**Cubic HfO$_2$ Doped with Y$_2$O$_3$ Epitaxial Films on GaAs (001) of Enhanced Dielectric Constant**

Nanometer thick cubic HfO$_2$ doped with Y$_2$O$_3$ of 19 at. % (YDH) epitaxial films were grown on GaAs (001) using molecular beam epitaxy. Structural studies using high-resolution X-ray scattering and transmission electron microscopy determined an epitaxial orientation relationship between the cubic YDH films and GaAs to be (001)$_{\text{GaAs}}$// (001)$_{\text{YDH}}$ and [100]$_{\text{GaAs}}$//[100]$_{\text{YDH}}$. The YDH structure is strain relaxed with a lattice constant of 0.5122 nm, a small mosaic spread of 0.023° from the (002) rocking curve, and a twist angle 2.9° from the (400) azimuthal scan. The YDH/GaAs interface is atomically abrupt without evidence of reacted interfacial layers. From C-V and I-V measurements a cubic epitaxial YDH film 7.7 nm thick has an enhanced dielectric constant $\kappa \approx 32$, an equivalent oxide thickness $\sim 0.94$ nm, an interfacial state density $D_{it} \sim 7 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$, and a low leakage current density of $6 \times 10^{-5}$ A/cm$^2$ at 1 V gate bias.

The aggressive scaling of Si complimentary metal-oxide-semiconductor (CMOS) device has called for alternative high $\kappa$ gate dielectrics replacing conventional SiO$_2$. HfO$_2$ and its derivatives have now emerged as the choice of materials, for the high $\kappa$ value and thermal stability in contact with Si. Moreover, feverish research activities are now being taken on high $\kappa$ dielectrics on GaAs, as Si channel will be replaced with higher mobility channels such as GaAs for technologies beyond the 22 nm CMOS mode.

Molecular beam epitaxy (MBE) or atomic layer deposited (ALD) hafnium dioxide (HfO$_2$) is of monoclinic phase with $\alpha \sim 20$ (or less). The MBE epitaxial HfO$_2$ films have the monoclinic crystal structure ($\alpha = \gamma = 90^\circ$ and $\beta \sim 99^\circ$) with their a and b axes aligned with the in-plane (100) axes of GaAs, and formed four equivalent in-plane domains rotating 90° about surface normal. Higher dielectric constants $\kappa$ being ~30 and 70 are theoretically predicted in crystallographic structures of cubic and tetragonal phases. Unfortunately the tetragonal and cubic phases can be transformed thermodynamically at approximately 1720 and 2600°C, respectively, whereas the monoclinic phases appeared at room temperature. Nevertheless, the HfO$_2$-Y$_2$O$_3$ phase diagram suggests a possible cubic phase formation at relatively lower temperatures with Y$_2$O$_3$ doping to HfO$_2$.

In this work, nano thick HfO$_2$ doped with Y$_2$O$_3$ (denoted as YDH) films were epitaxially grown on GaAs (001) by MBE. High-resolution x-ray diffraction studies found that the film crystal structure is altered from the common monoclinic phase of a dielectric constant $\kappa \sim 17$ to the cubic phase of a $\kappa$ value exceeding 30, as determined from C-V measurements in YDH MOS diodes. In-situ angle-resolved x-ray photoelectron spectrometry (XPS) revealed that Y$_2$O$_3$ is
uniformly distributed through the YDH films with an atomic percentage of Y to be 19.2±0.5, as confirmed by anomalous x-ray diffraction (AXD). The oxide/semiconductor interfaces are atomically sharp as observed from high-resolution transmission electron microscopy (HR-TEM). The attainment of the cubic YDH has effectively eliminated the number of azimuthal domains, thus significantly improved electrical leakage. The fact that the YDH films are grown in single crystalline at typical dopant activation temperature has alleviated the problem of poly crystalline formation of most amorphous dielectrics during post annealing, and the consequent increase of electrical leakage.

All oxides were prepared in a multi-functional integrated ultrahigh vacuum system as previously described. The YDH films were co-evaporated using electron beam evaporation from two separate targets of HfO₂ and Y₂O₃ ceramic pallets at substrate temperatures of 550°C. The majority of the deposited species arriving at the substrate were HfO₂ and Y₂O₃ molecules or clusters, thus avoiding direct exposure of GaAs surface to oxygen and preventing formation of AsOₓ and GaOᵧ. The surface morphology of epitaxial YDH films as monitored by in-situ reflection high energy electron diffraction indicates a smooth two-dimensional film growth exhibiting four-fold symmetry in the plane. Typical YDH layer thickness varies between 4 and 12 nm. Crystallographic structures of the epitaxial YDH films on GaAs were analyzed by high-resolution x-ray diffraction at beamline BL17B of National Synchrotron Radiation Research Center (NSRRC). HR-TEM was performed using a Philips TECNAI-20 FEG type TEM. Electrical characteristics of the MOS diodes of 7.85 x 10⁻⁵ cm² in area with Au electrodes were measured using Agilent 4156C and 4284. X-ray photoemission spectroscopy (XPS) was taken in-situ by using a SPECS-PHOIBOS-150 hemispherical electron analyzer and a dual anode x-ray source (Mg Kα and Al Kα). The pass energy of electron analyzer was fixed at 10 eV, and the binding energies of the spectra were calibrated using Ag 3d₅/₂ peak (368.3 eV) of an Ag foil. After removal of a Shirley background, the peak fitting was made by using a least-square fit of the spectra to a Gaussian-Lorentzian function.

X-ray scattering radial scans for an YDH epitaxial film along GaAs [002], [040] and [111] directions, are shown in Fig. 1 (a), (b) and (c), respectively. The abscissa is in units of GaAs reciprocal lattice unit (rlu₆₆₆₆), 2π/a₆₆₆₆= 1.11 Å⁻¹ where a₆₆₆₆ denotes the lattice constant of GaAs. The intense sharp peaks centered at 2, 4 and 1 are GaAs (002), (040) and (111) Bragg peaks; the broad peaks centered at 2.2, 4.4 and 1.1 are reflections from YDH. The fact that for each GaAs reflection, there is always an YDH reflection located at 1.104 times the position of the GaAs peak in radial scans manifests that YDH has the same symmetry as GaAs, i.e. cubic. By comparing the obtained inter-planar spacing with database, the broad peaks in Fig. 1 (a), (b) and (c) were indexed as (002), (400) and (111) reflections of cubic YDH, respectively. A large lattice mismatch of approximate -9.4 % exists between the YDH layer and GaAs substrate. Furthermore, the azimuthal scans, i.e. Φ scans, across YDH in-plane (400), shown in the inset of Fig. 1(b), and off-specular (111) reflections exhibit four-fold symmetry and the peak positions coincide with the GaAs reflections of the same Miller Indices. These observations verify the cubic structure of the grown YDH and its epitaxial relationship with GaAs substrate follows YDH {100} || GaAs {100}. The lattice constant of the films is 0.5122 nm as determined by fitting the scattering angles of more than 10 reflections. No sign of tetragonal deformation was observed, indicating the YDH lattice is well relaxed for films of thickness of 4 nm or even less. In view of the large lattice mismatch between YDH and GaAs, the generation of defects near the interfacial region to accommodate the mismatch is expected.

The additional oscillations beside the two Bragg reflections in the radial scan along surface normal, Fig. 1(a), are the thickness fringes, originating from the interference between the X-rays reflected by the top and bottom
interface of the YDH layer. From the oscillation period $\Delta q = 0.08 \text{ nm}^{-1}$, the film thickness of 7.7 nm was derived for the sample shown. The coherence length along the growth direction, estimated from the width of YDH (002) reflection using the Scherrer equation, is 7.4 nm. The comparable size of the film thickness and coherence length indicates that the structural coherence extends throughout the whole film thickness. The small mosaic spread of 0.023° and twist angle 2.9°, determined from the width of the YDH (002) rocking curve and (400) azimuthal scan, respectively, demonstrate its high crystalline quality.

Interfacial structure of the YDH layer was examined by both HR-TEM and X-ray reflectivity (XRR). HR-TEM cross sectional image shown in Fig. 2 indicates that the interface between YDH and GaAs is atomically sharp. This observation agrees with the XRR results, i.e. one-layer model is sufficient to fit the experimental data. The root-mean-square (rms) roughness of the oxide/GaAs interface obtained by reflectivity is ~0.3 nm. The YDH surface is rougher than the buried interface and its roughness increases with layer thickness. For the YDH layer 11 nm thick, the measured rms roughness of free surface is about 1.0 nm. Unlike (001) monoclinic HfO$_2$ epitaxial films on GaAs, no features associated with azimuthal domain boundaries were observed in Fig. 2. The continuity of the film structure is helpful to minimize the pathways of leakage current.

The content and distribution of Y in YDH films were determined using AR-XPS at O 1s, Y 3d and Hf 4f core levels with the spectra shown in Fig. 3 (a), (b) and (c), respectively. The relative sensitivity factor (R.S.F) of O 1s, Y 3d and Hf 4f was 2.93, 5.98 and 7.52, respectively using Al K$_\alpha$. Spectra were quantified using CasaXPS (version 2.3.12, Casa Software Ltd.). Hf and Y are homogeneously distributed in the YDH films, as evidenced by the constant ratios between the area of O 1s, Y 3d and Hf 4f peaks at various electron takeoff angles of 0, 45 and 75°. The curves in Fig. 3(a) can be de-convoluted into two different kinds of oxygen bonding of Hf-O (531.5 eV) and Y-O (532.55 eV). Compositions of the hafnium oxide and yttrium oxide are close to stoichiometric HfO$_2$ and Y$_2$O$_3$, respectively. Furthermore, the atomic percentage of Hf : Y was estimated to be 80.8±0.5:19.2±0.5, equivalent to the mole fraction of $(\text{HfO}_2)_{0.895}(\text{Y}_2\text{O}_3)_{0.105}$. We have also determined the absolute Y content incorporated in the YDH films using anomalous x-ray diffraction (AXD). AXD spectra were measured across Y $k$-edge at the YDH (222) and (220) reflections. Comparing the relative intensity attenuation at absorption edge with the calculated one assuming a random substitution of Hf by Y, we determined that the Y content was about 19±2 at%, in good agreement with the XPS analysis, thus confirming that Y substitutes Hf in the crystalline lattice and forms a solid solution.

The C-V characteristics of a MOS capacitor with a YDH film 7.7 nm thick measured at frequencies varying from 10 k to 100 kHz are illustrated in Fig. 4. The C-V curves show the standard depletion to accumulation transition with little frequency dispersion. A dielectric constant $\kappa$ of 32 was obtained from the C-V curve, significantly higher than that of the monoclinic pure HfO$_2$ in 16-18 range and close to the theoretically predicted value 29 for cubic HfO$_2$. Typical $D_i$ value is deduced to be $7-8 \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ using the Terman method, and an equivalent oxide thickness of 0.94 nm was obtained as given by $t_{YDH} \times (k_{SiO_2} / k_{YDH})$ where $t$ is the thickness of YDH layer. A flat band shift in the C-V measurement was observed at frequencies over 100 kHz. This is probably caused by the presence of interfacial...
Research Highlights

- MBE-Y$_2$O$_3$ doped HfO$_2$ (YDH, a cubic phase) on GaAs - epitaxial single crystal growth, and structural studies using high-resolution x-ray diffraction
- Strongly enhanced dielectric constant in cubic HfO$_2$ doped with Y$_2$O$_3$

Experiment Stations

- X-ray scattering end station
- 7-circle X-ray Scattering Station

References


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Fig. 4: C-V curves of a MOS capacitor of an YDH layer 7.7 nm thick measured at frequencies between 10 and 100 kHz. The inset shows a J-E curve of the same sample (filled circles) and of a monoclinic HfO$_2$ layer of similar thickness (open squares).

states induced by the large lattice mismatch between YDH and GaAs. The complex bonding of mixed oxide may also attribute to the shift.

The electrical leakage versus biasing field (J-E curve) of the same sample is shown by the filled circles in Fig. 4 inset. The leakage current density measured at gate bias voltage of 1 V is $6 \times 10^{-5}$ A/cm$^2$, about two orders of magnitude lower than the value of an epitaxial monoclinic HfO$_2$ layer with similar thickness (open squares). The attainment of cubic on cubic epitaxy via modest doping Y$_2$O$_3$ has reduced the number of azimuthal domains in YDH, thus lowering the electrical leakage current by about two orders of magnitude.

In conclusion we have demonstrated the attainment of the high temperature high dielectric constant phase of HfO$_2$ as stabilized through Y doping and thin film epitaxy on GaAs. Accompanying the structural transformation from HfO$_2$ monoclinic phase to YDH cubic phase, a significant increase of dielectric constant $\kappa$ from $\sim$17 to as high as 32 is obtained. In addition the reduction of the number of azimuthal domains in cubic YDH has notably improved the electrical leakage. The fact that the YDH films are grown in single crystalline offers an important advantage of maintaining low leakage during high temperature anneals for dopant activation compared to the amorphous counterparts.

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