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Monocliniclike local atomic structure in amorphous ZrO₂ thin film

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The local atomic structure and electronic structure of amorphous ZrO_2 (a- ZrO_2) thin film were examined using the Zr *K*- and O *K*-edge x-ray absorption spectroscopy and x-ray photoelectron spectroscopy. It was found that a monoclinic local structure is stabilized in several nanometers-thick a- ZrO_2 films due to the structural disorder. The distinct local structure in a- ZrO_2 from the ordinary tetragonal ZrO_2 (t- ZrO_2) films results in different electronic structure with a decrease in the band gap by 0.5 eV. The reduced band gap and dielectric constant of a- ZrO_2 suggest inferior gate leakage current performances compared to the t- ZrO_2 films. © 2010 American Institute of Physics. [doi:10.1063/1.3497077]

A high dielectric constant (k) is essential for gate oxides in metal-oxide-semiconductor field effect transistors because it prevents the current leakage through the gate oxide. Following the intensive research to find oxides with higher kand reasonably large band gaps, the Hf-based oxide system is currently being used as the gate dielectric in several high performance logic chips.¹ Recently, Zr-based oxides are also drawing an increasing amount of attention because they are expected to exhibit similar electrical performances with a more superior interface, which may lead to an improvement in interface related reliability properties compared to the Hfbased oxides.^{2–4} Thus it is undoubtedly important to study their electronic structure theoretically and experimentally.

The bulk hafnia (HfO₂) and zirconia (ZrO₂) are remarkably alike in terms of electrochemical properties. They have a monoclinic crystal structure $(m; P2_1/c)$ at room temperature with almost identical lattice constants.^{5,6} The similarity originates from the identical valences (+4) and orbital configurations (d^0) , along with the similar ionic radii (within difference of only 0.02 Å) of the Hf and Zr ions.⁷ When in nanoscale structures such as ultrathin films (which are only several nanometers thick) or nanoparticles, however, their preferred crystal structures are different from each other; the HfO₂ nanostructure still prefers the monoclinic structure while the ZrO₂ nanostructure favors a tetragonal structure $(t; P4_2/nmc)$ (Ref. 8) even at room temperature.⁹ The stabilization mechanism of the tetragonal structure has been exploited extensively but is still rather controversial; perhaps, it could be summarized as a combination of the effects of surface and stress.^{9,10}

It has been reported the k value in Zr-based oxides is mainly determined from the local atomic structure, although the charge transfer between the adjacent clusters or structural units also have a minor influence.^{11,12} The k value of t-ZrO₂ is about two times larger ($k \sim 40$) than that of m-ZrO₂ ($k \sim 20$) due to the difference in local structure.¹³ Therefore, it is much encouraged to use tetragonal ZrO₂ for Zr-based oxide gate dielectrics to obtain a higher k. Also an amorphous gate oxide is frequently desired due to its homogeneous and isotropic electrical properties. In a HfO₂ thin film, the dielectric properties are rarely influenced by amorphization because the monoclinic local structure is preserved even in the amorphous phase, which is why the *k* of amorphous HfO₂ (*a*-HfO₂) is roughly similar to that of monoclinic HfO₂ (*m*-HfO₂).¹⁴ However, this experimental study shows that in amorphous ZrO₂ (*a*-ZrO₂) thin films, a monoclinic local structure is re-stabilized due to the structural disorder, so the *k* of the *a*-ZrO₂ film would become similar to that of *m*-ZrO₂.¹⁴ This suggests that *a*-ZrO₂ may have inferior dielectric performance compared to crystalline *t*-ZrO₂ in next-generation high-*k* dielectric applications.

ZrO₂ films were prepared on a Si wafer by plasma enhanced atomic layer deposition (PEALD) using $Zr[N(C_2H_5)(CH_3)]_4$ as the Zr-precursor and plasmaactivated O₂ as the oxygen source at a wafer temperature of 280 °C. The film thickness was controlled by tuning the number of the PEALD cycles and was confirmed by ellipsometry. The 40 and 80-Å-thick as-grown films were amorphous, which was confirmed by the absence of Bragg peaks in grazing angle x-ray diffraction (GAXRD). Postdepositionannealing (PDA) was also performed at 950 °C in a N₂ ambiance to make the films crystalline. The GAXRD confirmed that the PDA films crystallized with a tetragonal symmetry ($P4_2$ /nmc). The local structures were examined by Zr K-edge x-ray absorption spectroscopy (XAS) and the x-ray absorption near-edge structure (XANES) was analyzed. The electronic structure and chemistry were examined by O K-edge XAS and x-ray photoelectron spectroscopy (XPS). The Zr K- and O K-edge XAS were performed at the 3C1 and 2A beamlines in the Pohang Light Source (PLS), respectively. The XPS was performed using a monochromatic Al $K\alpha$ source, after cleaning the film surfaces with a moderate Ar-ion sputtering (acceleration voltage <0.5 keV).

Figure 1 shows the Zr *K*-edge XANES of the (a) PDA and (b) as-deposited ZrO_2 films.¹⁵ The overall XANES features are almost thickness independent; the results of the 80-Å-thick PDA and as-deposited films are quite similar to those of the 40-Å-thick PDA and as-deposited films, respectively.

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FIG. 1. Zr K-edge XANES of the (a) PDA and (b) as-deposited ZrO_2 films. The simulation results based on tetragonal and monoclinic local structures were appended in [(a) and (b)], respectively. The spectrum of a polycrystal-line ZrO_2 powder was also attached.

However, the features of the PDA films are quite different from those of the as-deposited films, as highlighted by the arrows in Fig. 1. This indicates the PDA process rather than the film thickness is responsible for the spectral evolution. In order to interpret the features in detail, the theoretical spectra obtained by FEFF8¹⁶ and appended.¹⁵ Here, the full multiple scatterings within a radius of 6 Å around the photon absorber were considered. The simulations were performed based on the representative tetragonal and monoclinic local structures.^{17–19} The simulated spectra of t-ZrO₂ and m-ZrO₂ well reproduce all the features in the experimental spectra of the PDA and as-deposited films, respectively, indicating that the PDA films have a tetragonal local structure while the as-deposited films have a monoclinic local structure. Therefore, the discrepancy in the experimental spectra in Figs. 1(a) and 1(b), denoted by arrows, can be regarded as the signatures of tetragonal co-ordinations.

The intensities of the oscillatory features in the spectrum of the 40 Å-PDA film appears to be slightly reduced compared to those of the 80 Å-PDA film due to the reduced crystallinity in the thinner film. This is because the reduced crystallinity would enhance the structural disorder, which attenuates the fine structure oscillation. The extinction of the features in the spectra of the as-deposited films [Fig. 1(b)], however, cannot be attributed to the influence of the structural disorder, since the main peak near $h\nu \sim 18.01$ keV survived. For clarity, the spectrum of a polycrystalline ZrO₂ powder (*m*; P2₁/c), which had distinct Bragg peaks in the XRD (not shown here), was appended in the figure. The coincidence of the XANES features clearly shows the asdeposited films have monoclinic local structure.

In a bulk form, zirconia prefers to have an *m* structure than a *t* structure because the bulk free energy of the *m* phase is lower than that of the *t* (or cubic) phase.¹⁰ However, in a nanostructural form, the surface free energy becomes comparable to the bulk free energy. Since the surface free energy of the *t* phase is much lower than that of the *m* phase, the total free energy of the *t* phase could be lower than that of the *m* phase at the nano-scale.¹⁰ This can be formulated as follows:



FIG. 2. (Color online) O *K*-edge XAS spectra of 80 Å-thick ZrO_2 and HfO_2 films. *t*-ZrO₂ (*m*-HfO₂), tetragonal (monoclinic) PDA films; *a*-Zr(Hf)O₂, as-deposited amorphous film.

$$\Delta F_{\text{bulk}} = F_{\text{bulk}}(t) - F_{\text{bulk}}(m) > 0,$$

$$\Delta F_{\text{surf}} = F_{\text{surf}}(t) - F_{\text{surf}}(m) < 0,$$

$$\Delta F_{\text{tot}} = F_{\text{tot}}(t) - F_{\text{tot}}(m) < 0,$$
(1)

where F's are the free energies for the total, bulk, and surface terms, and t and m in the parentheses indicate the tetragonal and monoclinic *local* structures, respectively.

However, it is shown in Fig. 1 that the monoclinic local structure is stabilized in the amorphous zirconia films, even though the as-deposited films are identical in geometric terms with the tetragonal PDA films. The structural disorder in the *a*-ZrO₂ possibly enables this type of stabilization by lowering the $F_{bulk}(m)$ due to the additionally increased bulk entropy $(S_{bulk};F_{bulk}=E_{bulk}-TS_{bulk})$. This would allow the $F_{tot}(m)^*$ in the *a*-ZrO₂, which is quite different from the $F_{tot}(m)$ in a hypothetical *m*-ZrO₂, to become lower than $F_{tot}(t)$. The existence of a monoclinic local structure in the *a*-ZrO₂ thin films can be understood using this rationale.

The different local structures between the amorphous and crystalline ZrO₂ films result in distinct electronic structures. Figure 2 shows the unoccupied electronic structures of the 80-Å-thick films probed by O K-edge XAS. From now on, t-ZrO₂ (a-ZrO₂) refers to the 80-Å-thick PDA (asdeposited) film. The spectra of 80-Å-thick crystalline m- and a-HfO₂ films, which were prepared through a similar procedure to this experiment except for the precursor, are appended for comparison.¹⁵ The overall features in the spectra of a-ZrO₂ and a-HfO₂ are broadened out from their respective crystalline phases due to the structural disorder. Interestingly, the line shapes of the a-ZrO₂ and a-HfO₂ films are very similar to each other except for an energy shift due to the band gap difference.²⁰ This suggests a similarity in the local structure, since the OK-edge XAS probes the local density of states of the O 2p wave function that hybridizes with the neighboring Zr or Hf d/sp bands, where the hybridization symmetry is determined by the local structures. It is well known a-HfO₂ thin films have a monoclinic local structure,²¹ so the results above reconfirm the monoclinic local structure of a-ZrO₂.

Generally, the dielectric property is determined from the local structure and the electronic structure. The dielectric response of media, ε or $k = \varepsilon/\varepsilon_0$, can be decomposed into two This article $E_{tot,\overline{c}}$, F_{bulk} , $E_{surf-licated in the article. Reuse of AIP content is subjectors; an optical term and a vibronic term.^{22,23}$



FIG. 3. (Color online) (a) Zr 3*d* and (b) O 1*s* XPS spectra of the 80 Å *a*and *t*-ZrO₂ films, indicating identical chemistry.

is related to the optical electronic transition which is determined by the electronic structure, and the latter concerns the phononic vibrations which are sensitive to the local structure. Thus, the monoclinic local structure of *a*-ZrO₂ suggests that the *k* should be similar to monoclinic ZrO₂, $k \sim 20$, not t-ZrO₂, $k \sim 40$.¹⁴

Now, the influence that local structural change during amorphization has on the chemistry and valence bands/ conduction bands (VBs/CBs) of the films are described. Figure 3 shows the (a) Zr 3d and (b) O 1s core level XPS spectra of the *t*-ZrO₂ and *a*-ZrO₂ films.¹⁵ Negligible differences between the spectra of the two films were found at both core levels. The same binding energy (BE) and intensity of the main peaks at both core levels suggest an identical chemistry of the Zr^{4+} and O^{2-} ions in the *t*-ZrO₂ and *a*-ZrO₂ films. The additional tiny features in the t-ZrO₂ at BE ~ 181 eV in Fig. 3(a) and at BE ~ 532 eV in Fig. 3(b), might reflect the Zr-silicide formation at the interface and the remaining adsorbed molecules at the surface, respectively. The identical O²⁻ chemistry allows a direct comparison of energies in the O K-edge XAS spectra without any uncertainty on the core hole effect in the O 1s-2p photoabsorption process. In Fig. 4, the CBs near the band gaps of the two films were redrawn from Fig. 2, being shifted by a same amount of energy to reproduce the band gap of t-ZrO₂ to the well known value of $\sim 5.2 \text{ eV.}^{24}$ The XPS VB spectra are also appended.¹⁵ The edge energies were determined by ex-



FIG. 4. (Color online) VB structures measured by XPS and CB structures measured by O *K*-edge XAS of the 80 Å *a*- and *t*-ZrO₂ films. The band edge energies were determined by extrapolating the steepest slopes (arrows).

trapolating the steepest slopes in the features near the band gap. The VB edge energies almost coincided with each other with a BE of ~3.2 eV while the CB edge energy of a-ZrO₂ (E-E_F~+1.5 eV) differs from that of t-ZrO₂ (E-E_F~+2.0 eV) by approximately -0.5 eV. The reduced band gap and lower CB edge will deteriorate the performance of the high-*k* gate oxide by facilitating leakage current.

In conclusion, it was confirmed that a-ZrO₂ thin films have a monoclinic local structure, so it was expected to have a *k* value lower than that of crystalline *t*-ZrO₂. The CB edge energy of *a*-ZrO₂ was lower than that of *t*-ZrO₂ by ~0.5 eV. Due to these reasons, the dielectric performance of the *a*-ZrO₂ dielectrics would be less desirable compared to *t*-ZrO₂ films although more uniform characteristics are expected from the *a*-ZrO₂ dielectrics.

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