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Spectroscopic ellipsometry characterization of the optical properties and thermal stability of ZrO₂ films made by ion-beam assisted deposition

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The optical properties, interface structure, and thermal stability of the ZrO_2 films grown on Si(100) were investigated in detail. A 2 nm thick interfacial layer (IL) is formed at the ZrO_2 –Si interface for the as-grown ZrO_2 . The optical constants of ZrO_2 films and IL correspond to amorphous- ZrO_2 and amorphous-SiO₂, respectively. The oxidation and IL growth at 900 °C, as a function of annealing time, exhibit a two-step behavior with a slow and a fast growth-rate zones. The transition from a zone of slow to fast rate is attributed to structurally modified ZrO_2 facilitating the faster oxygen transport to the ZrO_2/Si interface. © 2008 American Institute of Physics. [DOI: 10.1063/1.2811955]

Zirconia (ZrO_2) is an important material with a potential for a wide range of technological applications.¹⁻¹² The outstanding chemical stability, electrical and mechanical properties, high dielectric constant, and wide band gap of ZrO₂ make it suitable for several industrial applications in the field of electronics, magnetoelectronics, and optoelectronics.^{1-4,6-12} ZrO₂ is employed in superplastic structural ceramics that demonstrate excellent strength and fracture toughness.⁵ Zirconia is also considered to be an excellent nuclear waste form for the direct geological disposal. Most importantly, ZrO₂ is considered as a promising dielectric to replace SiO₂ in advanced metal oxide semiconductor devices in gate stack.^{7–11} However, it is well known that the electrical and optical properties of ZrO₂ thin films are highly dependent on the film-substrate interface structure, morphology, and chemistry, which are in turn controlled by the filmfabrication technique, growth conditions, and postdeposition processes.^{1-4,6-15}

The chemical reaction between ZrO_2 and Si substrate during fabrication or postdeposition annealing process resulting in the formation of interfacial layer (IL), with silicon oxide (SiO₂), or metallic Zr clusters, or Zr-silicate (ZrSi_xO_y), or a combination of these, has been found in most of the earlier investigations, although the proposed mechanism varies greatly.^{6–11,13–15} Interfacial chemical compounds from the interfacial reaction suppress the effective dielectric constant and degrade the device performances. As such, elucidation of the ultramicrostructure, and electronic properties of ZrO₂ films has recently been the subject of numerous investigations. However, the existing data and reports on the optical properties of ZrO₂ films are meager. In this context, the present investigation has been performed to understand the optical properties of ZrO₂ films grown on *n*-type Si(100) substrates using ion-beam assisted sputter deposition. Spectroscopic ellipsometry (SE), which is known to be a sensitive and nondestructive method for the structure and optical characterization of thin-films,^{16,17} has been employed in combination with the reflection high energy electron diffraction (RHEED) and high-resolution transmission electron microscopy (HRTEM) to study the optical properties and thermal stability of the ZrO_2/Si system. The qualitative and quantitative information, based on the SE and HRTEM results, on the thermal stability, interfacial oxide layers, and optical properties of ZrO_2 films grown on Si is reported in this letter.

The ZrO_2 films were deposited on *n*-type singlecrystalline Si(100) substrates using an ARC-12M sputtering device using Zr metal as a target. The Si substrate was subjected to chemical cleaning procedure and treatment in diluted HF to remove the native oxide layer on the surface. An argon $(Ar)/oxygen (O_2)$ mixture was introduced into the vacuum chamber, which was initially pumped down to a pressure of 10⁻⁶ Torr, during film deposition. The pressure in the chamber was kept at 10^{-3} Torr during deposition, and the films were made at a low substrate temperature (T_s) of 70 °C. TEM measurements were performed on the crosssectional ZrO₂/Si specimens using a JEOL JEM2010F at an accelerating voltage of 200 kV. RHEED measurements were performed using an EFZ4 device (Carl Zeiss) on the asgrown and finally annealed ZrO₂ samples to assess their surface structure. The technical details of HRTEM, RHEED, and cross-sectional sample preparation procedures are described elsewhere.¹⁸⁻²⁰ SE measurements were made on ZrO₂ films using a Spectroscan ellipsometer in the spectral range of 250 nm $<\lambda < 900$ nm at an incidence angle of 70°. Annealing of the ZrO₂/Si samples was performed in air using a conventional furnace. Two sets of annealing experiments were performed: (a) in the temperature range of 600–900 °C at a constant annealing time of 1 h and (b)

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FIG. 1. HRTEM image of ZrO_2 films grown on Si(100) substrate. The formation of an amorphous interfacial layer is evident in the micrograph. The estimated thickness of the amorphous interface layer is about 2 nm.

high-temperature annealing at 900 $^\circ\mathrm{C}$ as a function of annealing time.

The RHEED analysis indicates the amorphous nature of as-grown ZrO_2 films. The HRTEM micrograph of the ZrO_2/Si cross-sectional structure is shown in Fig. 1. The existence of an IL between the ZrO_2 and Si is evident in the HRTEM image, which indicates that the reaction between the Si substrate and growing ZrO_2 film readily takes place even without a high- T_S . HRTEM results indicate the amorphous nature of the IL, which is about 2 nm thick (Fig. 1). The chemical analyses (not shown) indicate that the grown ZrO_2 layers are stoichiometric with all of the Zt ions in the Zr^{4+} state.^{19,20}

Optical properties and interfacial oxide growth behavior of ZrO_2/Si system have been primarily probed by SE, which measures the relative changes in the amplitude and phase of the linearly polarized monochromatic incident light upon oblique reflection from the film surface.^{16,17} The experimental parameters obtained by SE are the angles Ψ (azimuth) and Δ (phase change), which are related to the microstructure and optical properties, defined by

$$\rho = R_p / R_s = \tan \Psi \exp(i\Delta), \tag{1}$$

where R_p and R_s are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively. The spectral dependencies of Ψ and Δ can be fitted with appropriate models to extract the film thickness and the optical constants, i.e., the refractive index (*n*) and extinction coefficient (*k*), based on the best fit between the experimental and simulated spectra.¹⁷ The spectral dependencies of Ψ and Δ determined for ZrO₂ films on Si are shown in Fig. 2 as a function of time of the high-



FIG. 2. (Color online) The spectral dependences of Ψ and Δ for the asgrown and annealed ZrO₂ films. A significant shift of Ψ and Δ of the annealed ZrO₂ films when compared to that of the as-grown ZrO₂ films is evident, which indicates the modification of the ZrO₂/Si interface structure.



FIG. 3. (Color online) The spectral dependence of the optical constants, n and k, of ZrO_2 films derived from SE data. The curves shown indicate the corresponding phase as amorphous ZrO_2 . Inset shows the dispersion of refractive index obtained for the IL, which matches with that of amorphous SiO₂.

temperature annealing at 900 °C along with those for films without annealing. Two important observations derived from the spectra are (a) the evolution of the ellipsometric functions $\Psi(\lambda)$ and $\Delta(\lambda)$ is remarkably different for the asdeposited and annealed ZrO₂ films, and (b) the thermal annealing of ZrO₂ films at 900 °C results in a noticeable spectral shift of $\Psi(\lambda)$ and $\Delta(\lambda)$ with increasing time of annealing. The dispersion relations of the optical constants, i.e., *n* and *k*, of as-grown ZrO_2 films are derived using a simple model based on a double-layer system consisting of (air)/ (isotropic homogeneous layer)/(Si substrate). The standard models^{17,21} employed for amorphous dielectrics have been used for the determination of $n(\lambda)$ and $k(\lambda)$. The spectral dependences of n and k calculated for ZrO_2 films is shown in Fig. 3. The $n(\lambda)$ and $k(\lambda)$ dispersion curves are in good agreement with those reported for amorphous ZrO2.²¹ The extinction coefficient (k) being low and very close to zero indicates very small optical loss due to absorption. The dispersion relation of $n(\lambda)$ evaluated for the IL is shown as an inset in Fig. 3. The $n(\lambda)$ vs λ curve is very similar to that of amorphous SiO_2 ²² thus indirectly confirming the SiO₂-based chemical nature of the IL. SE is very sensitive to the IL formation and the simple model as described for the asgrown ZrO₂/Si structure was not suitable to fit the experimental results in the case of annealed samples. Thus, a more complicated two-layer model is adopted not only to take the growing ILs into consideration. The system consists of an array (air)/(first isotropic homogeneous layer with thickness L_1)/(second isotropic homogeneous layer with thickness L_2 /(Si substrate), whereby thicknesses L_1 and L_2 are varied during fitting. Excellent fitting of $\Psi(\lambda)$ and $\Delta(\lambda)$ is obtained for the annealed ZrO_2 films using the model adopted. The values of L_1 and L_2 are presented in Fig. 4 along with the representation of the model adopted. The data are presented as a function of the square root of the annealing time to indicate the two-step behavior of the thermal oxidation process noticed in the present work. A continuous increase in L_2 adjacent to Si substrate with annealing time is due to the oxidation of the Si substrate by oxygen diffused from air through the ZrO_2 layer. Thus, this IL, which is L_2 in SE model notations, is mostly SiO₂ in chemical composition,



FIG. 4. (Color online) The quantitative information obtained on the ZrO₂ layers and interfacial SiO₂ layer as a function of time of annealing at 900 °C. Linear fits to the data are shown with solid lines. The slow rate of the IL with almost no change in ZrO2 film thickness in zone I is attributed to the oxygen diffusion alone. The fast-rate growth rate of the IL along with a slight decrease in ZrO₂ film thickness observed in the zone II is attributed to the oxygen diffusion coupled with structural transformation of ZrO2 from amorphous to crystalline state.

but possible Zr-doping cannot be excluded. The growth rate of IL is controlled by three elemental stages, namely, adsorption of oxygen on the top surface of ZrO₂, diffusion through the ZrO_2 layer, and diffusion through the SiO₂ layer to the oxidation front at the interface SiO₂/Si.

A model can be formulated to explain the observed effects of high-temperature annealing, stability, and growing ILs of the ZrO_2/Si system. The as-deposited ZrO_2 layer is completely amorphous as confirmed by RHEED and HR-TEM observations. The IL thickness increases, with the time of annealing, which is due to the oxidation of the ZrO_2/Si interface. Oxygen needed for this process is provided by the interaction of the topmost surface layers with air at high temperature. Subsequently, the diffusion of oxygen through ZrO₂ layer causes further oxidation of the Si substrate layers into SiO_2 or a mixed composition of $ZrSi_rO_v$. The interesting point is that the IL oxide growth as a function of annealing time shows a two-step behavior (Fig. 4) with a clear distinction of two regions, which are labeled zone I and zone II. The growth rate is rather slow in zone I, where the oxygen transport is, perhaps, controlled by a slow-diffusion process through the relatively thick amorphous ZrO₂ layer at the surface. Continued annealing for more than 3 h shows a transition of the oxidation behavior into zone II, where the growth rate of the IL is fast. A slight decrease in thickness of the ZrO_2 layer is noticed corresponding to the fast-rate zone II. This observation indicates the crystallization of the amorphous ZrO₂ layer with increasing annealing time. Crystallization of amorphous ZrO2 results in a drastic shrinkage of the film volume because of intensive crystal grain formation with dense atomic packing and structural ordering. As a result, the interstitial diffusion mechanism of oxygen in ZrO₂ becomes less important and oxygen transport is mainly taken over by high-rate crystal grain boundary diffusion that facilitates the faster oxygen transportation to SiO_2/Si interface. Therefore, crystallization of ZrO₂ with formation of grain boundaries is mainly responsible for initiating zone II stage of the oxidation process. Crystallization of ZrO_2 at 700–900 °C as reported in several earlier studies^{13–15} and confirmed by the RHEED pattern in the present work provides evidence that the change in oxidation behavior is due to a transition from a disordered to ordered state. Further- Subject Phys. 85, 7646 (1999).

more, Busch et al. reported the fast interfacial oxidation at the ZrO₂/Si based on oxygen diffusion at the crystalline boundary.²³ A higher oxygen diffusivity $(10^3 - 10^4 \text{ times})$ faster) was also reported for polycrystalline ZrO₂ than that in the bulk crystal. We, therefore, conclude that thermally induced structural modification of the ZrO₂ film from amorphous to crystalline state causes the transition from slow to fast interfacial oxidation zone.²⁴

Summarizing the results, ZrO₂ films were fabricated on Si(100) substrates using ion-beam assisted deposition, and their surface/interface structure and optical properties were investigated. HRTEM analysis reveals a 2 nm thick IL with a refractive index profile similar to that of amorphous SiO₂ as determined from SE. The as-deposited ZrO₂ films exhibit profiles of optical constants corresponding to the amorphous-ZrO₂ phase. A two-step behavior is established for the hightemperature annealing of ZrO2 at 900 °C as a function of annealing time. The slow-rate growth of IL in zone I is due to oxygen transport in amorphous ZrO2. The faster-rate growth in zone II is attributed to the transition from disordered to ordered state of ZrO₂. Crystallization and grain boundary formation in ZrO₂ enhance oxygen diffusion through the layer to the Si substrate and, hence, the oxidation leading to the interfacial oxide layer at the ZrO_2/Si interface.

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