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Citation: *Applied Physics Letters* **89**, 122907 (2006); doi: 10.1063/1.2356895

View online: <http://dx.doi.org/10.1063/1.2356895>

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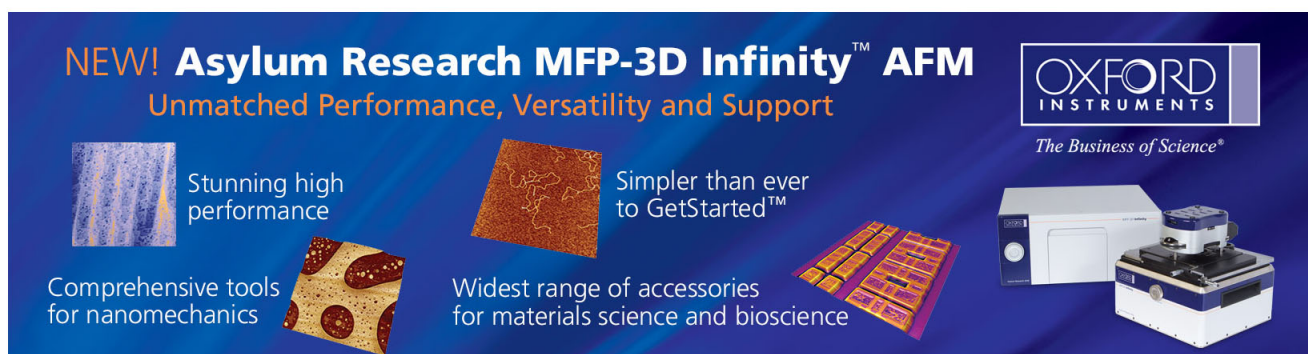
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Structure of HfO₂ films epitaxially grown on GaAs (001)

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(Received 6 June 2006; accepted 1 August 2006; published online 20 September 2006)

High-quality HfO₂ 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 (001)-plane epitaxy between the HfO₂ films and GaAs, in spite of a large lattice mismatch of >8.5%. © 2006 American Institute of Physics.

[DOI: 10.1063/1.2356895]

The continuous scaling in Si-based device technology has called for identifying alternative high κ dielectrics to replace SiO₂ in gate and other applications. HfO₂ is a promising material as a high κ gate dielectric. Amorphous HfO₂ has been profoundly studied but may not be adequate due to the low recrystallization temperatures.^{1,2} 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 temperature annealing. Therefore, the employment of single crystal HfO₂ may provide advantages as the gate dielectric.

It is known that there exist three different low-pressure polymorphs of HfO₂: a cubic phase with lattice constant $a = 0.508$ nm,³ a metastable tetragonal phase with $a = 0.503$ nm and $c = 0.511$ nm,⁴ and a monoclinic phase with $a = 0.512$ nm, $b = 0.518$ nm, $c = 0.529$ nm, and $\beta = 99.22^\circ$.⁵ Dielectric constants of the three phases are 29, 70, and 16, respectively; all are much higher than that of SiO₂, i.e., 3.9.⁶ 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 HfO₂ films have been polycrystalline and often more than one phase exists in the film.^{1,7,8}

Recently, single crystal nanothick HfO₂ films were grown epitaxially on GaAs (001) with a two-step method⁹ as briefly described below. The oxide dielectric films were grown in a multichamber molecular beam epitaxy (MBE) system.¹⁰ A GaAs epilayer was grown in a solid-source GaAs-based MBE chamber. The sample was then moved *in situ* (under a vacuum of $\sim 10^{-10}$ torr) to an arsenic-free oxide chamber. Compacted and sintered HfO₂ ceramic pellets were used as the e-beam evaporation source to avoid direct expo-

sure of the GaAs surface to oxygen, thus preventing the formation of AsO_x. The initial deposition of HfO₂ was performed at room temperature and an amorphous layer was formed. *In situ* annealing to 530–540 °C leads to the formation of an epitaxial single crystal HfO₂. This also serves as a template for a subsequent epitaxial overgrowth of HfO₂ at higher temperatures (580 °C).

In this letter, the epitaxial nanothick single crystal HfO₂ films on GaAs were found to be a monoclinic phase with an atomically sharp interface with the substrate.

Measurements of x-ray reflectivity, crystal truncation rod (CTR), and grazing incidence x-ray diffraction^{11,12} were carried out at beamline BL17B of the National Synchrotron Radiation Research Center, 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 HfO₂ overlayer of different thicknesses 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 letter we mainly present the results of the films with thicknesses of 4–10 nm, which give stronger scattering signals. High-resolution transmission electron microscopy (HRTEM) specimens were prepared with mechanical polishing, dimpling, and ion milling using a Gatan PIPS system operated at 3 kV. The TEM sample analytical work was performed using a Philips Tecnai-20 TEM with a field emission gun source.

The intensity profile of a θ - 2θ scan along the surface normal, i.e., the (00L) CTR, of a sample consisting of a HfO₂ template layer of ~ 2 nm thick plus an epitaxial overlayer of ~ 7 nm thick is illustrated in Fig. 1. The abscissa is in units of GaAs reciprocal lattice unit (rlu_{GaAs}), $2\pi/a_{\text{GaAs}}$ = 1.11 \AA^{-1} , where a_{GaAs} denotes the lattice constant of GaAs. The part of small L ($\leq 1 \text{ rlu}_{\text{GaAs}}$) stems from the (000) Bragg peak and is commonly known as x-ray reflectivity. The peri-

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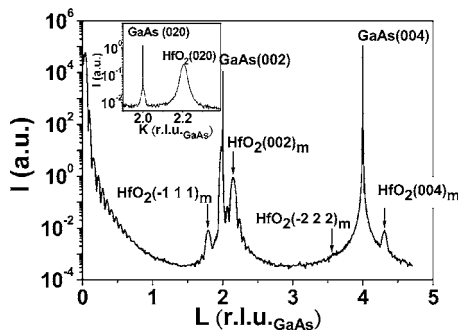


FIG. 1. Intensity profile of (00L) crystal truncation rod. Inset displays the in-plane radial scan across GaAs (020) and HfO₂ (020) reflections.

odic 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 HfO₂/GaAs interface is determined to be 0.27 nm and the roughness of HfO₂ surface, which is sensitive to the film thickness, is $\sim 0.5 \text{ nm}$.

Indeed, a HRTEM cross sectional image for a sample with an overall oxide of 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,¹³ no intermediate (interfacial) layer between HfO₂ and GaAs was observed.

As compared with the crystalline HfO₂ 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.⁹ Along the (00L) rod, the intense sharp peaks centered at 2 and 4 rlu_{GaAs} are the (002) and (004) Bragg reflections of the GaAs substrate. Additional broad peaks centered at 2.153 and 4.306 rlu_{GaAs} correspond to interplanar spacings of 0.2626 and 0.1313 nm , respectively. The values of (HKL) were determined to be (002) and (004) by referencing to the interplanar spacing of the monoclinic HfO₂ single crystal, $d_{(002)}=0.2610$ and $d_{(004)}$

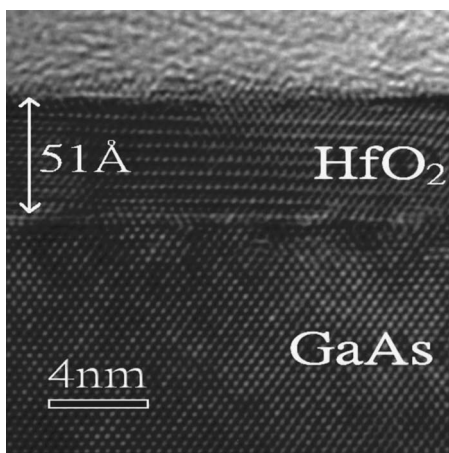


FIG. 2. Cross sectional HRTEM image of a 51 \AA thick HfO₂/GaAs sample. The image clearly shows the atomically sharp interface and the high crystal quality of the HfO₂ film (including the epitaxial single crystal template and the overgrown film).

$=0.1305 \text{ nm}$. The full width at half maximum (FWHM) of the HfO₂ (002) and (004) reflections are 0.59 and 0.63 nm^{-1} [as a comparison, the FWHM of GaAs (004) reflection is 0.014 nm^{-1}], which give a coherent length of $\sim 10 \text{ nm}$ along the growth direction. This value is comparable to the film thickness, thus indicating that the atomic structure of the HfO₂ remains coherent throughout the whole thickness of the film.

Another weak diffraction peak centered at $1.7945 \text{ rlu}_{\text{GaAs}}$ has a planar spacing close to $d_{(-111)}$ of monoclinic HfO₂ and thus is indexed as the (-111) reflection. The weak HfO₂ (-222) reflection, located at twice the L value of HfO₂ (-111), can barely be seen in Fig. 1. The linewidth of the (-111) reflection is approximately 0.64 nm^{-1} , corresponding to a vertical coherence length of $\sim 9 \text{ nm}$, which is again comparable to the film thickness. The intensity of the (002) reflection is more than two orders of magnitude stronger than that of the (-111) reflection and the ratio increases with reducing film thickness. This implies that the films are predominantly made of domains with (001) normal, especially in the case of ultrathin films.

In the following, we will first focus on the structural properties of the dominant (001) oriented domains. A θ -rocking scan at the HfO₂ (002) reflection has a FWHM of 0.17° . As a comparison, the FWHM of nearby GaAs (002) reflection is 0.006° , which practically represents the instrumental resolution. Therefore, the 0.17° linewidth gives an upper limit of the mosaic spread of the HfO₂ overlayer. An additional fringe on the (00L) rod near the GaAs (002) 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 HfO₂ films and GaAs (001) substrates, careful analysis of the crystal structure using four-circle x-ray diffraction was carried out. Illustrated in the inset of Fig. 1 is the scattered x-ray intensity variation of a radial scan across the GaAs (020) surface reflection, where the broad peak centered at $2.2048 \text{ rlu}_{\text{GaAs}}$ is indexed as the (020) reflection of the monoclinic HfO₂. The linewidths of HfO₂ (020) and (040) 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 method¹⁴ to separate the strain induced broadening from the finite-size effect, we estimated the lateral domain size of approximately 100 nm . With the monoclinic reference frame defined by the (002) and (020) reflections, we indeed found many other Bragg reflections and confirmed the monoclinic structure of the dominant domain of the deposited HfO₂ films.

If the monoclinic HfO₂ films were c -plane epitaxy, they would give characteristic twofold and onefold symmetries in the intensity distribution of the azimuthal scan, i.e., ϕ scan, of the HfO₂ (040) and (400) reflections, respectively. The observed fourfold rotational symmetry in both azimuthal scans shown in Fig. 3 strongly suggest that the (001)-plane epitaxial HfO₂ 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 HfO₂ (400) reflection with the axes displayed in the rlu of monoclinic HfO₂. The

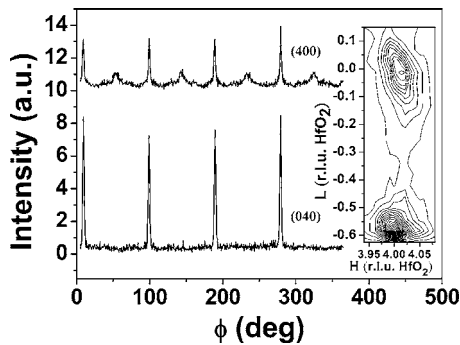


FIG. 3. Intensity distribution of the azimuthal scan, i.e., ϕ scan, of the HfO_2 (040) and (400) reflections. The panel to the right illustrates a contour plot of the H - L mesh of a set of (040) and (400) Bragg peaks.

lobe on the top is the (400) reflection of one domain and the lobe on the bottom, centered at $(40-0.572)_{\text{HfO}_2}$, matches perfectly the location of the (040) reflection of another monoclinic HfO_2 frame whose in-plane rectangular lattice net is rotated 90° from the former one.

The peak positions in ϕ scans of HfO_2 {400} and {040} reflections coincide with that of GaAs {400} and their FWHM are all $\sim 2.1^\circ$. This observation evidences the perfect alignment of the a and b axes of the HfO_2 with $\langle 100 \rangle$ axes of the underneath GaAs and the high crystal quality of the grown films. The weak peaks halfway between the HfO_2 {400} reflections, shown on Fig. 3, are ascribed to the CTRs of GaAs {3-31}. From the position of measured Bragg reflections, the lattice parameters of the monoclinic film are determined to be $a=0.512 \text{ nm}^{-1}$, $b=0.513 \text{ nm}^{-1}$, $c=0.532 \text{ nm}^{-1}$, and $\beta=98.8^\circ$, slightly different from the bulk value reported previously.⁵ 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 $1.7945 \text{ rlu}_{\text{GaAs}}$ in Fig. 1, it is speculated that there exist minor domains with the (-111) normal in addition to the dominant c -plane epitaxial domains. To verify this, we performed a θ -rocking scan at (-111) reflection and found that its FWHM is 2° , indicating a mosaic spread much worse than that of the dominant (002) reflection. Furthermore, we looked for off-normal reflections associated with the same monoclinic phase but with (-111)

normal and have found the (111) and (020) reflections. However, the widths of ϕ scans of HfO_2 (111) and (020) associated with this minor orientation are very wide, more than 12° , and their intensities are only about twice as high as the background. This reveals that this minor orientation has a (-111) preferred columnlike 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 atomically 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 (001) in parallel to the normal (001) of the substrate epitaxy with their a and b axes aligned with the in-plane $\langle 100 \rangle$ axes of GaAs.

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

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