Spectroscopic characterization of high k dielectrics: Applications to interface electronic structure and stability against chemical phase separation

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Extensive spectroscopic characterization of high k materials under consideration for replacing Si oxide as the gate dielectric in Si-based microelectronic devices has been accomplished. Band offset energies of Zr silicates with respect to Si have been determined as a function of silicate alloy composition by combining near-edge x-ray absorption fine structure spectroscopy, vacuum-ultraviolet spectroscopic ellipsometry, x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, and *ab initio* calculations on cluster models. These studies provide insight that applies to both transition metal- and rare earth-based dielectrics, including binary oxides and silicate and aluminate alloys. Results have been used to estimate the electronic conduction through Hf silicate films as a function of alloy composition. Thermally induced chemical phase separation in Zr silicate films has been characterized using XPS, Fourier transform infrared spectroscopy, x-ray diffraction, high-resolution transmission electron microscopy, and extended x-ray absorption fine structure spectroscopy. Our results indicate separation into a noncrystalline, Si-rich phase and either nano- or microcrystalline ZrO_2 , depending on the original film stoichiometry. © 2004 American Vacuum Society. [DOI: 10.1116/1.1755714]

I. INTRODUCTION

The search for a material of high dielectric constant (high k) to replace nitrided silicon oxide as the gate dielectric in advanced microelectronic devices has been concentrated on Hf and Zr-based materials. The pure transition metal oxides are naturally attractive due to their high k values, but silicate alloys have shown enhanced thermal stability against crystallization. Additional issues that have been addressed regarding thin high k films on Si include: band alignment, interfacial electronic states, fixed charge, charge trapping, electron mobility at the interface with Si, and reliability with respect to dielectric breakdown. The vast knowledge base available regarding the SiO_2/Si interface has been of limited use, and new understandings need to be developed.

In this article we use spectroscopic data to address (i) the band alignment of transition metal silicates with Si and (ii) chemical phase separation during thermal annealing of Zr silicate alloys. In the first case, we build models that ultimately identify the optimal silicate alloy composition regarding suppression of direct electron tunneling. In the second, we present a wealth of experimental data that support a recent analysis of the thermodynamics of the Si–O–Zr system. Our experimental data are the result of extensive spectroscopic characterization of Hf and Zr silicate alloys using x-ray absorption spectroscopy (XAS), including extended x-ray absorption fine structure (EXAFS) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopies, vacuum-ultraviolet spectroscopic ellipsometry (VUV SE), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), Fourier transform infrared spectroscopy

(FTIR), x-ray diffraction (XRD), and high-resolution transmission electron microscopy (HRTEM).

II. EXPERIMENTAL PROCEDURES

XPS, AES, XAS, VUV SE, and HRTEM measurements were performed on Hf and Zr silicate films ranging in thickness from 20 to 50 nm on Si(100); films thicker than 150 nm were deposited: (i) on Si(100) for FTIR and XRD and (ii) on fused silica for XAS measurements. The remote plasma enhanced chemical vapor deposition (RPECVD) process used for sample preparation is described in detail elsewhere.^{1,2} In summary, radio frequency excitation (13.56 MHz, 15 W) of a He/O_2 (20:1) mixture produces a plasma. Excited species reach the sample holder in the plasma afterglow region as a result of gas flow. Si and Zr (Hf) source gases [2% SiH_4 in He and $\text{Zr(IV)} t$ -butoxide ($\text{Hf(IV)} t$ -butoxide) carried by He] are delivered directly onto the substrate by two different shower-head injectors. The substrate is kept at 300 °C, and the total pressure during deposition is 0.3 Torr.

Changing the flow rates of the transition metal and Si source gases varied the composition of the deposited films. Substrates were treated in a $\text{H}_2\text{O}/\text{HF}$ (100:1) solution prior to film deposition to remove the superficial native oxide. Also, ~ 3 nm of a - SiO_2 were deposited on the Si substrates by RPECVD before silicate deposition. This had two purposes: (i) to suppress reactions of the Zr(Hf) source gas with the Si substrate and (ii) to prevent reactions between the alloy and the Si substrate during postdeposition annealing. Thermal annealing was performed *ex situ* in an inert Ar ambient for 1 min.

The composition of silicate alloys, reported as x in $(\text{MO}_2)_x(\text{SiO}_2)_{1-x}$ ($\text{M}=\text{Zr}, \text{Hf}$), was obtained from on-line

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AES measurements using the ratio of the derivative spectrum peak-to-peak heights of $Zr_{MNN(MVV)}$ and $O_{KLL(KVV)}$ features. The Auger process was initiated by a 3 keV electron beam, which was defocused to prevent damage to the samples. These measurements were once calibrated against Rutherford backscattering spectrometry, which indicated that the alloy films are homogeneous and fully oxidized; the uncertainty in composition is $\delta x = \pm 0.03$. FTIR absorption measurements, in the mid-IR ($4000\text{--}400\text{ cm}^{-1}$) and far-IR ($700\text{--}50\text{ cm}^{-1}$), were performed in the transmission mode. XPS measurements of O $1s$, C $1s$, Zr $3d$, and Si $2p$ core levels were made using nonmonochromatized Mg $K\alpha$ radiation (1253.6 eV) and a pass energy of 20 eV. Data were corrected for charging effects using the C $1s$ peak at 284.6 eV from adventitious carbon contamination on the sample surface. EXAFS and NEXAFS measurements were made at the National Synchrotron Light Source at Brookhaven National Laboratory. Absorption spectra for the O K_1 edge NEXAFS were recorded by detecting the primary photoelectron yield, and absorption data for EXAFS and NEXAFS at the Zr K_1 edge were obtained by monitoring x-ray fluorescence. *Ab initio* calculations have been discussed in detail elsewhere.³

III. BAND ALIGNMENT WITH RESPECT TO Si

In the following we show the application of various spectroscopic techniques to the determination of band alignment at the transition metal silicate/Si interface *as a function of silicate composition*.^{2,4,5} Our results qualitatively apply to transition metal *aluminate* alloys as well. Starting from the electronic structure of ZrO_2 , we use spectroscopic data to analyze the silicate conduction and valence band edges, thus building the complete band diagram. We then consider atomic d -state energy as a scaling variable for the electronic properties of transition metal- and rare earth-based dielectrics. Finally, we develop a model to estimate electron tunneling through silicate alloys *as a function of silicate composition*.

Figure 1 is a schematic representation of the intra- and interatomic electronic transitions for ZrO_2 that are addressed in this article. The intra-atomic transitions are dipole allowed and reflect the atomic states of Zr, while the interatomic transitions terminate in mixed Zr and O states, and therefore are qualitatively different than the intra-atomic transitions. The relative ordering of the conduction band states is supported by molecular orbital calculations of small clusters incorporating group IVB Ti, Zr and Hf atoms in octahedral and tetrahedral bonding arrangements with oxygen neighbors.^{6–8} The top of the valence band is associated with nonbonding oxygen $2p\pi$ states, and the first two conduction bands are associated with transition metal d states. The energy separation between the top of the valence band in ZrO_2 and the threshold absorption to the O $2p^*$ states mixed with Zr $5s^*$ states defines an *ionic band gap* of essentially the same width as in nontransition metal insulating oxides such as MgO or Al_2O_3 , $\sim 8\text{--}9\text{ eV}$.^{7,9}

The lowest conduction band states of ZrO_2 as determined from XAS and VUV SE measurements are associated with

Fig. 1. (Color online) Schematic representation of the intra-atomic $Zr M_{2,3}$, and interatomic O K_1 and band edge transitions for ZrO_2 . The ordering of the energy states is derived from *ab initio* molecular orbital calculations on small neutral clusters.

$Zr 4d^*$ states. Figure 2(a) displays the deconvolved Zr $M_{2,3}$ NEXAFS spectrum of crystalline ZrO_2 , which displays features associated with transitions from Zr $3p_{3/2}$ states to Zr $4d^*$ (split) and Zr $5s^*$ states. The symmetry-determined splitting of the $4d^*$ states in Table I is designated as $\Delta(d^*)$, and the energy separation between the lowest $4d^*$ state, and the center of the $5s^*$ band is designated as $\Delta(d^*, s^*)$. The table includes experimental results for $ZrO_2 M_{2,3}$ and $HfO_2 N_3$ spectra. The splitting of the $5d^*$ states in the $Hf N_3$ spectrum is not spectroscopically resolved due to an increase in linewidth that scales with atomic number. Table II includes the spectroscopically determined spin-orbit splittings of Ti, Zr, and Hf $p_{1/2}$ and $p_{3/2}$ states. Figure 2(b) displays the O K_1 NEXAFS spectrum of crystalline ZrO_2 . The two bands at the low photon energy edge are associated with transitions to mixed O $2p^* - Zr 4d^*$ states. A third multi-component band has considerable O $2p^*$ character, mixed with Zr $5s^*$, and additional features at higher energies due to mixing with Zr $5p^*$ states. Table I includes the $\Delta(d^*)$ splitting, as well as the energy separation between the lower energy d^* state and the first spectral peak of the $5s^*$ band, $\Delta(d^*, s^*)$. Figure 2(c) displays the band edge optical absorption constant α of ZrO_2 obtained from analysis of VUV SE data. The lowest lying transitions in the crystalline ZrO_2 O K_1 edge and band gap transitions are associated with Zr $4d^*$ states.

The assignments in Fig. 2 are based in part on comparisons with the results of our *ab initio* calculations. The *ab initio* method used is based on a self-consistent field Hartree–Fock calculation, followed by a configuration interaction (CI) refinement utilizing the variational theorem. Proceeding in this way, the calculations include final state effects, in particular the Coulomb attractions between core and valence band holes, and the excited electrons. Table I summarizes the energy splittings, $\Delta(d^*)$ and $\Delta(d^*, s^*)$, of the band edge electronic states for ZrO_2 and HfO_2 as determined

FIG. 2. ZrO₂ spectra: (a) Zr M_3 and (b) O K_1 edges from XAS measurements, and (c) optical absorption constant from VUV SE.

TABLE I. Experimentally determined $\Delta(d^*)$ and $\Delta(d^*, s^*)$ energy splittings for ZrO₂ and HfO₂.

Spectrum	Energy (± 0.2 eV)			Energy (± 0.3 eV)	
	d_1^*	d_2^*	s^*	$\Delta(d^*)$	$\Delta(d^*, s^*)$
ZrO ₂ -Zr M_2	345.9	347.7	357.5	2.2	11.7
ZrO ₂ -Zr M_3	332.6	334.8	344.5	2.2	11.9
ZrO ₂ -O K_1	532.2	535.4	542.3	3.2	10.1
HfO ₂ -Hf N_3^a	382.7 ^a	382.7 ^a	392.7	<3.5 ^b	10 ^a
HfO ₂ -O K_1	532.5	536.8	541.5	4.3	9.0

^aDoublet is not spectroscopically resolved.

^bEstimated from linewidth.

from experiment. The agreement between calculations and experiment is in the range of ± 0.3 eV.

Figure 3(a) compares O K_1 NEXAFS data for a Zr silicate alloy ($x \sim 0.6$) after a 900 °C anneal in (i), and as deposited in (ii). The spectrum in (i) is well approximated by a linear combination of the crystalline ZrO₂ O K_1 spectrum of Fig. 2(b), and the SiO₂ O K_1 spectrum. In the noncrystalline as-deposited film (ii), the higher energy component of the Zr d^* doublet overlaps the Si $3s^*$ band and is not spectroscopically resolved. The Si $3s^*$ and Zr $5s^*$ states overlap with no resolvable features that can be assigned to either atomic state. The Zr $4d^*$ state remains the lowest-lying conduction band state, and hence defines the onset of band gap transitions as in ZrO₂. Studies of Zr silicate alloys with $0.35 < x < 0.70$ establish that the separation between the Zr $4d^*$ and Si $3s^*$ features is constant, but their relative intensities scale with alloy composition. A similar behavior occurs for Hf silicate alloys. This is shown in Fig. 3(b) for noncrystalline Hf silicate alloys, where the Hf $5d^*$ state replaces the Zr $4d^*$ state as the lowest energy transition. Our most important observation is that the conduction band edge, and therefore the conduction band offset energy with respect to Si in Zr and Hf silicate alloys is associated with the respective transition metal d^* states and does not change in energy with silicate bonding. It is effectively pinned at the transition metal oxide value. A similar conclusion applies to Zr and Hf aluminate alloys, where the decrease in the band gaps between noncrystalline Al₂O₃ and SiO₂, results in increased overlap between the Al $3s^*$ state and respective transition metal d^* states.

Having analyzed the transition metal silicate (and aluminate) conduction band edge, we now address the valence

TABLE II. Spin-orbit splittings of p -state.

Oxide	p -state spin-orbit splitting (± 0.5 eV)		
	TiO ₂ 2p	ZrO ₂ 3p	HfO ₂ 4p
XAS spectra	5.6	13.3	57.0
Data Handbook ^a	6.4	13.7	57.5

^aX-ray Data Handbook, Lawrence Berkeley National Laboratory.

FIG. 3. Comparison of XAS O K_1 edges for (a) Zr and (b) Hf silicates. (a) Compares crystalline and phase-separated Zr silicate with $x \sim 0.6$, and (b) compares Hf silicate alloys with the SiO₂ concentration increasing from ~ 0.25 to 0.75 (bottom to top).

band edge. For the AES O K_{LL} process in SiO₂ it has been demonstrated that L refers to nonbonding O $2p$ π states at the top of the valence band.¹⁰ Thus

$$E_K(O_{KLL}) = E_B(O\ 1s) - 2E_B(O\ 2p) - \Omega, \quad (1)$$

$$E_B(O\ 2p) = 1/2[E_B(O\ 1s) - E_K(O_{KLL}) - \Omega],$$

where E_K is the electron kinetic energy from AES, E_B is an electron binding energy from XPS, and Ω includes all final state and Coulomb effects. Under the hypothesis that the same applies to the high k materials under consideration, Eq. (1) can be used to estimate $E_B(O\ 2p)$ within Ω using O K_{LL} AES and O $1s$ XPS data. This sets the stage for establishing $E_B(O\ 2p)$, the valence band edge energy, as a function of high k alloy composition.

Figure 4(a) displays O K_{LL} AES and O $1s$ XPS data for Zr silicates in the whole range of possible compositions ($0 < x < 1$). XPS and UPS measurements have established that the valence band offset energies with respect to Si ΔE_V are 4.6

FIG. 4. (a) XPS O $1s$ binding energy and AES O K_{LL} kinetic energy as a function of Zr silicate alloy composition. (b) Valence band offset with respect to Si ΔE_V as given by Eq. (2).

eV for SiO₂ ($x=0$) and 3.1 eV for ZrO₂ ($x=1$).^{11,12} Starting from these values we apply a scaling with silicate composition that follows Eq. (1) to arrive at

$$\Delta E_V(x) \approx -A \cdot 1/2 \cdot [E_B(O\ 1s) - E_K(O_{KLL})] + B, \quad (2)$$

with $A=0.44$ and $B=1.2$. Figure 4(b) displays the data corresponding to Eq. (2). The nonlinear change in valence band edge with silicate composition corresponds to changes in the average O-atom bonding coordination, which increases from 2 in SiO₂ to 3 in (ZrO₂)_{0.5}(SiO₂)_{0.5}, and to 4 in ZrO₂. Figure 5 is the result of merging our findings regarding

FIG. 5. Compositional dependence of band offset energies for Zr silicate alloys with respect to Si.

FIG. 6. Scaling of band gap and conduction band offset with respect to Si with transition metal and rare earth atomic d -state energy.

high k conduction and valence band edges and alignment to Si. With x increasing from 0 (SiO_2) to 1 (ZrO_2), one observes that:

- the conduction band offset is reduced. It is the same for the silicates and ZrO_2 and does not change with silicate composition;
- the valence band offset is reduced. It is higher for the silicates as compared to ZrO_2 ;
- the band gap of the dielectric decreases. The silicates show a wider band gap than ZrO_2 due to the changing valence band edge.

We have obtained similar results for Hf silicate alloys using VUV SE, XAS, and XPS. XPS data from Hf aluminates show the same trend.¹³ Suitable weighting of our spectroscopic data reproduces the experimental¹⁴ optical band gap of Zr and Hf silicates.

Before addressing direct tunneling in silicate alloy systems, we consider transition metal and rare earth atomic d -state energy as a general scaling variable for high k band gap and conduction band offset energy. Figure 6 displays the results of an empirical model originally deduced from a combination of experiment and model predictions.⁹ The model demonstrates a monotonic correlation of (i) oxide optical band gaps and (ii) oxide conduction band offset energies with respect to Si to transition metal and rare earth atomic d -state energy in the $s^2d^{\gamma-2}$ configuration ($\gamma=3$ for Sc, Y, and La, 4 for Ti, Zr, and Hf, and 5 for V, Nb, and Ta). Based on the previously shown results and discussion, this model qualitatively applies to silicate and aluminate alloys as well. The linear behavior between Ti and Hf and the extension to small d -state energies by Y and La defines the oxides that have received the most interest as potential candidates for replacing SiO_2 and Si oxynitrides in complementary metal-oxide-semiconductor (CMOS) applications. V, Ti, Nb, Ta, and Sc-based materials have been eliminated due to low conduction band offset with respect to Si—less than ~ 1 eV, taken as a threshold for technological applications due to the

need to suppress electron tunneling. Due to the relevance of this issue we have also investigated electron tunneling through high k silicates as a function of alloy composition.

Equation (3) indicates the tunneling transmission T through a rectangular potential barrier, taken as an approximation for the case of a metal-dielectric-Si capacitor at low bias voltage

$$T \propto \exp[-2at(E_b m^*)^{0.5}], \quad (3)$$

where a is a constant, t is the barrier width (dielectric layer thickness), E_b is the barrier height (conduction band offset) and m^* is the tunneling electron mass. Taking SiO_2 as a benchmark, t can be rewritten as $t_{\text{ox}}k/k_{\text{ox}}$, where t_{ox} is the equivalent SiO_2 thickness,¹⁵ k is the dielectric constant of the high- k under consideration, and k_{ox} is the dielectric constant of SiO_2 . Based on this picture we define a tunneling figure of merit given by

$$\Phi = k(E_b m^*)^{0.5}. \quad (4)$$

Significant increases in k to values of 15–25 in transition metal and rare earth oxides are generally accompanied by decreases in E_b and m^* . Using an experimental approach,¹⁶ our group has determined the product $E_b m^*$ for HfO_2 as 0.23 ± 0.01 eV m_0 (where m_0 is the free electron mass). Based on the spectroscopic studies of Zr oxide and alloys, $E_b = 1.5$ eV has been inferred for Hf oxide and alloys. This corresponds to $m^* = 0.15 \pm 0.02 m_0$, in good agreement with other analysis of tunneling through HfO_2 films.¹⁷ This mass

FIG. 7. (a) Compositional dependence of the tunneling figure of merit Φ for different high k alloys. (b) Calculated tunneling current as a function of alloy composition (1 V bias, 1.2 nm equivalent SiO_2 thickness).

Fig. 8. XPS O $1s$ spectra for Zr silicate films of various compositions: (a) as deposited and (b) after annealing at 900 °C.

is significantly smaller than $m^* \sim 0.55 m_0$ for electrons in SiO_2 and is consistent with the Franz two band model of Ref. 18.

In order to evaluate how Φ changes with composition for high k alloys, one needs to know the dependence on composition of k , E_b , and m^* . We use averages of the values corresponding to the end-member oxides weighted by x ; m^* in the high k oxide is either estimated from the Franz two band model or experimentally determined. This procedure yields $\Phi(x)$ as displayed in Fig. 7(a). The monotonically increasing function for Y silicates predicts that tunneling with respect to SiO_2 will be reduced over the entire alloy range, while the qualitatively different behavior predicts that the tunneling reduction in Hf silicate alloys will display a minimum at an intermediary composition. A Wentzel–Kramers–Brillouin solution of the tunneling problem for 1.2 nm equivalent SiO_2 thickness and a potential drop of 1 V across the dielectric yields the results displayed in Fig. 7(b). Experimental data are scaled to an equivalent SiO_2 thickness of 1.2 nm assuming tenfold increase in tunneling current per 0.2 nm decrease in equivalent SiO_2 thickness.¹⁹ The excellent agreement between simulated and experimental data supports our models. Based on our results, $x \sim 0.6$ provides the strongest suppression of electron tunneling in Hf silicates. In terms of Si technology, this also means that such silicate—not HfO_2 —is the most scalable Hf-based replacement for SiO_2 . Although Hf oxide indeed has a higher k , that effect is mitigated by a decrease in m^* .

IV. CHEMICAL PHASE SEPARATION

We now restrict ourselves to Zr silicates and compare spectroscopic data obtained as deposited and after annealing.

Fig. 9. FTIR spectra for Zr silicate films of various compositions [(a)–(c)], as deposited and after annealing at the temperatures indicated.

We show that there is thermally induced chemical phase separation above 800 °C, and that the mode of separation depends on the metal content of the silicate.²⁰

Figure 8 displays O $1s$ XPS data. The systematic changes in line shape with alloy composition have been interpreted in terms of changes in the oxygen atom coordination,² as noted above regarding the valence band edge. The spectra in Fig. 8(a) show asymmetric line shapes, whereas those in Fig. 8(b) clearly indicate two discrete and separated spectral components. The two features in these spectra are assigned to SiO_2 - and ZrO_2 -rich phases. This experimental result supports a recent analysis of the mixing thermodynamics of the ZrO_2 – SiO_2 system in which the phase separation has been predicted as a result of spinodal decomposition.²¹

FTIR data are shown in Fig. 9. As a point of reference, the spectral range includes the Si–O–Si asymmetric stretching signal between 900 and 1300 cm^{-1} , the Si–O–Si symmetric stretching (or bending) signal at about 810 cm^{-1} , and the Si–O–Si out-of-plane rocking signal at about 450 cm^{-1} , all for noncrystalline SiO_2 .^{22,23} The spectral changes from Figs. 8(a) to 8(c) in the as-deposited sample are brought about by alloying with ZrO_2 . The shoulder at 970 cm^{-1} is not present in noncrystalline SiO_2 ; it has been assigned²⁴ to a stretching vibration of a terminal Si–O bond formed by disruption of the SiO_2 network upon formation of a pseudobinary alloy with ZrO_2 .^{25,26} The spectrum for $x = 0.50$ in Fig. 9(b) is for a

FIG. 10. XRD data for Zr silicate films of different composition [(a),(b)], as deposited and after annealing at the temperatures indicated.

chemically ordered alloy in which the SiO_2 network has been completely disrupted. It is comprised of $(\text{SiO}_4)^{4-}$ ions and Zr^{4+} ions, where the oxygen atoms have a threefold coordination.² For the samples as-deposited and annealed below 900 °C, the first broad feature centered at about 900 cm^{-1} is the signature of the $(\text{SiO}_4)^{4-}$ ion. The second broad feature, centered at approximately 410 cm^{-1} , is due to Zr–O vibrations. This assignment is supported by the IR absorption spectrum of a crystalline ZrO_2 sample (not shown). Spectra in Fig. 9 show essentially no change for annealing at up to 800 °C, consistently with no detectable OH or H_2O bands in the infrared spectrum (at high wave numbers, not shown). The changes observed after annealing at 900 °C are consistent with the chemical phase separation inferred from analysis of the O 1s XPS data. In particular, a significant decrease of the feature at 970 cm^{-1} is consistent with a restriction of terminal Si–O bonding to the boundaries of the SiO_2 - and ZrO_2 -rich phases.

XPS and FTIR results are complemented by XRD data. The broad feature shown for an as-deposited sample with $x = 0.50$ in Fig. 10(b) does not change after annealing at up to 800 °C, but data obtained after annealing at 900 °C clearly identify the tetragonal crystalline phase of ZrO_2 . In contrast, no indication of crystallinity appears in Fig. 10(a), which corresponds to a sample with $x = 0.23$. This suggests that the details of phase separation depend on the original composition of the silicate. It is interesting to note that the thermodynamically favored phase of crystalline ZrO_2 at room temperature and pressure is monoclinic. At room temperature,

FIG. 11. HRTEM images for Zr silicate samples after annealing at 900 °C: (a) $x \sim 0.25$; (b) $x \sim 0.50$.

the tetragonal phase becomes favored at high pressures, which in our sample would be a result of the surrounding SiO_2 -rich phase.

Figure 11 displays HRTEM images obtained after annealing at 900 °C. The darker regions are assigned to the ZrO_2 -rich phase. Figure 11(a) evidences ZrO_2 crystallites in a sample with $x \sim 0.25$. Based on the spacing of lattice planes in the Si substrate, the crystallite size ranges from 3 to 5 nm. As mentioned above, *these nanocrystallites were not detected by XRD*. For example, XRD can readily detect crystallites as small as 10 nm; however, as the crystallite size decreases, the width of an XRD peak increases, and it is generally difficult to detect features as small as 3–5 nm. Figure 11(b), which corresponds to a sample with $x \sim 0.50$, shows a *microcrystallite* that is about 2–3 times larger than the ones in Fig. 11(a). Thus, HRTEM identifies the original silicate composition as determining the size of the ZrO_2 crystallites resulting from phase separation.

Figure 12 displays radial distribution functions (RDFs) obtained from the analysis²⁷ of $\text{ZrM}_{2.3}$ EXAFS data. As-deposited samples with $x \sim 0.25$ and 0.55 yield essentially the same result, except for a narrowing of the Zr–O peak and reduction of a satellite feature at about 3 Å for low x . Annealing at 900 °C results in a distinguished feature slightly above 3 Å and in weaker signals below 5 and 7 Å. The peak labeled Zr–Zr corresponds to a second-nearest neighbor dis-

FIG. 12. Radial distribution functions from $Zr M_{2,3}$ EXAFS data for Zr silicates of different composition [(a),(b)], as deposited and after annealing at 900 °C.

tance, and the additional features, to more distant Zr–O and Zr–Zr coordination shells. The three signals resulting from annealing are stronger in the sample with $x \sim 0.55$. The emergence of second-nearest neighbor Zr–Zr features is clear evidence of order on a crystalline scale. The differences between the RDFs after annealing are consistent with increased crystalline order (crystallite size) in the alloy with $x \sim 0.55$ as compared to that with $x \sim 0.25$, in agreement with HRTEM data.

V. CONCLUSIONS

We have presented a comprehensive spectroscopic characterization of Zr and Hf silicate alloys. Band alignment with respect to silicon has been shown as a function of alloy composition. The atomic d -state energy of transition metal and rare earth elements has been shown to be a valuable scaling variable for the electronic properties of high k materials. Electron tunneling has been predicted as a function of high k alloy composition in remarkable agreement with experimen-

tal data, showing that $(HfO_2)_x(SiO_2)_{1-x}$ with $x \sim 0.6$ is the most scalable Hf-based high k substitute to Si oxide (oxynitrides). Chemical phase separation was observed in the Zr silicate system after annealing at 900 °C and is a point of concern regarding technological applications.

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