

High sensitivity attenuated total reflection Fourier transform infrared spectroscopy study of ultrathin ZrO₂ films: A study of phase change

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Attenuated total reflection Fourier transform infrared spectroscopy (FTIR ATR) was performed on ultrathin ZrO₂ films as thin as ≈ 3.0 nm deposited on silicon. An observed vibrational mode near 710 cm^{-1} undergoes a very pronounced absorption line shape change, corresponding to a structural phase change, as a function of film thickness and thermal processing. This absorption, attributed to the $E_u(\text{LO}2)$ and $A_{2u}(\text{LO})$ modes of tetragonal ZrO₂, marks the first experimental measurement and verification of vibrational modes for tetragonal ZrO₂ in this spectral range. The FTIR-ATR method shows promise as an extremely sensitive and nondestructive tool for high- κ dielectric film characterization. © 2008 American Vacuum Society. [DOI: 10.1116/1.2830642]

I. INTRODUCTION

The need for a high permittivity (high- κ) material for future nanoelectronic devices is clear.¹ HfO₂ and ZrO₂ are being considered as potential replacements for SiO₂ in future complementary metal-oxide semiconductor devices on Si as well as higher mobility substrates due to their appreciably higher dielectric constant as well as to their moderately large band gaps.² Although many reports of high- κ /silicon gate stack structures have appeared, most of which explore HfO₂ and ZrO₂ based materials including their silicate derivatives, a consensus on the best dielectric material has yet to be reached.

The electrical properties of these materials are dependent on their microstructure. A variety of factors such as the degree of crystallinity, interface roughness, chemical homogeneity, and stoichiometry can have a direct effect on the dielectric properties and leakage currents across such a dielectric layer.² It is therefore important to characterize the microstructure of these materials. There have been many reports on the electrical properties of zirconia films for application as gate dielectrics, but detailed reports on microstructural characterization along with electrical characteristics are much less common.³⁻⁵

Most high- κ metal oxides, unlike SiO₂, have a strong tendency to form a crystalline phase. In many cases, including ZrO₂, multiple phases are known to exist, each having different values for their dielectric constants. The characterization of the crystalline phase of these materials is thus quite important. The known crystal phases of ZrO₂ 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

the stabilization, or predominance, of one or more of these phases. Ultrathin films are expected to have different electronic and dielectric responses depending on thickness, preparation method: chemical vapor deposition, atomic layer deposition (ALD), or physical vapor deposition, and thermal processing history.³

Zhao and Vanderbilt performed first principles density functional theory (DFT) calculations on all crystal phases of HfO₂ and ZrO₂, where it was shown that the dielectric response and bandgap of the material are strongly phase dependent.^{6,7} For example, the permittivity of the tetragonal phase of ZrO₂ was estimated to be 38, whereas that of the monoclinic phase is estimated to be about 20.

Optical studies of zirconia (ZrO₂) include theoretical calculations of the infrared active vibrational modes that occur for various phases including the tetragonal phase.⁸ However, experimental verification of the theoretical results has been difficult because of the lack of high quality single crystals (especially for tetragonal zirconia). Previous results have been obtained from reflectance data performed mainly on pure powders consisting of small ($5\ \mu\text{m}$) particles and doped powders (e.g., yttrium doped). However, there is no consensus on the values for the vibrational modes of absorption peaks.

For the characterization of the ultrathin films studied here, a single-reflection attenuated total reflection (ATR) Ge crystal was used to obtain mid-IR absorption data. This method has the advantages of (a) having a high sensitivity to very thin dielectrics on silicon wafers, (b) not having to cleave large Si wafers, and (c) not needing to polish the wafer backside. On the other hand, the Ge crystal does limit the spectral range to wavenumbers higher than $\approx 650\text{ cm}^{-1}$.

Recently we have reported x-ray diffraction (XRD), x-ray absorption (XAS), and spectroscopic ellipsometry (SE) results on the phase of the ultrathin ZrO₂ films,³ where we

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have shown that the films are predominantly amorphous below a critical thickness (≈ 5.4 nm) and transform to the tetragonal phase upon annealing, while thicker films appear tetragonal as grown. In this contribution, we experimentally explore crystal structure determination in similar ultrathin films of ZrO₂ on silicon using attenuated total reflection Fourier transform infrared spectroscopy (FTIR-ATR); we also present complimentary results to our previously reported XAS, SE, and XRD studies.

II. EXPERIMENT

A series of thicknesses of ZrO₂ films (in the range of 3.6–9.9 nm) were deposited on silicon substrates (with either a chemical oxide or an oxynitride layer) at 300 °C by ALD using ZrCl₄ and H₂O as precursors. A four-phase model consisting of silicon substrate, SiO₂ interfacial oxide, ZrO₂ film, and air ambient was employed to extract the real and imaginary part of dielectric functions ($\epsilon = \epsilon_1 + i\epsilon_2$) in ellipsometry studies of the ZrO₂ films, where the interfacial thicknesses are extracted from high resolution transmission electron micrographs. All thicknesses reported in this manuscript are the optically determined thicknesses of the ZrO₂ film. 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 in nitrogen (RTA/N₂), and an 800 °C vacuum anneal at 1.33×10^{-7} Pa, (10^{-9} Torr).

Measurements were performed at room temperature in an evacuated Bomem DA-8 FTIR instrument with the ATR component in one of the sample chambers. A Harrick Scientific Corp. GATR (a single-reflection hemispherical Ge crystal ATR) was used because of its sensitivity to thin dielectrics on silicon and its ease of use with 200 mm silicon wafers.⁹ Repeatability of measurements is a function of the cleanliness of the ATR crystal surface, and this was monitored by using a thin (14 nm) oxide on silicon as a reference sample and observing the longitudinal optical (LO), and transverse optical (TO) modes around 1000 cm⁻¹. Scans were set to measure the spectral interval, 650–4000 cm⁻¹, with a resolution of 4 cm⁻¹.

The XAS measurements were performed at the National Synchrotron Light Source (NSLS) at Brookhaven on beamline X19A in the total electron yield mode.

III. RESULTS AND DISCUSSION

Figure 1 shows the FTIR-ATR spectra obtained from four as-deposited samples of ZrO₂ films of different thicknesses. The spectra for thinner samples (3.6 and 4.9 nm) have a different spectral shape than those for the thicker ones (6.4 and 8.0 nm). For the thicker samples, the strongest absorption peak is in the 710–720 cm⁻¹ range, while the spectra for thinner ones indicate a broad absorption peak in the range of ≈ 725 cm⁻¹, with a broad shoulder around 750 cm⁻¹. The broadness of these bands suggests a wide dispersal of vibrational states which is one of the characteristics of an amorphous network.

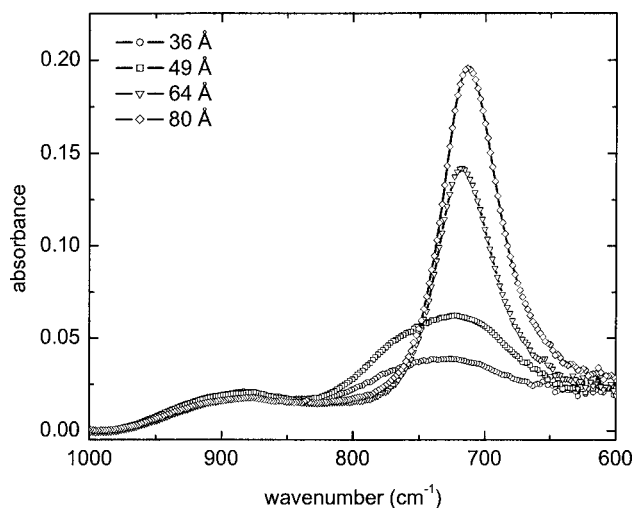


FIG. 1. Absorption spectra for as-deposited ZrO₂ films with thicknesses of 3.6, 4.9, 6.4, and 8.0 nm.

The broad band in the spectral range of 850–950 cm⁻¹ is common to all spectra and is assigned to Zr–O–Si bonds in an amorphous network as suggested by Neumayer and Cartier.¹⁰

We have recently reported on XAS and XRD studies of the same ultrathin ZrO₂ films as used here.³ In that work it was shown that the peak splittings and relative intensities apparent in the XAS Zr-L₂ edge measurements provide a convenient tool for identifying the structural changes in these ZrO₂ films. Figure 2 presents the XAS L₂-edge spectra of ZrO₂ films of thicknesses 3.6, 4.9, 6.4, and 8.0 nm. The XAS spectra of 3.6 and 4.9 nm thick films were not consistent with that of any pure single phase (i.e., tetragonal, cubic, or monoclinic). Our previous XRD measurements on samples of similar thickness indicated that these films were predominantly amorphous. The assignment of a crystalline phase to a predominantly amorphous structure for the films thinner than 4.9 nm can be justified with the following precautions: (a)

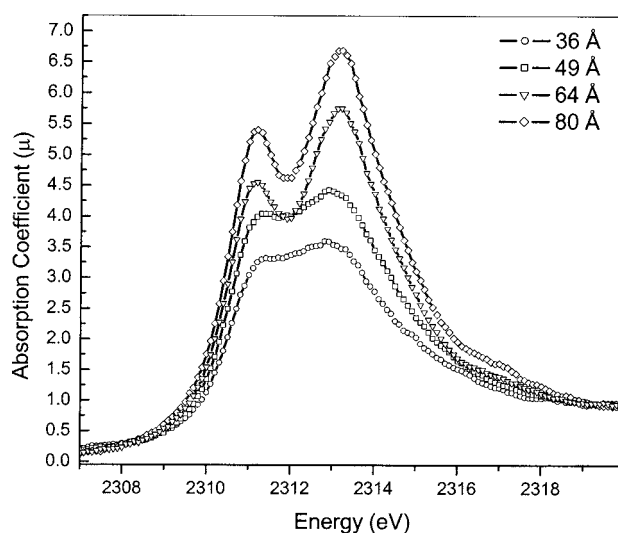


FIG. 2. Zr-L₂-edge XAS spectra of 3.6, 4.9, 6.4, and 8.0 nm ZrO₂ films.

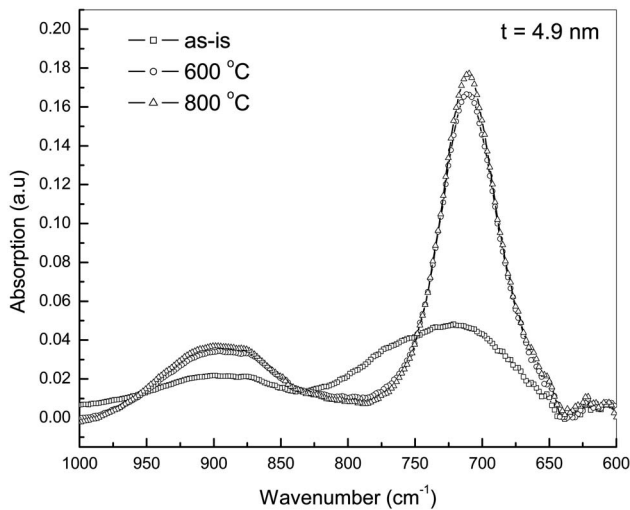


FIG. 3. Absorption spectra of 4.9 nm ZrO₂ film before and after RTA at 600 and 800 °C.

line broadening due to small (<1 nm) crystallite domain sizes, which may exist in thinner films and may not be distinguishable from amorphouslike structure; (b) the strain in the film may also lead to broad or asymmetrical diffraction bands, hence making their identification less certain; and (c) the experimental conditions provide sufficient photons and sample volumes to observe any diffraction signal.

The Zr-L₂-edge XAS spectra obtained for as-deposited thicker films (e.g., the 6.4 and 8.0 nm films in Fig. 2) are consistent with that of the tetragonal phase, indicating that, as the films get thicker, the tetragonal structure forms. This film thickness dependence of crystal structure (e.g., tetragonal phase crystal growth) is consistent with the behavior of the infrared absorption peak ≈ 710 cm⁻¹ as mentioned above.

Rignanese *et al.* studied dynamical and dielectric properties of tetragonal zirconia by using variational DFT.⁸ The infrared active fundamental frequencies of tetragonal zirconia were calculated to be 338.5 cm⁻¹ [$A_{2u}(\text{TO})$], 663.8 cm⁻¹ [$A_{2u}(\text{LO})$], 152.7 cm⁻¹ [$E_u(\text{TO1})$], 270.5 cm⁻¹ [$E_u(\text{LO1})$], 449.4 cm⁻¹ [$E_u(\text{TO2})$], and 734.1 cm⁻¹ [$E_u(\text{LO2})$]. The band we observed in the 710–720 cm⁻¹ range for thicker films possessing the tetragonal structure is consistent with the study reported by Rignanese *et al.*, and therefore can be assigned to $E_u(\text{LO2})$ modes of tetragonal zirconia. The shoulder on the lower energy side of this band (≈ 660 cm⁻¹) can be assigned to the [$A_{2u}(\text{LO})$] mode of tetragonal ZrO₂, in agreement with the theoretical results presented in Ref. 7.

Several different anneals were performed on samples in various ambient and temperature regimes as noted in the experimental section. The *ex situ* FTIR spectra of 4.4 and 6.4 nm thick ZrO₂ films as a function of rapid thermal anneals performed at 600 and 800 °C in N₂ ambient are shown in Figs. 3 and 4, respectively. An amorphous to tetragonal phase transformation was observed as a result of all annealing treatments tested. While the 4.4 nm thick film underwent a phase transition from an amorphous phase to a tetragonal

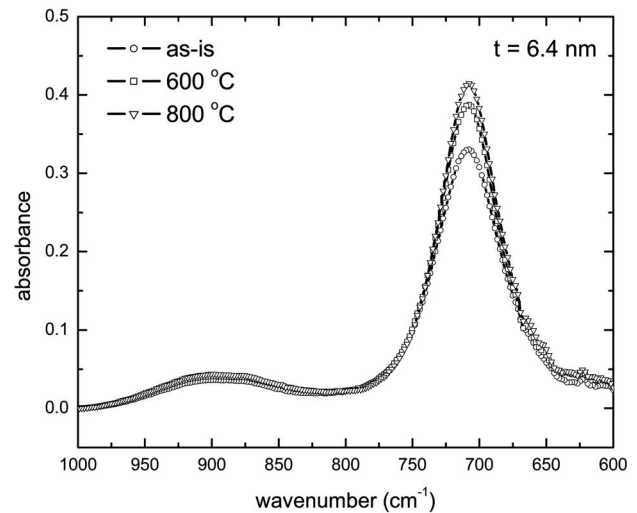


FIG. 4. Absorption spectra of 6.4 nm ZrO₂ film before and after RTA at 600 and 800 °C RTA.

one, the 6.4 nm thick film remained tetragonal as evidenced by FTIR. The same behavior is also seen in the XAS L₂-edge spectra (not shown).

The FTIR spectra for a 4.4 nm ZrO₂ film was measured before and after RTA at 600 and 800 °C (Fig. 3). As the annealing temperature is increased, the peak strength is enhanced, and the peak width is reduced possibly due to a change in absorption coefficient due to phase change and/or intensity reduction on the shoulder on the high wavenumber side.

Figure 4 shows the FTIR spectra from a 6.4 nm ZrO₂ film measured before and after anneals at 600 and 800 °C. Here the annealing temperature is seen to have a much smaller effect on the absorption intensity. The variation in intensity most likely results from sample film thickness differences due to film nonuniformity in the wafer and/or the ATR crystal contact variation from sample to sample. However, the integrated areas under the strong sharp absorption bands were found to scale with film thickness. A thicker sample of 9.9 nm was also found to show similar features except for a more intense peak (not shown).

In the frequency range of 650 to 800 cm⁻¹ there are very few modes present in the phonon density of states of the theoretical amorphous “sample” of Zhao and Vanderbilt.¹¹ These modes predominantly originate from the twofold and threefold coordinated oxygen atoms. The broad spectral features, in this frequency range, observed for the as-deposited thinner samples (3.6 and 4.9 nm) may stem from these phonon modes related to undercoordinated oxygen atoms. However, due to the low level of statistics (from the theoretical calculations in this frequency region), it is difficult to make any strong claims.

Spectroscopic ellipsometry was also performed on these materials, as reported previously. Results of modeling the experimental data showed that coincident to the phase change from amorphous to tetragonal was a bandgap change.

Here the corresponding bandgap shifted from 5.1 to 5.5 eV, another important change in an optical property of these films.³

IV. CONCLUSION

Fourier transform infrared spectroscopy (FTIR) using the attenuated total reflection (ATR) method was used to study the crystal structure of ultrathin ZrO₂ films. For films that were >5.4 nm thick, or thinner films that were annealed, a strong absorption band was observed with a peak near $\approx 710\text{ cm}^{-1}$ with a line width of about $\approx 60\text{ cm}^{-1}$. This absorption was attributed to the $E_u(\text{LO}2)$ and $A_{2u}(\text{LO})$ modes of tetragonal ZrO₂ which is consistent with previous XRD and XAS studies.³ This paper presents the first experimental measurement and verification of vibrational modes for tetragonal ZrO₂ in the spectral range of 700–800 cm^{-1} , confirming the theoretical studies of Rignanese *et al.* For thinner as-deposited, films (<5.4 nm) that were studied, the IR line shape feature was much broader, less intense, and slightly shifted to longer wavenumbers. The FTIR-ATR method resulted in the acquisition of absorption spectra with very good signal-to-noise and high sensitivity characteristics on ultra-

thin films as thin as $\approx 3.0\text{ nm}$ and offers a very sensitive and nondestructive method for high- κ dielectric film characterization.

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