

## Structural, electronic, and dielectric properties of ultrathin zirconia films on silicon

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As high-permittivity dielectrics approach use in metal-oxide-semiconductor field-effect transistor production, an atomic level understanding of their dielectric properties and the capacitance of structures made from them is being rigorously pursued. We and others have shown that crystal structure of  $ZrO_2$  films have considerable effects on permittivity as well as band gap. The as-deposited films reported here appear amorphous below a critical thickness ( $\sim 5.4$  nm) and transform to a predominantly tetragonal phase upon annealing. At much higher thickness the stable monoclinic phase will be favored. These phase changes may have a significant effect on channel mobility. © 2005 American Institute of Physics. [DOI: 10.1063/1.1864235]

As the effective gate oxide thickness scales towards 1 nm, the use of  $SiO_xN_y$  dielectric layers become less viable due to high tunneling currents.<sup>1,2</sup> One solution being extensively explored is to increase capacitance by replacing  $SiO_2$ -based dielectrics with higher permittivity ones such as  $HfO_2$  and  $ZrO_2$ .<sup>2</sup> The dielectric constant values in the literature vary from 16 to 45<sup>3-7</sup> for  $HfO_2$  and 18 to 35<sup>8-10</sup> for  $ZrO_2$ . Similarly, the reported band gap values for these materials are in the range of 5.1 to 6.0 eV, with  $ZrO_2$  reported to have a smaller band gap.<sup>4,8,11,12</sup>

A variety of factors, such as degree of crystallinity, roughness, chemical homogeneity, and stoichiometry, can effect the dielectric properties and leakage currents across the dielectric layers.<sup>2</sup> There have been many reports on the electrical properties of zirconia films, but detailed reports on microstructural characterization along with electrical characteristics are scarce.<sup>13</sup>

The known crystal phases of  $ZrO_2$  are monoclinic, orthorhombic, cubic, and tetragonal (the latter three phases are metastable under ordinary temperatures and pressures). Film thickness, stress, grain size, and impurities may lead to changes in the relative of these phases. It is therefore quite reasonable to expect different electronic and dielectric responses for ultrathin films of different thicknesses, some of which may be in metastable states. In addition, films prepared by different methods (chemical vapor deposition, atomic layer deposition, or physical vapor deposition) can result in quite different physical and electronic properties.

Zhao and Vanderbilt performed first-principles density functional theory calculations on all crystal phases of  $HfO_2$

and  $ZrO_2$ , where it was shown that the dielectric response and band gap of the material are strongly phase dependent.<sup>14,15</sup> In this contribution, we experimentally explore the issue of crystal structure in ultrathin films of  $ZrO_2$  and the effect of structure on dielectric properties.

A series of thicknesses (in the range of 36 to 99 Å) of  $ZrO_2$  films were deposited on silicon substrates (on either a chemical oxide or an oxynitride layer) at 300 °C by atomic layer deposition using  $ZrCl_4$  and  $H_2O$  as precursors. Some of the samples were annealed in various ambient and temperature regimes including a 500 °C oxidation, a 400 °C forming gas anneal, 600 and 800 °C rapid thermal anneals (RTA/ $N_2$ ), and an 800 °C vacuum anneal ( $10^{-9}$  Torr).

The x-ray absorption spectroscopy (XAS) measurements were performed at Brookhaven (NSLS) in the total electron yield mode.<sup>16</sup>

Wide-angle x-ray scattering was performed to obtain x-ray diffraction (XRD) patterns of several  $ZrO_2$  thin-film samples using an area detector and a rotating anode x-ray generator equipped with a graphite monochromator (Cu  $K_\alpha$ ;  $\lambda = 1.5418$  Å).

Vacuum ultraviolet spectroscopic ellipsometry (VUV-SE) measurements were performed on a commercial instrument from 1.5 to 8.5 eV in steps of 0.02 eV. A four-phase model consisting of silicon substrate,  $SiO_2$  interfacial oxide,  $ZrO_2$  film, and air ambient was employed to extract the real and imaginary part of dielectric functions ( $\epsilon = \epsilon_1 + i\epsilon_2$ ) of the  $ZrO_2$  films, where the interfacial oxide thicknesses are extracted by high-resolution transmission electron microscopy.

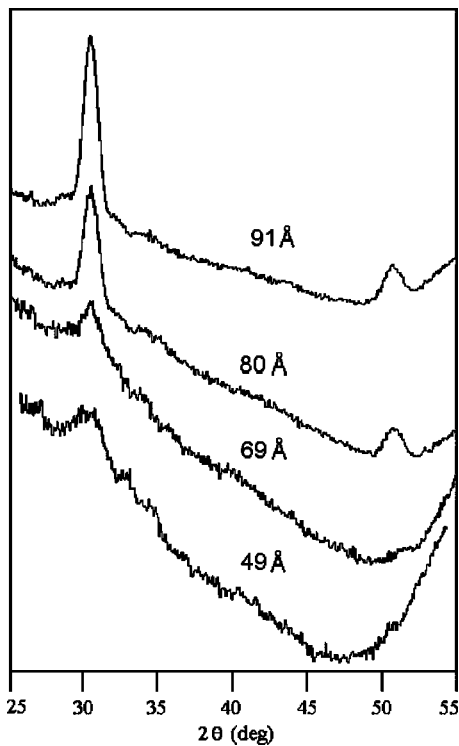


FIG. 1. XRD spectra of  $\text{ZrO}_2$  films of optical thickness 49, 69, 80, and 91 Å.

The thicknesses reported here are the  $\text{ZrO}_2$  optical film thicknesses.

Figure 1 presents selected XRD spectra for a series of as-deposited  $\text{ZrO}_2$  films. For the samples with optical thicknesses greater than  $\approx 49$  Å, only the tetragonal phase can be positively identified. Based upon the decreasing relative intensity and increasing relative peak width of the  $\langle 101 \rangle$  reflection ( $2\theta = 30.3^\circ$  for the tetragonal phase), the degree of crystallinity decreases with decreasing film thickness. The 49 Å as-deposited film is found to be predominantly amorphous. The measurements on thinner samples did not yield useful information because of insufficient scattering.

The XAS near-edge structure of the  $L_2$  and  $L_3$  edges of Zr compounds are dominated by transitions into unoccupied final Zr  $4d$  states (Fig. 2). Although both the  $L_2$  and  $L_3$  edges probe the  $4d$  density of states, we discuss the  $L_2$  edge here because it involves only  $4d_{3/2}$  final states and is less sensitive to multiplet effects.<sup>17</sup> The lower energy (less intense) and higher energy (more intense) peak features in the cubic  $\text{ZrO}_2$  spectrum at the bottom of Fig. 2 are due to  $e_g$  and  $t_{2g}$  final states, respectively. The additional splitting of the lower symmetry monoclinic phase is reflected by the additional Zr  $L_2$  edge spectral features (at around  $\approx 2311.8$  eV). In particular, the sharpening and narrowing of the splitting between the two peak features on going from the cubic to tetragonal phase (see the spectral overlay in Fig. 2 at the bottom) is supported by our band structure calculations and by the O  $K$ -edge electron energy loss spectroscopy measurements on these phases where a  $\approx 0.2$  eV narrowing is observed going from the cubic to the tetragonal phase.<sup>18,19</sup> A point to emphasize here is that the peak splittings and relative intensity in the Zr  $L_2$ -edge measurements provide a convenient tool to identify the structural changes in these  $\text{ZrO}_2$  films.

The XAS  $L_2$ -edge spectra of a thin, as-deposited  $\text{ZrO}_2$  film of 44 Å optical thickness are also given in Fig. 2. It is

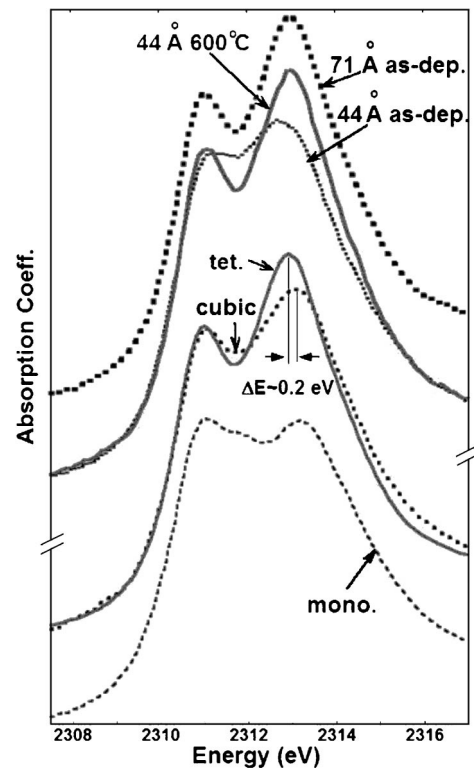


FIG. 2. Zr  $L_2$ -edge XAS spectra of bulk monoclinic and yttrium stabilized cubic phases of zirconia, a representative film spectrum of tetragonal  $\text{ZrO}_2$  (confirmed by XRD), and representative spectra of amorphous  $\text{ZrO}_2$  films before and after annealing. The distinct spectral changes associated with the tetragonal phase, induced by annealing (44 Å RTA 600 °C spectrum) or increased film thickness (71 Å as-deposited) should be noted.

not consistent with that of any pure single phase (i.e., tetragonal, cubic, or monoclinic). The XRD measurements indicate that thin as-deposited samples are predominantly amorphous. The spectrum obtained for as-deposited thicker films (e.g., the 71 Å film in Fig. 2) is consistent with that of the tetragonal phase, indicating that, as the films get thicker, the tetragonal structure becomes favored over an amorphous one.

Anneals were performed in various ambient and temperature regimes. An amorphous-to-tetragonal phase transformation was observed for the thinner films as a result of all annealing treatments tested, as represented by the 44-Å-thick annealed (600 °C RTA) sample, as shown in Fig. 2.

Figure 3 presents the real ( $\epsilon_1$ ) and imaginary ( $\epsilon_2$ ) part of dielectric functions of these films. Two important trends observed in the dielectric functions are the dependence on thickness and thermal annealing. As the thickness of as-deposited films increased above a transitional value, somewhere between 54 and 64 Å, the optical band gap determined by Tauc plots (not shown) increased from 5.1 to 5.5 eV and remained at 5.5 eV for thicker films. In addition, the dielectric function exhibits new interband transitions ( $\approx 6.0$ , 7.3, and 8.5 eV), and the overall magnitude increases with thickness. The band gap of the thin samples increase from 5.1 to 5.5 eV after being annealed at 600 °C and also display new interband transitions similar to those observed for thicker films (lower panel in Fig. 3).

A main finding is that there is a transition from an amorphous to a tetragonal phase in the thickness regime explored here. This phase change should increase the dielectric constant of the  $\text{ZrO}_2$  film to a large value, as predicted by Vanderbilt and Zhao.<sup>15,19</sup> XRD studies of an equivalently

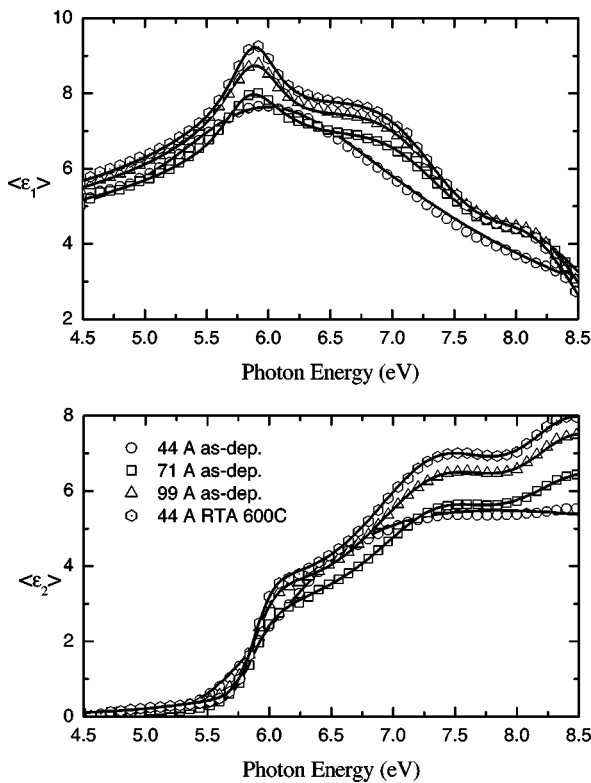


FIG. 3. Dielectric functions of  $\text{ZrO}_2$  films resulting from VUV spectroscopic ellipsometry for as-deposited films of 44, 71, and 99 Å and for a 53 Å film after RTA at 600 °C. Real (top) and imaginary (bottom) parts of dielectric functions.

produced 800 Å film that show the coexistence of similar amounts of tetragonal and monoclinic (the stable phase) components. Recent work by Navrotsky *et al.*<sup>20,21</sup> on bulk zirconia films of varying particle size has demonstrated that the total energy of the system is minimized by moving from amorphous to tetragonal to monoclinic with increasing particle size. We observe the same trends with thickness. In the thickness regime below some transitional value (of order 54 to 64 Å), the optical band gap of the as-deposited  $\text{ZrO}_2$  films (amorphous) is 5.1 eV, while above this regime it increases to 5.5 eV (in the predominantly tetragonal phase). Annealing of the amorphous films results in a transformation to the tetragonal phase, and the band gap increases to 5.5 eV. TEM results on similar films show the existence of tetragonal crystallites at a slightly lower nominal thickness.

These findings lead one to consider several issues when thinking of dielectric design and metrology. On one hand, one wants a high capacitance dielectric structure, while on the other, the film should result in a laterally smooth and homogeneous potential in the channel. (i) Since the tetragonal phase has the larger dielectric constant, it should be preferred if it can be made uniform. This can be achieved by tailoring film thickness or annealing the gate stack, both of which can lead to formation of the tetragonal phase. Another route is to stabilize by impurity incorporation, as is done for the cubic phase.<sup>22</sup> By growing under conditions that prefer (or stabilize) the tetragonal phase, one can take advantage of higher dielectric constant (lower equivalent oxide thickness), larger band gap, and lower leakage. Our results imply that if

the film is too thin, then it may exhibit a predominantly amorphous phase, whereas for intermediate thickness films (>5 nm), the more stable tetragonal phase is able to form. (ii) The change of crystal structure will also have important consequences from a band alignment point of view. As shown in Fig. 3, the tetragonal phase has a larger band gap than the amorphous phase by about  $\approx 0.4$  eV. This will lead to different band offsets and thereby affect charge transport and leakage. (iii) From a metrology point of view, effects of phase on the dielectric properties should be fully understood for any given system.

We have shown that both amorphous and tetragonal phases of  $\text{ZrO}_2$  can be observed in thin films. Film thickness is a key factor regulating which phase is observed under any set of specific conditions. Processing history (especially the maximum temperature a film experiences) also affects phase. In microelectronic applications, we suggest that the crystal structure of thin high- $\kappa$  films should be both determined and stated in comparative experimental studies of dielectric and electrical properties. Film stress, thickness, grain-size, and impurities may lead to stabilization or predominance of one or more phases, which in turn result in variations in dielectric and electronic response.

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