High κ Dielectric HfO_2 on GaAs with Atomically Sharp Interface - Growth, Structural Studies, and Increase in Dielectric Constant

Research Highlights
Part I: MBE-HfO_2 on GaAs—amorphous and epitaxial single crystal growth, and structural studies using high-resolution X-ray diffraction
Part II: Increase in dielectric constant in cubic HfO_2 doped with Y_2O_3

Beamline

17B1 W20 X-ray Scattering beamline

Authors

J. R. Kwo and M. Hong
National Tsing Hua University, Hsinchu, Taiwan

C. H. Hsu and H. Y. Lee
National Synchrotron Radiation Research Center, Hsinchu, Taiwan

High-quality HfO_2 films of technologically important thickness ranging from 1.8 to 17 nm have been grown epitaxially on GaAs (001) by molecular beam epitaxy. Thorough structural and morphological investigations were carried out by X-ray scattering and high-resolution transmission electron microscopy. The films exhibit an atomically sharp interface with the substrate and are of a monoclinic phase with predominant (0 0 1)-plane epitaxy between the HfO_2 films and GaAs, in spite of a large lattice mismatch of > 8.5%. Moreover, HfO_2 doped with Y_2O_3 was found to be a cubic phase with a dielectric constant of more than 30.

The continuous scaling in Si-based device technology has called for identifying new high-*k* dielectrics to replace SiO_2 in gate and other applications. HfO_2 is a promising material as an alternative gate dielectric. Amorphous HfO_2 has been profoundly studied but may not be adequate due to the low re-crystallization temperatures. A high electrical leakage occurs at grain boundaries, which are formed when amorphous films turn into polycrystalline. Epitaxial single-crystal oxide thin films and their interfaces with semiconductors are generally more robust during the high temperatures annealing. Therefore, the employment of single crystal HfO_2 may provide advantages as the gate dielectric.

It is known that there exist three different low-pressure polymorphs of HfO_2: a cubic phase with lattice constant a = 0.508 nm, a meta-stable tetragonal phase with a = 0.503 nm and c = 0.511 nm, and a monoclinic phase with a = 0.512 nm, b = 0.518 nm, c = 0.529 nm and $\beta = 99.22^\circ$. Dielectric constants of the three phases are 29, 70 and 16, respectively; all are much higher than that of SiO_2, i.e. 3.9. Judging from their crystal structures and the lattice constants, a large lattice mismatch is always present regardless of which phase is grown on Si(001) or GaAs(001) substrates,. Therefore, so far almost all the reported crystallized HfO_2 films have been polycrystalline and often more than one phase exists in the film.

Recently, single crystal nano-thick HfO_2 films were grown epitaxially on GaAs (001) with a two-step method as briefly described below. The oxide dielectric films were grown in a multi-chamber molecular beam epitaxy (MBE) system. A GaAs epi layer was grown in a solid-source GaAs-based MBE chamber. The sample was then moved in-situ (under a vacuum of ~10^{-10} torr) to an arsenic-free oxide chamber. Compacted and sintered HfO_2 ceramic pallets were used as the e-beam evaporation source to avoid direct exposure of the GaAs surface to oxygen, thus preventing the formation of AsO_x. The initial deposition of HfO_2 was

performed at room temperature and an amorphous layer was formed. In-situ annealing to 530~540˚C lead to the formation of an epitaxial single crystal HfO_2. This also serves as a template for a subsequent epitaxial over-growth of HfO_2 at higher temperatures (580˚C).

Measurements of X-ray reflectivity (XRR), crystal truncation rod (CTR) and grazing incidence X-ray diffraction (GIXD) were carried out at beamline BL17B of National Synchrotron Radiation Research Center (NSRRC), where X-rays are monochromatized by a pair of Si(111) crystals. A beam energy of 8 keV was employed in most of the measurements. A six-circle diffractometer with two pairs of slits between the sample and detector was employed. A typical resolution of better than 4×10^{-4} nm^{-1} is adopted for this work. Samples with HfO_2 over-layer of different thickness have been examined. Within the studied thickness, 1.8-17 nm, the qualitative structural properties of the samples are identical, independent of film thickness. Therefore, in this paper we mainly present the results of the films with thickness of 4-10 nm, which give stronger scattering signals. High-resolution transmission electron microscopy (HR-TEM) specimens were prepared with mechanical polishing, dimpling, and ion milling using a Gatan PIPS system operated at 3kV. The TEM sample analytical work was performed using a Philips TECNAI-20 FEG type TEM.

The intensity profile of a θ-2θ scan along surface normal, i.e., the (0 0 L) CTR, of a sample consisting of a HfO_2 template layer ~ 2 nm thick plus an epitaxial over-layer ~7 nm thick is illustrated in Fig. 1. The abscissa is in units of GaAs reciprocal lattice unit (r.l.u.$_{GaAs}$), $2\pi/a_{GaAs}$= 1.11 $Å^{-1}$ where a_{GaAs} denotes the lattice constant of GaAs. The part of small L (≤ 1 r.l.u.) stems from the (0 0 0) Bragg peak and is commonly known as X-ray reflectivity. The periodic intensity modulation on the reflectivity curve, the Kiessig fringe, originates from the interference between the X-rays reflected by the surface and buried film-substrate interface. From the fringe spacing 0.69 nm^{-1}, the total film thickness of 9.1 nm was derived. The pronounced oscillations persist over 8 nm^{-1} and no second periodicity is observed in the reflectivity curve, manifesting the existence of a sharp interface. The roughness of the HfO_2/Si interface is determined to be 0.27 nm and the roughness of HfO_2 surface, which is sensitive to the film thickness, is ~ 0.5 nm.

Indeed, a HR-TEM cross sectional image for a

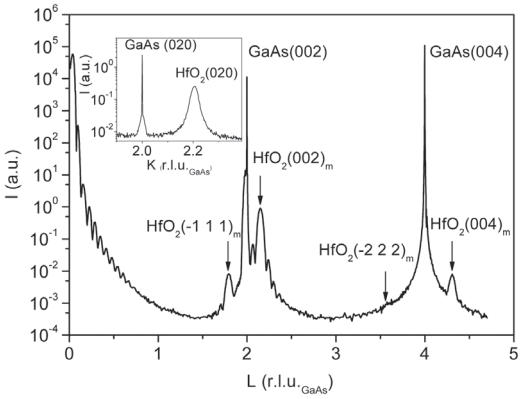

Fig. 1: Intensity profile of (0 0 L) crystal truncation rod. Inset displays the in-plane radial scan across GaAs (0 2 0) and HfO_2 (0 2 0) reflections.

sample with an overall oxide 5.1 nm thick, shown in Fig. 2, verifies that the oxide/GaAs interface is atomically sharp. Furthermore, there is no boundary between the template and the overgrown epitaxial oxide film. Unlike the films prepared by atomic layer deposition (ALD), no intermediate (interfacial) layer between HfO_2 and GaAs was observed.

As compared with the crystalline HfO_2 films grown at high temperatures, in which an interaction occurred between the oxide and GaAs, the interface of the samples prepared by this two-step method is sharp. Along the (0 0 L) rod, the intense sharp peaks centered at 2 and 4 r.l.u.$_{GaAs}$ are the (0 0 2) and (0 0 4) Bragg reflections of the GaAs substrate. Additional

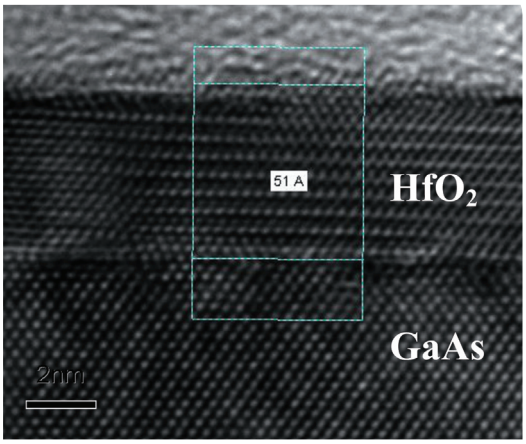

Fig. 2: Cross sectional HR-TEM image of a 51Å thick HfO_2/GaAs sample. The image clearly shows the atomic sharp interface and the high crystal quality of the HfO_2 film (including the epitaxial single crystal template and the overgrown film).

broad peaks centered at 2.153 and 4.306 r.l.u.$_{\_GaAs}$, correspond to inter-planar spacing of 0.2626 and 0.1313 nm, respectively. The values of (H K L) were determined to be (0 0 2) and (0 0 4) by referencing to the inter-planar spacing of the monoclinic HfO_2 single crystal, $d_{(002)}$= 0.2610 and $d_{(004)}$= 0.1305 nm. The full width at half maximum (FWHM) of the HfO_2 (0 0 2) and (0 0 4) reflections are 0.59 nm^{-1} and 0.63 nm^{-1} (as a comparison, the FWHM of GaAs (0 0 4) reflection is 0.014 nm^{-1}), which give a coherent length ~ 10 nm along the growth direction. This value is comparable to the film thickness, thus indicating that the atomic structure of the HfO_2 remains coherent throughout the whole thickness of the film.

Another weak diffraction peak centered at 1.7945 r.l.u.$_{\_GaAs}$, has an planar spacing close to $d_{(-1\ 1\ 1)}$ of monoclinic HfO_2 and thus is indexed as the (-1 1 1) reflection. The weak HfO_2 (-2 2 2) reflection, located at twice the L value of HfO_2 (-1 1 1), can barely be seen in Fig. 1. The line width of the (-1 1 1) reflection is approximately 0.64 nm^{-1}, corresponding to a vertical coherence length of ~ 9 nm, which is again comparable to the film thickness. The intensity of the (0 0 2) reflection is more than two orders of magnitude stronger than that of the (-1 1 1) reflection and the ratio increases with reducing film thickness. This implies that the films are predominantly made of domains with (0 0 1) normal, especially in the case of ultra-thin films.

In the following, we will first focus on the structural properties of the dominant (0 0 1) orientated domains. A θ-rocking scan at the HfO_2 (0 0 2) reflection has a FWHM of 0.17˚. As a comparison, the FWHM of nearby GaAs (0 0 2) reflection is 0.006˚, which practically represents the instrumental resolution. Therefore, the 0.17˚ line width gives an upper limit of the mosaic spread of the HfO_2 over-layer. An additional fringe on the (0 0 L) rod near the GaAs (0 0 2) reflection has the same origin as the Kiessig fringe in the reflectivity and again evidences the high crystal quality of the deposited film and the sharp interfaces.

To confirm the epitaxy between the HfO_2 films and GaAs (0 0 1) substrates, careful analysis of the crystal structure using four-circle X-ray diffraction were carried out. Illustrated in the inset of Fig. 1 is the scattered X-ray intensity variation of a radial scan across the GaAs (0 2 0) surface reflection, where the broad peak centered at 2.2048 r.l.u.$_{\_GaAs}$ is indexed as the (0 2 0) reflection of the monoclinic HfO_2. The line widths of HfO_2 (0 2 0) and (0 4 0) reflections are 0.34 and 0.62 nm^{-1}, respectively. The broadening of Bragg reflections in reciprocal space may be caused by small correlation length and heterogeneous strain. The obvious increase of the FWHM with K value indicates that strain induced peak broadening is the main contribution. Applying the Williamson-Hall method to separate the strain-induced broadening from the finite-size effect, we estimated the lateral domain size of approximate 100 nm. With the monoclinic reference frame defined by the (0 0 2) and (0 2 0) reflections, we successfully found many other Bragg reflections and confirmed the monoclinic structure of the dominant domain of the deposited HfO_2 films.

If the monoclinic HfO_2 films were c-plane epitaxy, they would give a characteristic two-fold and one-fold symmetry in the intensity distribution of the azimuthal scan, i.e. ϕ scan, of the HfO_2 (0 4 0) and (4 0 0) reflections, respectively. The observed four-fold rotational symmetry in both azimuthal scans shown in Fig. 3 strongly suggest that the (0 0 1)-plane epitaxial HfO_2 films consist of four domains which rotate 90˚ with respect to each other. The inset on the right of Fig. 3 shows an H-L mesh scan near the HfO_2 (4 0 0) reflection with the axes displayed in the r.l.u. of monoclinic HfO_2. The lobe on the top is the (4 0 0) reflection of one domain and the lobe on the bottom, centered at $(4\ 0\ -0.572)_{HfO_2}$, matches perfectly the location of the (0 4 0) reflection of another monoclinic HfO_2 frame whose in-plane rectangular lattice net is rotated 90˚ from the former one.

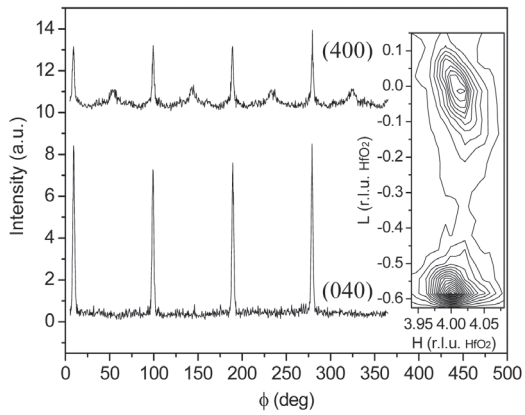

Fig. 3: Intensity distribution of the azimuthal scan, i.e. ϕ scan, of the HfO_2 (0 4 0) and (4 0 0) reflections. The panel to the right illustrates a contour plot of the H-L mesh of a set of (0 4 0) and (4 0 0) Bragg peaks.

The peak positions in ϕ scans of HfO_2 {4 0 0} and {0 4 0} reflections coincide with that of GaAs {4 0 0} and their FWHM are all ~2.1°. This observation evidences that the perfect alignment of a and b axes of the HfO_2 with <1 0 0> axes of the underneath GaAs and the high crystal quality of the grown films. The weak peaks half-way between the HfO_2 {4 0 0} reflections, shown on Fig. 3, are ascribed to the CTRs of GaAs {3 -3 1}. From the position of measured Bragg reflections, the lattice parameters of the monoclinic film are determined to be a = 0.512 nm^{-1}, b = 0.513 nm^{-1}, c = 0.532 nm^{-1}, and β = 98.8°, slightly different from the bulk value reported previously. The variations in lattice parameters (of the measured samples) with HfO_2 thickness between 4-17 nm are less than 0.2% and have no clear trend. This suggests that these films are fully relaxed in structure.

As implied by the peak centered at 1.7945 r.l.u.$_{\_GaAs}$ in Fig. 1, it is speculated that there exist minor domains with the (-1 1 1) normal in addition to the dominant c-plane epitaxial domains. To verify this, we performed a θ-rocking scan at (-1 1 1) reflection and found its FWHM is 2°, indicating a mosaic spread much worse than that of the dominant (0 0 2) reflection. Furthermore, we looked for off-normal reflections associated with the same monoclinic phase but with (-1 1 1) normal and successfully found the (1 1 1) and (0 2 0) reflections. However, the width of ϕ scans of HfO_2 (1 1 1) and (0 2 0) associated with this minor orientation are very wide, more than 12°, and their intensity are only about twice as high as the background. This reveals that this minor orientation has a (-1 1 1) preferred column-like structure with a rather poor in-plane alignment.

In conclusion, the HfO_2/GaAs heterostructures with the oxide stacks prepared by the two-step MBE-growth has an atomic sharp interface and no interfacial oxide layer. Our films, even with a thickness as thin as 1.8 nm, are made of monoclinic HfO_2 of highly epitaxial quality. The predominant domains have (0 0 1) in parallel with the normal (001) of the substrate epitaxy with their a and b axes aligned with the in-plane <100> axes of GaAs. We have recently successfully grown a cubic structure of HfO_2 doped with Y_2O_3 as shown in Fig. 4, whose dielectric constant is higher than 30.

We wish to acknowledge the support from Department of Natural Sciences at National Science Council (under grants of NSC-93-2120-M-007-007, NSC-93-2120-M-007-008 and NSC94-2112-M-213-014), Taiwan, Republic of China.

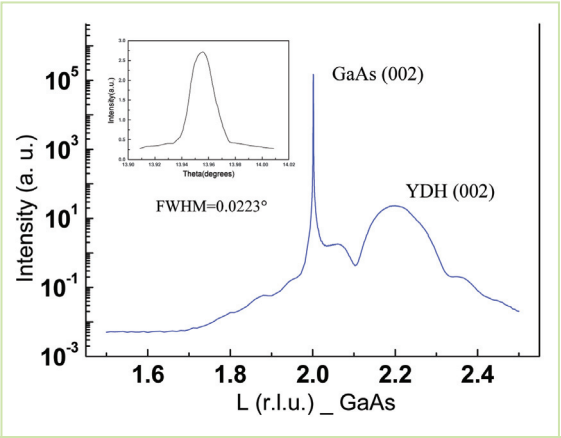

Fig. 4: Surface normal scan of cubic HfO_2 doped with Y_2O_3 5.1nm thick grown on GaAs (100)

Experimental Station

X-ray scattering end station

References

- M. M. Frank *et al.,* Appl. Phys. Lett. **86**, 152904 (2005).
- N. V. Nguyen *et al.,* Appl. Phys. Lett. **87**, 192903 (2005).
- S. Kremmer *et al.,* J. Appl. Phys. **97**, 074315 (2005)
- C. Wiemer *et al.,* Thin Solid Films **450**, 134 (2004).
- M.-H. Cho *et al.,* Appl. Phys. Lett. **81**, 472 (2002).
- X. Zhao *et al.,* Phys. Rev. B **65**, 233106 (2002).
- M. Hong *et al.,* J. Vac. Sci. Technol. B **14**, 2297 (1996).
- J. Wang, *et al.,* J. Mater. Sci. **27**, 5397 (1992).
- J. Adam *et al.,* Acta Crystallogr. **12**, 951 (1959); R. E. Hann, *et al.,* J. Am. Ceram. Soc. **68**, C-285 (1985).
- C. E. Curtis *et al.,* J. Am. Ceram. Soc. **37**, 458 (1954).
- G. K. Williamson *et al.,* Acta Metall. **1**, 22 (1953).

Contact E-mail

raynien@phys.nthu.edu.tw