMS at ORNL using the Nion U100 with X. Sang, operated at 100 kV with a 0.2 eV dispersion.

towards lower loss energies. The raw, normalized image shows this to be the case, but it is more apparent in the smoothed and normalized images.

A less pronounced though similar trend is observed in the K-edge of N. Figure 7.7 shows the K-edge of N from the lower loss regime of the same EEL line-scan. In the normalized images, the N peak maxima at \(\sim 402\) eV shifts slightly towards higher energies at the interface, and it likewise exhibits some broadening (compare to 1D line plots in Figure 7.8). This shifting towards the interface is opposite that of the O K-edge, which moves towards lower energies in the MgO at the interface, whereas the N K-edge here is progressing towards higher energies in the GaN at the interface.
Interestingly, N signal continues into the MgO, and the maxima is discontinuous and jumps towards lower-energy losses. The origin of this remains unclear, but it is evident in the un-normalized signal that the N intensity is weak compared to the N K-edge in the GaN region. In contrast, the GaN region remains relatively free of O (see Figure 7.6).

Further study, including additional STEM/EELS experimentation to confirm these results and explain them, is necessary for their validation. Several interface regions should be checked to ensure that these findings do not relate to intermixing or roughness at a specific portion of the interface. Step sizes, dwell times, and dispersion values should be varied to evaluate if this influences the peak shifting and broadening and to see if it can improve the signal-to-noise of the spectra. Additional experiments could also eliminate the possibility microscope energy drift, sample drift, or other experimental effects that could influence these spectra. Finally, these findings could be compared to future DFT simulations of the density of states of interfaces like these for validation through another technique. Likewise, more details are needed to understand the origin of the nitrogen signal in the MgO.

Lattice matched interfaces in rock-salt oxide∥nitride interfaces are desirable to decrease dislocation presence which could diminish the mobility of an interfacial metal state. As mentioned, this is commonly achieved with CaO alloying[114]. MgO reacts with water to form a hydroxyl phase. This is a process which can lead to etching of MgO particles over time in aqueous solution and absorption of water over time in ambient atmosphere [269–271]. CaO is even moreso prone to hydrating, and the electron beam energy in an electron microscope is sufficiently powerful to destroy hydrated CaO very readily [272]. CaO itself etches and facets under the electron beam, which has been visualized using HRTEM on pure CaO [273]. It is not precisely known how (1) alloying CaO with MgO and (2) intentionally growing the film such that it contains a polar interface will influence the etching energies and tendency of the film to hydrate. Thus, any predicted robustness of the material to the electron beam is uncertain.

Perhaps unsurprisingly, Mg$_{x}$Ca$_{1-x}$O proves even more challenging to prepare and image in the electron microscope than pure MgO. Figure 7.9a-b shows a HAADF STEM image and Bragg
Figure 7.8 Un-normalized EEL spectra of the N and O K-edges plotted for each position in the line-scan. Acquired at the CNMS at ORNL with X. Sang using the Nion U100 operated at 100 kV.
filtered image of a Mg$_x$Ca$_{1-x}$O-\{111\}|GaN-(00.1) thin film. The sample preparation and imaging conditions are comparable to that of the \{111\}-MgO||(00.1)-GaN shown in Figure 7.3a-b, i.e. 200 kV and no sample baking. First and foremost, the Mg$_x$Ca$_{1-x}$O film shows significantly more damage than the MgO. Only a few \{111\}-Mg$_x$Ca$_{1-x}$O planes are crystalline on the GaN, and above this the sample appears amorphous and/or highly damaged. The Bragg filtered image shows presence of no dislocations in the imaged region and that the interface is quite sharp. The bending of the Bragg planes at the interface does not change significantly across the image, indicating relatively uniform misfit and strain. The Bragg filtered image also shows that the damaged/amorphous region at the top of the film may possess some residual crystallinity, as the Bragg planes are still visible in the filtered images.

Due to the beam sensitivity of MgO and Mg$_x$Ca$_{1-x}$O and due to challenges associated with seeing changes in the nitrogen and oxygen EELS edges in these materials, some alternatives are proposed for consideration [274]. Among these are MnO ($a/\sqrt{2}=3.14 \text{ Å}$ [266]), CoO ($a/\sqrt{2}=3.01 \text{ Å}$ [266]), and EuO ($a/\sqrt{2}=3.63 \text{ Å}$ [275]). All of the materials are technologically relevant materials. CoO and its hydrate Co(OH)$_2$ are of interest for battery and photocatalyst applications [168]. MnO is of interest for battery applications [276, 277], for its magnetic properties [278], and for its relation to electrochemical water splitting compounds [279]. EuO is of interest for its ferromagnetic properties [275], and it has been integrated directly onto GaN as a spin polarized ferromagnetic layer [111]. For the present purposes, all three possess multiple oxidation states which is useful for spectroscopic determination of electronic charge compensation at interfaces. Mg and Ca adopt (II) oxidation states, while Mn can go (II,III,IV,VII), Co (II,III), and Eu (II,III). Moreover, MnO is misfit to GaN by ~5 pm (-1.4%), while CoO is -5.5% smaller than GaN and EuO is +14% larger (comparing the $a/\sqrt{2}$ rock-salt to the GaN $a$, $b$, and [11.0]). As such, these rock-salts could be used for lattice strain tuning as well. Because the CoO and MnO bandgaps approach or are below the bandgap of GaN ($\sim$2.4 eV for CoO [280] and $\sim$3.6-3.8 eV for MnO [280] versus 3.45 eV for GaN [261]), some alloying with MgO will be required for band gap tuning.

MnO films are targeted first because of many accessible oxidation steps and small misfit to
Figure 7.9 (a) HAADF STEM image of \([111]-\text{Mg}_x\text{Ca}_{1-x}\text{O}||\text{(00.1)}\)-GaN showing amorphous/damaged regions above a thin amount of crystalline film and (b) Bragg filtered image showing no dislocations. Image is acquired with an FEI Titan at 200 kV using RevSTEM.
the GaN, which both could contribute to successful formation of a polar interface. MnO thin films have been successfully prepared previously with a [111] out-of-plane orientation on c-Al₂O₃ and on MgO-{111} substrates [278], but they have not yet been prepared on GaN. Furthermore, Mn valence changes are rather pronounced and have been observed in combination with two-dimensional interfacial electron gas formation in perovskite systems [281].

MnO-{111} films are grown GaN-(00.1) with PLD similar to the MgO and MgₓCa₁₋ₓO films. They are prepared for STEM using wedge polishing and liquid nitrogen cooled ion milling. The films are capped with amorphous LaAlO₃ to protect the film during sample preparation. Figure 7.11a-b shows HAADF STEM images acquired with the ORNL CNMS Nion U100 operated at 100 kV with Xiahan Sang. The very low misfit (∼1.4%) of the MnO results in many large interface regions that are free of dislocations. Furthermore, they appear less prone to sample preparation and imaging related damage than the MgO and MgₓCa₁₋ₓO rock-salts presented earlier. The lower bandgap of MnO than MgO makes the films somewhat more conductive [280], which may increase their stability under the beam and makes them less prone to charging.

The large field of view image with Bragg filtering in Figure 7.11a-b reveals additional features of interest for these films. Across this image, dislocation cores are not visible in the HAADF and accompanying Bragg filtered images, and the bending of the lattice planes across the boundary is

**Figure 7.10** (a)-(b) HAADF STEM images of {111}-MnO||(00.1)-GaN. Acquired at the CNMS at ORNL with Xiahan Sang using the Nion U100 operated at 100 kV.
Figure 7.11 (a) HAADF STEM images of {111}-MnO||(00.1)-GaN and (b) Bragg filtered image. Arrows indicate regions with Mn$_3$O$_4$-like inclusions near the outer portion of the sample. Acquired at the CNMS at ORNL with X. Sang using the Nion U100 operated at 100 kV.
rather consistent and unvaried. Towards the sample surface near the LaAlO$_3$ cap, the MnO begins to roughen and distort. White arrows indicate a clear change in structure in one instance, and what might be a subtle inclusion in the other region. The structure of the inclusion appears consistent with the Mn$_3$O$_4$ spinel phase that Mn occupies in a mixture of Mn(II,III) oxidation states. From X-Ray diffraction of films during growth optimization (not shown), the Mn$_3$O$_4$ phase is a common phase that competes with the Mn(II) phase (MnO), and it thus is a common secondary phase. Growth optimization is able to minimize the spinel formation compared to the rock-salt, but small fractions can remain in the films.

From the image in Figure 7.11a, spinel formation may be localized to the outer portion of the sample near the rough interface with LaAlO$_3$. For this reason, it was first speculated that the spinel formation may have been some sort of surface reconstruction during growth to mitigate the polar interface. EEL spectrum imaging is performed using the Nion U100 operated at 100 kV at CNMS at ORNL with Xiahan Sang. The region for spectrum imaging is shown in Figure 7.12a. Mapping the shift in the Mn $L_3$-edge position from background subtracted spectrum maps reveals no noteworthy shift in the position of the peak at the interface (see Figure 7.12b) as would be expected for a change in oxidation state [282, 283] due to interface metallization [281]. Normalized integrated EEL spectra taken from the approximate regions of the overlays in Figure 7.12a show that the bulk and interface are in the same oxidation state, with no clear difference in either the peak position or the peak ratios of the $L_3/L_2$ Mn peaks (see 7.12c,d). As such, the Mn valence is not noticeably changing in local regions near the interface in the present samples.

On the other hand, the Mn $L_3$-edge onset shows a rather uniform shift to higher loss energies in the outer portion of the film near the cap (see Figure 7.12b). From the integrated EEL spectra (Figure 7.12c,d), it can be seen that the mean shift is on the order of $\sim$0.9 eV. A shift of the peak onset of $\sim$0.5 eV is consistent with MnO to Mn$_2$O$_3$ oxidation, while MnO to Mn$_3$O$_4$ oxidation results in a shift of the onset by $\sim$1.0 eV [282]. The present measured shift is $\sim$0.9 eV on the basis of the peak maxima, consistent with oxidation to Mn$_3$O$_4$. Moreover, the Mn $L_3$ and $L_2$ loss ratios changes, which is also consistent with Mn valence change [283].
Figure 7.12 \{111\}-MnO\[(00.1)\]-GaN (a) EELS HAADF image and (b) measured shift in the Mn $L_3$ peak position at each region in (a), where the colorbar is set manually to emphasize the features. A positive shift corresponds to a shift towards higher energy losses, and the mean shift and standard error of the mean shift are listed. (c,d) show normalized integrated EEL spectra taken from the approximate regions marked by overlays in (a), and demonstrate an $\sim$0.9 eV shift of the signal of the outer region of the sample towards higher losses. The integration windows were 2 pixels high and the full image width. Acquired at the CNMS at ORNL with X. Sang using the Nion U100 operated at 100 kV.
Thus, spectroscopy and imaging provide consistent evidence that indicate changes in oxidation state of the outer film portions, which may be driven by a polar discontinuity or due some process occurring during sample growth or lamella preparation. Furthermore, this change may be passivating the polar interface such that interface metallization is not occurring, as evidenced by no change in oxidation state near the interface (Figure 7.12b-d). Atomic force microscopy of the surface of a thickness series of uncapped MnO films reveals a transition from smooth film surfaces to rough film surfaces at a thickness of \( \sim 5 \) nm (not shown). This suggests that \( \sim 5 \) nm may be a critical thickness between some sort of structural transition. For instance, as polarity builds up in the film during growth, newly deposited layers may begin relaxing into another phase during growth to minimize the polar catastrophe by structural/surface reconstruction mechanisms \([86, 88]\). Polar surfaces often exhibit reconstructions or structural differences at the surface, such as GaN-(00.1) and AlN-(00.1) wurtzites \([91]\) and the (110)-SrTiO\(_3\) surface \([90]\).

To confirm whether this is the case, STEM is performed on 4 nm and 8 nm thick layers of MnO grown on GaN-(00.1)∥c-Al\(_2\)O\(_3\), which are capped with amorphous LaAlO\(_3\). These thicknesses sit on either side of the suggested critical film thickness that drives a surface morphology change, and both thicknesses are thinner than the film presented earlier (\( \sim 13 \) nm). Both the 8 nm film (Figure 7.13a-c) and the 4 nm film (Figure 7.14a-b) actually exhibit more of the secondary phase than the first sample (Figure 7.11a-b). With the improved signal to noise of the RevSTEM images, the secondary phase is conclusively identified as Mn\(_3\)O\(_4\) on the basis of structure, which is seen down the [010] zone axis in Figures 7.13a-b and 7.14b, and down the [101] zone axis in Figure 7.13c and 7.14a. In the case of Figure 7.13a, the small white arrows in the MnO/Mn\(_3\)O\(_4\) layer point along crystallographic directions that transition in structure a few nanometers in front of them. Likewise, the small black arrows show another transition along a different lattice direction. These features likely indicate incomplete phase changes between the MnO/Mn\(_3\)O\(_4\) structures which leads to a general increase in structural non-uniformity in the film.

The arrow in the GaN in Figure 7.13a points to a dislocation at the MnO∥GaN interface, and the angled arrow in the MnO/Mn\(_3\)O\(_4\) points at an inclusion of Mn\(_3\)O\(_4\) in MnO. Figure 7.13b shows a
Figure 7.13 (a-c) HAADF STEM of 8 nm thick MnO film capped with amorphous LaAlO$_3$ showing regions with Mn(II) MnO rock-salt and regions with Mn(II,III) Mn$_2$O$_4$ spinel. (a) Small arrows (both black and white) point along non-uniform lattice planes, with the larger white arrows in the film indicating what may be inclusions of one phase in another. The white arrow in the GaN indicates a dislocation core. (b) A higher magnification image of a portion of (a), where the bottom inclusion may have grown some in size between the image acquisitions. (c) The MnO/Mn$_2$O$_4$ type film viewed down the GaN-[12.0]. Images acquired at 200 kV using RevSTEM on an FEI Titan.
higher magnification view of the same region acquired at a later time during imaging. The same dislocation and inclusion are indicated by arrows. The inclusion may have grown some in size between the two images. At the point that image was acquired, the sample had been irradiated with the electron beam for some time. While the MnO may be less prone to beam damage, phase interconversion by irradiation needs further investigation. In all of the 8 nm and 4 nm film images shown in Figures 7.13a-c and 7.14a-b, the first few Mn cation planes tend to be \{111\}-rock-salt-like planes. This may suggest that the strain at the interface is favorable for the rock-salt MnO phase and less favorable for the Mn$_3$O$_4$. The misfit of the MnO and Mn$_3$O$_4$ phases with each other seems rather low, with no defects arising that appear driven by misfit alone.

The 4 nm thick sample possesses a smooth surface to AFM before lamella preparation, so it should have been below the critical thickness for the surface morphology change. For this reason, the MnO films may be oxidizing from the surface towards the interface due to (1) interactions with the LaAlO$_3$ cap or (2) during sample preparation. Typically, wedge polishing involves affixing the sample to a polishing stub at between $\sim$170-200°C in air to melt the wax used for bonding. To consider whether heating could result in formation of Mn$_3$O$_4$ in a film of pure MnO, uncapped MnO films on GaN-(00.1) are heated in atmosphere for either 25 minutes at $\sim$200°C or for 20 minutes at

\[12:0\]-GaN

\[10:0\]-GaN

Figure 7.14 (a-b) HAADF STEM of 4 nm thick MnO film capped with amorphous LaAlO$_3$ containing rock-salt and spinel phases down two zone axes of the substrate. Images acquired at 200 kV using RevSTEM on an FEI Titan.
100°C before being checked for phase changes with X-Ray diffraction (not shown). In both instances, the MnO pure film shows strong conversion to the spinel Mn$_3$O$_4$ composition. It is not known why the degree of conversion observed is different between the ∼13 nm thick film shown in Figure 7.11a-b and the 4 and 8 nm thick films, though the they could have spent different amounts of time on the hotplate during sample preparation. Interestingly, the sample in Figure 7.11a-b was heated overnight in vacuum at ∼160°C before insertion into the Nion, yet it exhibits less spinel phase than that in Figure 7.13a-c. Heating in oxygen-rich environments may thus be the primary source of oxidation. This understanding is consistent with growth of MnO films with ALD, which have exhibited some surface presence of a higher Mn oxidation state in their native state after growth, and which oxidize into Mn$_2$O$_3$ by annealing at elevated temperatures [279]. As such, preparation of STEM samples without converting the MnO phase partially into the Mn$_3$O$_4$ spinel phase is necessary for continuation of the study. Moreover, Mn$_2$O$_3$ and Mn$_3$O$_4$ films could conceivably be reliably produced on GaN by growth of [111]-MnO followed by heating in air ex-situ.

7.3 Rock-salt Conclusions: HfN, MgO, Mg$_x$Ca$_{1-x}$O, and MnO

The film and interface structure of rock-salt HfN thin films grown for use as a conductive layer and transducer for time domain thermoreflectance spectroscopy is considered for films grown on MgO-(001), c-Al$_2$O$_3$, and (00.1)-GaN||c-Al$_2$O$_3$ substrates. Growth on (001)-MgO yields an epitaxial or very highly textured (001)-HfN film, though the very high misfit (∼30 pm) leads to mosaicity and defects. Films using c-Al$_2$O$_3$ as a substrate are [111]-oriented, though the films possess rotation variants and defects which diminish the film quality. Finally, HfN grows [111]-oriented on (00.1)-GaN||c-Al$_2$O$_3$ with the highest crystal quality due to very low misfit and nitride/nitride growth. The film quality on GaN-(00.1) is limited by steps on the GaN surface which produces “V-shaped” defects by disrupting the stacking sequence of the HfN across it. “V-shaped” defect formation is equivalent to what was shown previously for oxide rock-salts on GaN [114].

STEM of [111]-MgO and [111]-Mg$_x$Ca$_{1-x}$O films grown on (00.1)-GaN exhibit similar interface features to those reported previously [114], namely misfit dislocations in the MgO and a smooth,
dislocation free interface for the Mg$_{x}$Ca$_{1-x}$O. Both MgO and Mg$_{x}$Ca$_{1-x}$O films are extremely beam sensitive which may be due to surface damage or surface hydroxide presence formed during sample preparation. The films may also be increasingly sensitivity to the beam because of the polar geometry of their growth or due to high point defect concentrations. Alloying of CaO/MgO into the Mg$_{x}$Ca$_{1-x}$O film appears to increase beam sensitivity even further. Imaging of MgO-{111} films at lower accelerating voltages (80 kV or 100 kV) and baking of samples in vacuum at ~150°C overnight appears to improve the ability to image {111}-MgO∥(00.1)-GaN for an extended period of time. Preliminary EELS work suggests that the O K-edge peak maximum broadens and bends to lower energies adjacent to the interface. On the other hand, the N K-edge bends slightly towards higher energies at the interface and may broaden as well. The MgO possesses a weak residual N K-edge peak signal at an energy shifted just below that of the GaN N K-edge peak. The origin of this is unclear. Further studies are needed to confirm these three EELS findings and to interpret whether their origin could be connected to states associated with interface metallization.

MnO is proposed and investigated as another suitable system for interrogating polar compensation of {111}-rock-salt∥(00.1)-GaN interfaces because it is low misfit to GaN and because Mn can change oxidation state. MnO films are fabricated and exhibit the Mn(II) rock-salt structure based on X-Ray diffraction and STEM measurements. STEM imaging reveals that misfit dislocations between MnO and GaN are very uncommon. Additionally, STEM provides evidence that (1) Mn(II,III) Mn$_3$O$_4$ spinel phase impurities occur in the MnO films and that (2) shifts in oxidation state due to these impurities are measurable using EELS. Evidence suggests the spinel impurities are occurring due to the current method of preparing lamella for STEM experiments which requires heating the films at elevated temperatures. This is confirmed by heating of phase pure MnO films in ambient atmosphere at temperatures lower than those utilized during lamella preparation, which converts the films into the Mn(II,III) spinel phase. Alternative means of sample preparation are required to generate STEM lamella without artificial oxidation state changes arising from sample preparation to further assess any changes in interface electron density due to polarity. Based on these collected findings, high-quality, low misfit MnO-{111}/GaN-(00.1) interfaces are achievable.
and are promising for probing interface polarity compensation through change in the Mn valence near the interface. Moreover, the ability of Mn(II) and Mn(III) to coexist within a single film is also promising, and means that local oxidation change due to electron redistribution could feasibly be manifest in a well-prepared sample.
Chapter 8

Conclusions and Future Work

The studies presented in Chapters 3-7 have demonstrated the power of STEM to develop a broader understanding of the complex chemical and physical structuring that occur in advanced materials, and how these sorts of chemical and physical processes can give rise to unique and controllable properties. In some of these examples, the interpretation of STEM data is relatively straightforward and can be performed on a qualitative level. Film quality and misfit accommodation can be understood rather simply on the basis of visualizing the film and any misfit dislocations or defects that are forming. Other times, a much more quantitative approach is necessary to measure precise changes in structure and composition. In these instances, more complex image analysis and image acquisition methods are necessary, and it becomes more of a process to interpret the various physical and chemical forces at play in a given micrograph. Image interpretation in parallel with structural modelling and simulation is often beneficial to provide a three-dimensional picture of what occurs at interfaces and in complex regions of film structuring. This work has sought to elucidate structural features in a variety of new functional oxide and nitride materials using both qualitative and quantitative STEM measurements and interpretations. In particular, this work has demonstrated the development of a broader understanding of polar oxide and nitride materials using STEM and related techniques. The various Chapters have especially focused on new materials containing either a ferroelectric and/or a rock-salt, using quantitative atomic-scale metrology
afforded by STEM. The conclusions of the individual Chapters are broadly summarized here, and suggestions for future studies are made building directly from these new results and conclusions.

8.1 HfO$_2$ and HfN Conclusions and Future Work

Studies involving structural investigations of polycrystalline HfO$_2$ thin films occupy the content of Chapters 3, 4, and 5. Broadly speaking, these sections involve a ferroelectric oxide that coexists and competes for stability with several non-polar polymorphs with the same formula unit. These films are all grown on a metallic rock-salt nitride that is integrated directly onto Si-(001) substrates. For this reason, the results are tangentially related to those results presented in the HfN portion of Chapter 7 and its discussion of a newly engineered metal-like rock-salt nitride. For this reason, HfN future work is included in this section as well.

Chapter 3 identifies changes in the structure of polycrystalline ferroelectric HfO$_2$ as it is field-cycled, which has important consequences for the electrical behavior [3]. Field-cycling of pristine devices leads to an increase in remanent polarization by device wake-up, and then further cycling results in a decrease in remanent polarization after the onset of fatigue. STEM reveals defect rich tetragonal interfacial layers at the interface between some bulk monoclinic/orthorhombic grains at the boundary with the TiN electrode. STEM and impedance spectroscopy show that these layers become more uniform and decrease in thickness with field-cycling, and thus contribute to changes in the remanent polarization and dielectric permittivity of the films over their lifetime. These tetragonal layers are stabilized by higher concentrations of oxygen vacancies in the HfO$_2$ near the electrode which are present due to gettering of oxygen by the TiN from these portions of the film during annealing. STEM also demonstrates the dominant phase in the films changes from monoclinic to orthorhombic with field-cycling, leading to an increase in the polar phase and thus the device remanent polarization. These findings give insight into the phase changes and defect changes that enable device wake-up. Static leakage current measurements suggest that fatigue relates to dielectric breakdown. This knowledge enables discussion of a model incorporating structural changes to explain poor endurance behavior of HfO$_2$ ferroelectrics, and provides targeted areas for processing
improvement to increase the endurance behavior of HfO$_2$ [3, 175].

Chapter 4 elucidates additional aspects of polycrystalline ferroelectric HfO$_2$ grain sub-structure [4]. 90° domains are identified in the polar orthorhombic phase of pristine samples but not field-cycled samples, suggesting field-cycling increases polar domain uniformity. Interphase boundaries between the polar orthorhombic and non-polar monoclinic phase are studied, and the observed boundaries indicate that certain boundaries form preferentially. Steps in domains and interphase boundaries are linked to misfit, and the monoclinic phase is shown to form twin defects. Interphase boundaries are discussed in terms of limiting the grain size artificially and in terms of the strains they exert. Evidence suggests that some of these interphase boundaries may be mobile, which would explain a mechanism by which phases may interconvert during field-cycling. Variation in boundary structure is suggested to arise due to differences in glide structure of the HfO$_2$ which is a means by which the monoclinic and orthorhombic phases may interconvert [59]. These findings provide additional insight into the electrical and cycling behavior of ferroelectric HfO$_2$.

TiN and HfO$_2$ local epitaxial relationships in polycrystalline ferroelectric HfO$_2$ films are discussed in Chapter 5. The bottom TiN electrode (Si-side) is found to be highly textured, while the top TiN electrode is more randomly oriented. TiN-{111} planes commonly exist in orientation relation to the low order HfO$_2$ planes of the monoclinic and orthorhombic phases. Models are derived for how a N-terminated {111}-TiN surface can form a natural growth surface for Hf-terminated planes of the HfO$_2$. In this growth modality, HfO$_2$ is suggested to commonly grow with its longest principal axis in plane to reduce strain, which has important consequences for the resulting orientation of the polar axis of the orthorhombic phase. Moreover, these findings provide insight into how the local epitaxy may be driving the tendency of the HfO$_2$ to adopt tetragonal symmetry near the electrode in an attempt to conform to the growth surface. These evidences of preferred orientation between the TiN||HfO$_2$ are suggestive of how other metal nitride and how {111}-Au substrates could be used to strain tune HfO$_2$ and enable growth of oriented films on different substrates. Growth on an electrode with a lower potential for oxidation (i.e. Au) could reduce formation of oxygen vacancies in the HfO$_2$, leading to better performance. Moreover, deliberately textured HfO$_2$ films could be grown to
optimize switchable polarization.

Based on the HfO$_2$ studies in Chapters 3-5, and based on the HfN reports from Chapter 7, some clear avenues for ongoing and further research can be easily seen. The first two HfO$_2$ chapters (Chapters 3-4) primarily consider the influence of the phases, interfacial layers, and grain sub-structure features on the electrical behavior of the films. From these studies, bulk phase change (presumably by nucleation and propagation of interphase boundaries), interfacial layer diminishment, and 90° domain reorientation are expected to influence the wake-up of HfO$_2$-based ferroelectrics. Many in situ heating and electric field electron microscopy studies could clarify various aspects of these phenomena.

The actual extent of monoclinic to orthorhombic phase change driven by field-cycling is unknown. Phase change between cycling states is challenging to measure with good statistics because of limited sampling in STEM [3] and the need for microspot optics and texture considerations for XRD [169]. Moreover, not all samples in as-grown pristine states possess the same amount of monoclinic phase [42, 61, 206], so these sorts of monoclinic to orthorhombic phase changes may be more influential for certain varieties of HfO$_2$ ferroelectrics than others. Nonetheless, monoclinic∥orthorhombic interconversion has been seen [53, 226] and mechanistically has been explained from a crystal chemistry perspective [59], suggesting its plausibility. Moreover, the identification of nearly identical phase presence in samples field-cycled to two separate states, and their vast difference in phase presence from the pristine sample, supports the hypothesis of monoclinic to orthorhombic phase conversion by field-cycling [3].

Field-cycling of HfO$_2$ capacitors using in situ electron microscopy would elucidate many aspects of phase change in these materials [3]. Can field-cycling confirm phase conversion of monoclinic to orthorhombic as a sample “wakes-up?” Can high electric fields nucleate formation of new interphase boundaries in phase-pure regions of the monoclinic phase? If so, what field magnitude is required for nucleation of new boundaries? Do as-grown monoclinic∥orthorhombic interphase boundaries move under the influence of an applied field? What magnitude of field is commonly required, and is there variation in mobilities and required fields to move boundaries aligned differently? Are any
as-grown interphase boundaries immobile, and if so, what aspects of a particular environment might be influencing that? Furthermore, in situ methods could enable direct visualization of 90° domain re-orientation as driven by field-cycling. Incorporating the EMPAD [235] into these experiments would easily enable direct strain mapping based on the positions of Bragg peaks in the diffraction patterns, and could be used to measure the influence of an external electric field on the lattice. More excitingly, it would enable measurement of the deflection of the electron beam based on the polarity of an orthorhombic grain. Likewise, this aspect of the EMPAD should enable its use in the identification of 180° domains.

More broadly, in situ heating and cycling could be applied to the study of other aspects of the interrelated phases of HfO₂ films. Amorphous films could be heated and crystallized in situ to study the crystallization dynamics and to observe the influence of the pre-crystalline electrodes on the phase and grain formation in the HfO₂. Similar to Hudak and coworkers who heated twinned monoclinic nanoparticles in situ to form the tetragonal phase [223], heating and cooling of crystallized films could be used to observe the reversible monoclinic to tetragonal phase change. In highly doped regimes of Si doped samples [206] and certain regimes of Zr alloyed samples [42] that favor formation of the tetragonal phase, the field-induced ferroelectric properties [11] of the tetragonal phase could be explored and validated in situ. Is the application of large electric fields capable of transiently stabilizing the orthorhombic phase out of the tetragonal phase, consistent with present understanding? During the switching of an orthorhombic grain, is it possible to observe the tetragonal intermediate phase predicted from first principles [33, 34, 36, 60]? Can in situ cycling give better insight into the switching dynamics in these materials? All of these questions can be addressed to varying degrees with in situ heating and biasing.

In terms of chemistry within the films, it is challenging to perform EELS on HfO₂ because of the strong elastic and inelastic scattering by heavy Z = 72 Hf atoms [49]. This is particularly problematic for the N and O edges which are much lighter (N Z = 7 and O Z = 8). Both N and O are quite prevalent in the films, but their signals are severely diminished by Hf atoms. One alternative is to perform similar sorts of experiments on pure ZrO₂ or Zr-rich (Hf,Zr)O₂ ferroelectric films, as
$Zr\ Z = 40$ is much lower than $Hf\ Z = 72$ which would reduce the elastic and inelastic scattering. This could improve signal to enable better mapping of changes in N and O fine structure near the electrode∥ferroelectric interfaces. Such measurements could elucidate changes in these elements due to bonding across the interface (i.e. Hf-N vs Ti-N and Hf-O vs Ti-O). Variation in the O signal may also give insight into the changes in O structure of the bulk grains as they relax into tetragonal interface layers. Moreover, it could yield information regarding motion of oxygen vacancies within the films similarly to a previous study that showed their motion during field-cycling [197]. Change and evolution in all of these EELS signals could be considered as a function of field-cycling. This could be done by comparing ex situ cycled lamella to each other, or by using in situ field-cycling to cycle a sample within the microscope directly.

Finally, the results of the texture section in Chapter 5 combined with that of the HfN work in Chapter 7 are suggestive of several aspects that could elucidate texture in these materials. Growth of ALD films on highly textured or epitaxial nitride substrates (with subsequent deposition of top electrodes with normal deposition procedures) could elucidate the importance of the orientation of the bottom electrode. The \{111\}-textured ZrO$_2$ films of Fan and coworkers [5] may be achievable directly on (001)-Si if the TiN is grown highly (001)-oriented by other means [236]. A means of preparing highly textured or epitaxial \{111\}-C-TiN could be devised to prepare substrates to confirm the present model that finds the \{111\}-C-TiN is commonly aligning to low order HfO$_2$ planes. Incorporation of area detectors like the EMPAD into these studies will likely prove tremendously useful in determining orientation relationships to the fullest extents possible.

Many other metal nitride materials exist that could be used to tune the lattice parameters, and thus the strain, of HfO$_2$ thin films. This could be used both to optimize control over the orientation of HfO$_2$, as well as to tune the strain to alter the ferroelectric performance. Moreover, metal nitride electrodes could be selected that are less prone to oxidation, which may result in fewer oxygen vacancies in the HfO$_2$ films to reduce performance instabilities. As one example, HfN can be grown highly textured and epitaxially with different out-of-plane orientations, as shown in Chapter 7. MgO substrates yield (001)-HfN films, while c-Al$_2$O$_3$ and GaN-(00.1) yield \{111\}-HfN with different
epitaxial qualities. This provides an opportunity to grow HfO$_2$ on two principle surfaces of HfN to study texture, and gives a means by which ferroelectric HfO$_2$ could possibly be integrated into sapphire and wide bandgap/high power electronic devices.

Importantly, both c-Al$_2$O$_3$ and GaN-(00.1) substrates yield $\{111\}$-HfN films with rotation variants present in the films to varying degrees. Different GaN growth conditions yield different step densities, which could be used as a means of artificially changing the grain size of highly textured HfO$_2$ films, since rotational variants in the HfN substrate would likely change the way the HfO$_2$ films nucleate and grow together during annealing. It is likely that other metal nitrides could also be grown on MgO, GaN, and c-Al$_2$O$_3$ systems for study of texture and ferroelectric strain tuning. In particular, VN may provide less misfit than TiN. Finally, noble metal $\{111\}$-Au films may actually provide a better misfit than metal nitride electrodes. Because Au does not oxidize like metal nitride electrodes, films prepared on Au may possess fewer oxygen vacancies and thus be less prone to poor endurance because of electrode and defect related effects.

### 8.2 CdO Conclusions and Future Work

Chapter 6 considers the interface and film structures of CdO layers grown for transparent conductive oxide applications and for mid-infrared plasmonic properties. Intrinsic films are investigated on MgO-(001) substrates grown by oxide molecular beam epitaxy [81] and on c-Al$_2$O$_3$ using DC and RF reactive co-sputtering [243]. The (001)-CdO/$\parallel$(001)-MgO films grow with $+11.4\%$ misfit which is accommodated by the formation of edge misfit dislocations which form a square lattice in the interfacial plane with an $\sim3.25$ nm periodicity in good agreement with calculated values. The dislocations are of type $\xi_1 = [110] \perp b_1 = [\bar{1}10]/2$ and $\xi_2 = [\bar{1}10] \perp b_2 = [110]/2$ similar to those seen in other high misfit rock-salt systems [249–251]. The strains at the interface are measured and are shown to oscillate. In confined heterolayers that are very thin ($\sim < 3$ nm), dislocation cores on opposite interfaces form overlapping strain fields which generate complex strain networks that zig-zag through the films. On the other hand, CdO films grown on c-Al$_2$O$_3$ are much lower misfit ($a=4.70$ Å for CdO versus $a=b=[11.0]/2=4.76$ Å for Al$_2$O$_3$), but the mismatch in symmetry is
quite striking. Regardless, CdO accommodates the growth by forming misfit dislocations and by growing (052)-oriented, as revealed via STEM in Chapter 6 and by X-Ray previously \[238\]. Three structurally equivalent rotation variants form due to the hexagonal symmetry of the \(c\)-\(Al_2O_3\) surface, and intergrowth of these variants limits the grain size which is nonetheless quite large. Substrate steps do not necessarily introduce rotation variants, but they are associated with formation of threading dislocations. The threading dislocations and intergrowth of rotation variants are suggested as possible origins of slightly decreased mobility in films on \(c\)-\(Al_2O_3\) compared to MgO-(001).

Several future studies could elucidate some structural aspects of these materials. The dislocation core structures in the MgO∥CdO heterostructures appear to vary in structure from core to core. In these instances, the composition of the atom columns in the cores is not always clear. EELS could be utilized to determine the species that are occupying the core-region of the dislocations. This sort of information can be important for determining whether dislocation cores are charged \[267\]. Furthermore, the dislocations are very periodic at both top and bottom MgO interfaces, yet the dislocations on transverse interfaces are typically offset from each other. Presently, the offset of the dislocations periods at the top and bottom electrodes is not understood. Does it change with thickness? Are there any interruptions in the films where the offset shifts? Does it change the nature of the internal film strain for the ultrathin (∼1-1.7 nm) films? Further study and image analysis can provide clarifying information on the influence of these features.

In the case of the CdO films grown on \(c\)-\(Al_2O_3\), several avenues of future study also exist. Threading dislocations may have an influence on the electrical behavior of CdO thin films, similarly to how they influence the properties of GaN films on sapphire \[253\]. Plasmonic properties are influenced by defect scattering \[82\]. Growth parameters could be altered to try to increase or decrease the density of threading dislocations to observe whether this influences the electrical behavior (particularly the carrier mobility). Likewise, the rotational variants may be influencing the mobility. Similarly, varying growth conditions to alter the variant density could validate this hypothesis. In spite of these defects and rotation boundaries, the mobilities are still remarkably high and CdO films on \(c\)-\(Al_2O_3\) still afford a tremendous opportunity for plasmonic devices \[243\].
8.3 Rock-salt on Nitride Epitaxy Conclusions and Future Work

Chapter 7 considered the structure of several new functional rock-salt materials. To begin, the film and interface structures of HfN films grown for refractory applications [78] are presented for growth on MgO-(001), c-Al₂O₃, and (00.1)-GaN∥c-Al₂O₃ substrates. The best HfN film quality is achieved for growth on (00.1)-GaN∥c-Al₂O₃ substrates which yields highly-oriented {111}-HfN films with low misfit. The films are epitaxial and possess multiple {111}-HfN oriented rotational variants due to steps on the GaN substrate, which leads to stacking induced defects similar to those seen for growth MgₓCa₁−ₓO on GaN [114]. The HfN films remain {111}-oriented when grown on c-Al₂O₃, but the quality of the epitaxy and of the films deteriorates significantly. Presence of many more rotation variants leads to more defective and dislocation-rich films than those grown on GaN. Finally, MgO-(001) as a substrate yields (001)-HfN oriented films, but large lattice mismatch diminishes the film quality and they are rich in dislocations.

Several avenues exist for future work involving the metal-like nitride rock-salt HfN. The first and chief of these is as a bottom electrode for growth of HfO₂, which is discussed earlier and at length in the HfO₂ conclusions and future work section. To briefly recap here, (001)- and {111}-HfN orientations of HfN can be grown, and the {111}-HfN can be prepared with different film qualities. This provides a great opportunity for experimental growth of HfO₂ on this new metal-nitride. Such films may be epitaxial or highly textured. Furthermore, this should enable incorporation of HfO₂ into GaN-based devices. Furthermore, {111}-MgO∥Cu interfaces have previously been shown to form metal-induced gap states which are manifest in the oxygen and copper EEL fine structure [284]. Similar changes may be visible in the EEL fine structure of N or possibly one of the cation species in the {111}-HfN∥(00.1)-GaN interfaces.

In terms of the MgO and MgₓCa₁−ₓO films on GaN-(00.1), STEM imaging reveals interface structures consistent with prior reports [114]. The highly misfit {111}-MgO∥(00.1)-GaN grows with frequent misfit dislocations at the interface, while the lattice-matched MgₓCa₁−ₓO grows effectively free from dislocations. Beam damage and general sensitivity of these films to imaging limits the
achievable structural and spectroscopic data that is obtainable from these specific rock-salts on GaN. Vacuum baking and decreasing the accelerating voltage to 80-100 kV appears to prolong the ability to image these samples, yet beam currents still must be very low to avoid damage. Preliminary EEL spectra of the N and O K-edges suggests that the edge peak maxima may shift towards higher loss energies for the N and towards lower loss energies for the O as the interface is approached for the GaN and MgO, respectively. The shift in peak energy is more pronounced for O, and is present to a lesser extent for N. The O K-edge peak maxima also broadens towards the interface for the MgO. The MgO portion of the film contains some (weak) N signal but at a lower energy than it appears for the GaN. Further EELS experiments are needed to confirm these findings and to explain their origin in terms of interface states, interface metallization, and interface structure. This may require development of an understanding of the GaN∥MgO interface band structure through computational methods.

The growth and interface characterization of \{111\}-MnO∥(00.1)-GaN∥c-Al₂O₃ is presented for the first time. The films exhibit low misfit and infrequent misfit dislocations. The films adopt the Mn(II) rock-salt MnO structure, though traces of Mn₃O₄ Mn(II,III) is also identified. Based on growth and X-Ray studies, the Mn₃O₄ competing phase can be minimized or even eliminated based on growth conditions. Evidence of Mn₃O₄ in STEM lamella is linked to its formation by sample heating during lamella preparation, as X-Ray diffraction on ex-situ heated samples reveals phase transformation from MnO to Mn₃O₄. STEM EELS reveals no changes in the Mn L₂,₃ peaks in the interface compared to the bulk, however an approximately 0.9 eV shift to higher energies occurs near the surface, consistent with oxidation into Mn₃O₄. Atomic force microscopy identifies changes in surface morphology of samples above and below a critical thickness of ~ 5 nm, suggesting that polar compensation mechanisms may be occurring by electronic or structural means in these samples.

Fortunately, alternative means can be utilized to prevent the necessity of heating the samples during sample preparation, and are the first course of action for suggested further study. Certain Loctite® adhesives cure near-instantly and dissolve in acetone. Loctite super-glues of these sorts can be used for mounting, sectioning, and polishing purposes. M-Bond 610 Adhesive (Micro-Measurements)
can and should still be used for forming cross-sectioned glue lines and for mounting to TEM grids, as heating is not required for curing and because it does not dissolve in acetone. As such, the entire mechanical wedge polishing and Ar ion milling process should be achievable without the need for heating the sample at all. In the event that this still fails, the sample surface can be lightly scratched with a diamond scribe tip submerged in a drop of a solvent (like methanol), which can be dispersed with a pipet onto a lacy-carbon TEM grid. These fragments in some instances can be thin enough that they are transparent to the electron beam without requiring ion milling. Both of these methods can be employed to prevent the need for any heating during the sample preparation process.

Typically, rock-salt oxides etch in the Ar ion mill more rapidly than the GaN and Al$_2$O$_3$. For this reason, sacrificial capping layers are typically used to protect the samples from Ar ion milling damage during lamella preparation. Presently, it is unclear whether any reaction is forming between the amorphous LaAlO$_3$ and the crystalline MnO layer to form Mn$_3$O$_4$ or other inclusions. If Mn$_3$O$_4$ presence still accompanies samples that are prepared without heating, alternative cap layers can be considered such as SiO$_x$ or a metal such as Cu. Uncapped samples should be achievable with the scratch/disperse method of sample preparation. Uncapped samples may also be achievable with wedge polishing in combination with sector Ar ion milling where the ion guns are aligned so portions of the sample shadow the film regions to minimize damage [285]. Using these methods, samples free of artificial Mn$_3$O$_4$ should be achievable.

Upon achieving a suitable $\{111\}$-MnO/$\{001\}$-GaN STEM lamella, RevSTEM imaging and EELS studies need further attention. Any remaining presence of Mn$_3$O$_4$ should be investigated, as well as any valence changes near the MnO surface and the MnO/GaN polar interface. Does Mn valence change anywhere in the sample? Is there any local structural changes and distortions in the vicinity of the interface? Strain can be measured directly from the RevSTEM images, and any non-uniformities should be identified. Moreover, the lattice parameters of the film should be compared to known values for MnO bulk samples. Chemical and structural features should be compared between samples that have thicknesses above and below the $\sim$5 nm thickness that appears to lead to a change in surface morphology as measured by AFM. Alloying of MnO with MgO can also be performed to in-
crease the bandgap difference between film and heterolayer. Also, strain tuning could be performed by alloying with other rock-salts. CoO and EuO films can be explored as well on GaN, as they each can access multiple oxidation states. Ultimately, polarity and polar compensation mechanisms at these novel rock-salt∥nitride interfaces are not well understood. MnO seems like a promising step forward to investigate these questions, and several clear avenues exist for interrogating this system. Likewise, recent MgO∥GaN EELS results are promising and can be investigated in parallel with MnO∥GaN EELS.
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