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In situ low-angle x-ray scattering study of phase separation in initially mixed HfO_2 -SiO₂ thin film interfaces

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In this letter, we report on phase separation kinetics at initially mixed interfaces of HfO_2 -SiO₂ multilayers measured by low-angle x-ray scattering. Multilayers were fabricated by sputtering and ultraviolet ozone oxidation of ultrathin Hf and Si precursor films. The multilayers were subjected to isothermal anneals in the temperature range 680–762 °C during *in situ* x-ray scattering measurements. The evolution of the intensity of the multilayer x-ray satellite peaks, the Fourier components of the composition modulation, were consistent with diffusional phase separation of HfO₂ and SiO₂ during the anneals. The effective interdiffusivity \tilde{D}_L of the HfO₂-SiO₂ alloy present at the interfaces in the as-deposited multilayers was estimated from the measured intensity change of the first-order satellite reflection as a function of annealing time. The extracted activation energy for the phase separation process was 2.06±0.15 eV for the multilayer samples studied. © 2004 American Institute of Physics. [DOI: 10.1063/1.1831554]

As scaling of field-effect transistors continues to sub-0.1 μ m channel lengths, the gate capacitance density must increase to provide sufficient control of the transistor channel. Silicon dioxide (SiO₂) has conventionally been used as the dielectric, but further dimensional scaling of the dielectric thickness will lead to physical limitations such as very high gate leakage current densities resulting from direct tunneling of carriers across the gate. High permittivity (high-*k*) insulators which give higher gate capacitances with physically thicker dielectric films are needed to address these issues.¹

Hafnium (Hf) and zirconium (Zr) silicates are promising candidates for alternative gate dielectric materials because they are thermally stable with respect to solid state reaction with Si, and appear to have adequate band gaps to ensure a sufficient conduction band offset to Si.² Their relative compatibility (compared to high-*k* metal oxides) in fabrication with conventional CMOS processing also makes them attractive.³

However, it has been demonstrated that these amorphous metal silicates can decompose into silicon-oxide-rich and metal-oxide-rich regions due to the positive enthalpy of mixing of SiO₂ and metal oxides such as zirconium oxide (ZrO_2) and hafnium oxide (HfO_2).^{4,5} This degrades the film's dielectric and electrical properties. Further investigations are needed to study the thermal stability of the silicates and phase separation effects on their properties. Additionally, metal oxide insulators deposited onto ultrathin SiO₂-based interface layers are also candidate high-*k* gate dielectrics for Si transistors. Consequently, the stability of high-*k* metal oxide/SiO₂ interfaces and their tendencies for either interdiffusion or phase separation are also of great practical interest.

There have been a number of techniques used to measure interdiffusion or phase separation at film interfaces. Rutherford backscattering spectrometry, Auger electron spectroscopy, and secondary-ion-mass spectrometry are the most commonly used techniques which can give concentration profiles for chemical species across interfaces. However, the spatial resolution of the profiling technique is an important concern, as the resolution should be less than the diffusion distance \sqrt{Dt} of interest in order to produce meaningful results. In order to characterize diffusion processes with relatively short length scales, multilayer x-ray scattering is very advantageous. With this method, which probes changes in the Fourier components of the real-space composition modulation of artificially structured multilayer thin films, interdiffusivity values less than 10^{-23} m²/s can be measured.⁶

In this letter, we present results of a systematic *in situ* x-ray scattering investigation of phase separation phenomena which occur at interfaces in deposited HfO_2/SiO_2 multilayer (ML) structures. The magnitude of the interdiffusivity was estimated from the time evolution of the first-order multilayer satellite peak intensity during isothermal anneals in the x-ray diffractometer. An effective activation enthalpy for the process of diffusional phase separation at initially intermixed HfO_2/SiO_2 interfaces was extracted from observed temperature dependence of the interdiffusivity.

The HfO₂/SiO₂ multilayer sample was fabricated by alternately depositing and oxidizing sputter-deposited Hf and Si layers upon a passivated Si substrate (Fig. 1). The Si (100) substrate was first etched in 18% HF and then subjected to room temperature UV ozone exposure at 600 Torr for 60 min in the load-lock of ultra high vacuum (base pressure $<10^{-8}$ Torr) sputter deposition system. Hafnium and silicon layers were deposited by dc magnetron sputtering with the deposition rate of 0.36 Å/s for Hf and 0.095 Å/s for Si. The sputtering gas used was argon at a pressure of 20 mTorr. Nominal deposited layer thicknesses for Hf and Si were 20 and 10 Å, respectively, as measured by a quartz crystal rate monitor. Oxidation of each layer was accomplished by UV ozone exposure at 600 Torr for 60 min in the load-lock of the sputtering chamber. Samples were not exposed to air during any point in the deposition and oxidation processing. A mercury vapor lamp was used to generate UV-light with strong emission at 254 and 185 nm wavelengths in order to create atomic oxygen and ozone from the high purity oxygen (99.999%) source gas.

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FIG. 1. TEM image of as-grown UVO $(\rm HfO_2/SiO_2)_4$ multilayer structure on Si.

It should be pointed out that we have previously seen evidence for the initial mixing of 5–7 Å at metal oxide/SiO₂ interfaces prepared by the UVO method.⁷ This initial mixing may be a result of the sputter deposition process used to deposit the metal precursor layers prior to their oxidation. Energetic neutral species impacting the film during sputter deposition are likely capable of mixing metal atoms into the underlying layers. Furthermore, metals such as Hf and Zr are sufficiently reactive with oxygen to partially decompose an underlying SiO₂ layer. Therefore, there may be a chemical component to the initial intermixing at HfO₂/SiO₂ interfaces prepared by the UVO technique.

Transmission electron microscopy (Fig. 1) failed to detect evidence of crystallinity in the as-grown UVO synthesized MLs. This is consistent with previous experiments on individual UVO HfO₂ films which indicated that the asgrown films were amorphous. Therefore, the intermixed region in the vicinity of each interface in the ML can be thought of as an amorphous HfO₂–SiO₂ alloy. This amorphous alloy region should, however, experience a chemical driving force for phase separate system due to the large and positive enthalpy of mixing of HfO₂ and SiO₂ which is evident from the liquidus behavior observed in the reported binary phase diagram for this system.⁵ Diffusion-limited phase separation is expected to occur in the initially intermixed layers during postdeposition annealing.⁵

The interfacial phase separation kinetics in the HfO_2/SiO_2 MLs were examined primarily by low angle multilayer x-ray scattering. Figure 2(a) shows satellite peaks around the incident x-ray beam obtained in a symmetric scan. The small beating between the primary peaks in Fig. 2(a) is a consequence of the finite thickness of the multilayer samples.⁸ Each scan was performed for a range of diffraction angles in which one can detect out to the third-order satellite peak for this multilayer structure. After scanning the asdeposited sample, the same multilayer was heated *in situ* in the x-ray diffractometer to a temperature of interest in a nitrogen ambient. While at the annealing temperature, symmet-



FIG. 2. (a) Low angle XRD data for $(HfO_2/SiO_2)_4$ multilayer structure; (b) n=1 peak intensity of low angle XRD spectra for $(HfO_2/SiO_2)_4$ multilayer during continuous annealing.

The rate of phase separation can be estimated by observing first-order (n=1) multilayer satellite peak intensity as a function of annealing time through⁶

$$\left|\frac{d}{dt}\ln\left(\frac{I(t)}{I(0)}\right)\right| = \frac{8\pi^2}{L^2}|\tilde{D}_L|,\tag{1}$$

where *I* is the first-order peak intensity, *L* is the bilayer period of the multilayer, and \tilde{D}_L is a bilayer period dependent effective interdiffusivity of the system.^{6,9,10} This equation is derived from the linear diffusion approximation, in which the Fourier components of a composition wave are assumed to evolve via an interdiffusion process that is independent of time. Thus Eq. (1) is only an approximation for the interdiffusivity of samples such as those studied in this work, in which the amplitude of the composition modulation is relatively large and the composition changes across interfaces are sufficiently abrupt that the composition dependence of the interdiffusivity may be significant. For a phase separating system, the first-order peak intensity increases as diffusional segregation of the components takes place.

The n=1 peak intensity obtained from successive scans during the isothermal annealing of HfO₂/SiO₂ MLs are shown in Fig. 2(b). The intensity increases as annealing proceeds, as expected for phase separation at the initially intermixed as-deposited HfO₂/SiO₂ interfaces. The shift of the peak position to higher 2θ values indicates that bilayer spacing becomes smaller during the annealing procedure. This may arise from the molar volume change which occurs while the phase separation of the initially intermixed HfO₂–SiO₂ alloy layers proceeds.



FIG. 3. TEM image of UVO $(HfO_2/SiO_2)_4$ multilayer structure after annealing at 752 °C for 280 min.

A rapid and nonlinear increase of n=1 satellite intensity is evident [Fig. 4(a)] during the early stages of the anneals at each temperature. The rate of change of the scattered x-ray intensity stabilizes, producing the linear characteristic observed in Fig. 4(a) over much of the annealing time range investigated. The initial jump in n=1 satellite intensity may result in part from the densification and crystallization of the HfO₂ layers in MLs, which occurs during the anneals. Figure 3 presents the cross-section TEM image of the ML sample after an anneal at 752 °C for 280 min, which confirms crystallization as expected. Moreover, the composition dependence of \tilde{D} can give rise to nonlinear satellite intensity decay curves for multilayer samples with large-amplitude composition modulations.^{6,11–13} The satellite intensity data saturated



FIG. 4. (a) n=1 peak intensity change as a function of annealing time at various annealing temperatures. (b) Arrhenius plot of the HfO₂–SiO₂ inter-

after a certain period of time at each annealing temperature. The asymptotic value of the measured intensity obtained from fully phase-separated MLs will be determined by factors such as the interface roughness between adjacent HfO_2/SiO_2 layers. This saturation of the n=1 intensity is consistent with the completion of substantial phase separation in the initially partially intermixed HfO_2-SiO_2 multilayer.

A fit to the data in the linear regime in Fig. 4(a), can be used to estimate the interdiffusivity, \tilde{D}_L , at each annealing temperature using Eq. (1). Uncertainty in the I/I_0 data in Fig. 4(a) results from the fluctuation of the x-ray source intensity, and numerical errors resulting from background subtraction and satellite peak integration. Also, we estimate an uncertainty of about 900 s in annealing time, because of the time interval which a sample experiences while the stage is heated from room temperature to the high temperature of interest. The combination of these uncertainties results in the error bars for D_L shown in the Arrhenius plot in Fig. 4(b). The estimated interdiffusivity at T=762 °C is omitted from this figure because of the very small number of data points obtained before the multilayer satellite intensity saturated. However, one should note that D_L may be strongly dependent on the bilayer thickness as a consequence of gradient energy effects and differing molar volumes of HfO2 and SiO₂ molecular units.⁵ Therefore, the interdiffusivity values plotted in Fig. 4(b) are specific to the bilayer structure investigated in the present experiments and are subject to the important assumption that D_L is approximately independent of composition.

Approximate diffusion lengths calculated from estimated interdiffusivity and observed n=1 intensity saturation time for each sample were ~4 Å. This value is consistent with the reported interface abruptness of as-grown UVO metal oxide/SiO₂ interfaces measured by scanning transmission electron microscopy and electron energy loss spectroscopy.⁷ The activation enthalpy of the extracted HfO₂–SiO₂ interdiffusivity obtained from the slope of the Arrhenius plot in Fig. 4(b) is 2.06 ± 0.15 eV.

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