Nonlinear composition dependence of x-ray photoelectron spectroscopy and Auger electron spectroscopy features in plasma-deposited zirconium silicate alloy thin films

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The local bonding of Zr, Si, and O atoms in plasma-deposited, and post-deposition annealed Zr silicate pseudobinary alloys [(ZrO2)x(SiO2)1-x] was studied by x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Systematic decreases in XPS binding energies, and increases in AES kinetic energies with alloy composition x are consistent with an empirical chemical bonding model based on electronegativity equalization; however, there are significant departures from the predicted linear composition dependencies of that model. Deviations from linearity in the XPS compositional dependencies are correlated with dipolar network atom fields as determined from ab initio calculations. The nonlinearities in the x dependence of ZrMVV and OVV AES spectral features are determined primarily by oxygen–atom coordination dependent shifts in valence band offset energies. The energy spread in the compositional dependence of binding energies (~1.85 eV) for the XPS Zr 3d5/2 and Si 2p features combined with x-ray absorption spectroscopy data indicates that the conduction band offset energies between the Si substrate and Zr silicate dielectrics are alloy composition independent. Changes in O 1s XPS features in alloys with x~0.3 to 0.6 as function of annealing temperature are consistent with a previously identified chemical phase separation that occurs after 60 s anneals at 900 °C in a nonoxidizing ambient, Ar.

I. INTRODUCTION

Interest in noncrystalline dielectrics for advanced silicon microelectronic devices with increased dielectric constants (k) relative to amorphous (a-) SiO2 (k~3.9) and Si oxinitride alloys (k~5–7) has focused on transition metal (TM) oxides, and TM silicate and aluminate alloys.1 Increases in the relative dielectric constants of these high-k dielectrics compared to a-SiO2 allow use of physically thicker films to obtain the same effective capacitance and equivalent oxide thickness (EOT) as devices with physically thinner a-SiO2. This provides for the possibility for many order of magnitude reductions in direct tunneling current. However, decreases in tunneling anticipated from increases in physical thickness are in part mitigated by reductions in effective conduction band offset energies that define the tunneling barrier between the Si substrate and the high-k dielectric.2–4

The local bonding in a TM silicate alloy, where the ratios of each constituent oxide are fixed, can vary substantially depending on the deposition process and subsequent post-deposition heat treatments. This article presents the results of an XPS/AES investigation of the local bonding in pseudobinary Zr silicate alloys [(ZrO2)x(SiO2)1-x] prepared by remote plasma processing.5–7 This processing approach minimizes OH and C impurities, and ensures complete oxidation of Si and Zr. Local bonding in SiO2-rich alloys (x<0.5) approximately 2000 Å thick has been previously investigated by x-ray diffraction (XRD) and infrared (IR) spectroscopy.6 Results from that investigation indicated that films, deposited at 300 °C and annealed in a nonoxidizing ambient such as Ar at temperatures up to 800 °C, are amorphous and pseudobinary in character with Si–O and Zr–O bonds, but not Zr–Si, Si–Si, or Zr–Zr bonds. Similar IR studies have also been conducted on ZrO2-rich alloys and indicate a pseudobinary character as well. In addition, it has also been shown that a chemical phase separation into ZrO2 and either SiO2 or a low ZrO2 concentration alloy (x<0.1) occurs in these pseudobinary alloys when they are annealed at 900 °C for 60 s in a nonoxidizing ambient such as Ar.8 The XPS and AES results of this article provide additional insights to local bonding that are complementary to what has been previously revealed in the IR studies, and in addition confirm directly the chemical phase separation that occurs for annealing in inert ambients at temperatures greater than 900 °C.

The compositional dependence of the XPS and AES spectral features will be interpreted in terms of a bonding model that has previously been used to (i) interpret the results of IR experiments6 and (ii) describe systematic changes in amorphous morphology and bonding coordination (a) from SiO2 with a continuous random network (crn), (b) to silicate alloys in which the crn is disrupted and modified by alloying transition metal oxides, and finally to (c) amorphous transition metal oxides in which the bonding is ionic.8 It was noted in Ref. 8 that these changes in morphology were accompanied by a continuous increase in the average bonding coordination of O atoms. For the Zr silicate alloys of this study, this increase in O-atom coordination derives from the different coordinations of the Si and Zr atoms in the respective end-member oxides, four for Si in SiO2 and eight for Zr in ZrO2, and an assumption in Ref. 8, supported by experiment, that these coordinations are maintained throughout the entire alloy regime. Based on the bonding model of Ref. 8, the coor-
dination of O atoms increases from two in SiO₂ to between two to three in the SiO₂-rich Zr silicate regime up to \( x = 0.5 \), and then further increases from three to four in the ZrO₂-rich alloy regime from \( x = 0.5 \) to 1.0.⁸

In the SiO₂-rich regime there are four different bonding environments for O atoms (see Fig. 1): (i) twofold coordinated O atoms bonded only to Si atoms, the so-called bridging O atoms of the crn structure of SiO₂;⁹ (ii) twofold coordinated O atoms bonded to one Si and one Zr atom, the so-called terminal O atoms that result from network disruption by the ionic bonding of the Zr atoms;⁹ (iii) threefold coordinated O atoms that are covalently bonded to two Si atoms of the crn, and additionally make one donor–acceptor pair or dative bond with one Zr atom,¹⁰ and (iv) threefold coordinated O atoms that make (a) one bond to a Si atom and two terminal O atom bonds to Zr atoms. The donor–acceptor pair bonds of these alloys are qualitatively the same as the bonding of sixfold coordinated Al atoms in noncrystalline Al₂O₃.¹⁰ As the concentration of ZrO₂ increases and network disruption becomes more prevalent, donor–acceptor bonds as in (iii) are replaced by the second type of threefold coordinated O atom bond as in (iv). At the compound silicate composition, ZrSiO₄, \([\text{ZrO}_2]_{0.5}\cdot[\text{SiO}_2]_{0.5}\) network disruption is effectively complete, and all O atoms are threefold coordinated to one Si atom of a silicate ion, SiO₄²⁻, and two Zr⁴⁺ ions.

In the ZrO₂-rich regime there are threefold coordinated O atoms in the same bonding arrangement as in the compound silicate phase, as well as fourfold coordinated O atoms bonded only to Zr atoms. As \( x \) is increased from 0.5 to 1.0, the silicate ions are replaced by O²⁻ ions, and the coordination of O increases to four. This bonding model serves as a basis for the interpretation of the XPS and AES results. It differs from previous attempts to analyze XPS spectra from bulk silicate glasses¹¹ with respect to the specific inclusion of the donor–acceptor pair bonds that are required to satisfy the coordination requirements of the strongly electropositive ions. For example, in Ref. 11, the O 1s core level spectral features were analyzed solely in terms of bridging and nonbridging O atoms designated as BO and NBO, respectively, neglecting other O atom bonding arrangements which would increase the O atom coordination to levels consistent with the ionic bonding of the metal atoms of the silicate alloy glasses.

II. EXPERIMENTAL PROCEDURES

Films approximately 20–50 nm thick were deposited onto Si(100) substrates at 300 °C by a remote plasma process described in detail elsewhere.³ The respective Si and Zr source gases, 2% SiH₄ in He, and Zr(IV) t-butoxide, Zr[OC(CH₃)₄]₄, were delivered directly into the substrate region of a remote plasma reactor through two different shower-head injectors. The Zr:Si ratio in the deposited films is determined by the relative flow rates of the respective Zr and Si source gases. An O₂/He (20:1) mixture was subjected to remote plasma excitation, 15 W at 13.56 MHz, and used to initiate the remote plasma enhanced chemical vapor deposition (RPECVD) process. Substrates were treated in a H₂O/HF (100:1) solution prior to film deposition to remove the superficial native oxide. Prior to the Zr silicate alloy deposition, an a-SiO₂ layer approximately 3 nm thick, was deposited on the Si substrate by RPECVD to provide a chemical buffer layer between the deposited plasma-deposited Zr silicate alloys and the Si substrate to suppress Zr source gas reactions with the Si substrate. The alloy composition (Zr:Si ratio) was determined by Rutherford back-scattering spectrometry (RBS) and indicated that the (ZrO₂)(SiO₂)₁₋ₓ alloy films were homogeneous, and fully oxidized with an uncertainty in composition, \( \delta x = \pm 0.03 \).⁵ The RBS results were used to calibrate on-line AES results where a linear dependence was demonstrated between the ratio of the derivative spectrum peak–peak heights for OₓKVV(KLL) and ZₓMNN(MNN) features (see Fig. 2). Films were annealed \textit{ex situ} in an inert Ar ambient utilizing an AG minipulse 310 rapid thermal annealing (RTA) apparatus with an uncertainty in annealing temperature of \( \pm 15 \) °C.

XPS measurements of O 1s, C 1s, Zr 3d, and Si 2p core levels.
were made using a Riber LAS-3000 spectrometer with nonmonochromatic Mg $K_x$ radiation (1253.6 eV) and a pass energy of 20 eV. The system base pressure for XPS measurements was $3 \times 10^{-10}$ Torr. Data were corrected for charging effects using the C 1$s$ peak at 284.6 eV from adventitious carbon contamination on the film surface. The repeatability of measuring peak spectral positions was found to be $< 0.2$ eV. The as-deposited films were also characterized online by AES using a Phi system at a base pressure of $8 \times 10^{-10}$ Torr with a $10–30$ $\mu A$ electron beam at 3 keV which was defocused to prevent damage to the film structure. $O_{KVV}$ and $Zr_{MVV}$ transitions were measured as a function of film composition and the repeatability of peak kinetic energy determinations was $< 0.2$ eV.

### III. EXPERIMENTAL RESULTS

XPS measurements of O 1$s$, Zr 3$d$, and Si 2$p$ core levels were made on the end-member oxides, SiO$_2$ and ZrO$_2$, and for 13 pseudobinary oxide alloy compositions distributed over the entire composition range (see Table I). XPS spectra of the end-member oxides annealed at 900 °C for 60 s in an Ar ambient are shown in Fig. 3. The measured peak binding energies of the O 1$s$ and Si 2$p$ core level features of $a$-SiO$_2$ are $532.9 \pm 0.1$ and $103.1 \pm 0.1$ eV, respectively. The peak binding energies of the Zr 3$d_{s2}$ and O 1$s$ features in $c$-ZrO$_2$ are $181.9 \pm 0.1$ and $530.1 \pm 0.1$ eV, respectively. The spectral line shapes of the Si 2$p$ and Zr 3$d_{s2}$ features are symmetric, whereas the O 1$s$ features are asymmetric as indicated in the derivative spectrum in Fig. 3(b). There is broadening on the high energy side of this feature in $c$-ZrO$_2$, and on the low energy side in $a$-SiO$_2$. XRD and transmission electron microscopy (TEM) results have shown that plasma deposited ZrO$_2$ films annealed at 900 °C are in a polycrystalline monoclinic phase, $c$-ZrO$_2$.

XPS spectra of the as-deposited (ZrO$_2$)$_x$(SiO$_2$)$_{1-x}$ alloys are shown in Fig. 4. XPS films annealed at 500 °C were also analyzed by XPS, and the spectral results were essentially the same as those of the as-deposited films at a substrate temperature 300 °C; therefore, only the spectra of the as-deposited samples are addressed below. The derivatives of the O 1$s$ spectra in Fig. 4(b), obtained by numerical differentiation of the spectra in Fig. 4(a), reveal significant asymmetries in the alloy spectra. The Zr 3$d$ and Si 2$p$ features are more symmetric and show no evidence of multiple features or significant asymmetries in the respective derivative spectra, and hence these are not included in Fig. 4.

XPS core level O 1$s$ spectra of the pseudobinary oxides annealed at 900 °C for 60 s in Ar, and the associated derivative spectra, are shown in Fig. 5. The O 1$s$ spectra in Fig. 5(a) were fit using a two-component Gaussian model, and the results of the best fit are shown in Fig. 6 as a function of composition $x$. Based on the bonding in the end-member oxides, ionic in $c$-ZrO$_2$, and covalent in SiO$_2$, the low energy peak is correlated with non-network-bonded O atoms, primarily $O^2-$ ions, and the high energy peak with twofold and threefold coordinated bridging, and/or network-bonded O atoms.

The measured binding energies of O 1$s$, Zr 3$d_{s2}$, and Si 2$p$ core levels from Table I are presented in Fig. 7 as a function of composition $x$. The binding energies of all three of these features decrease with increasing $x$, but with different degrees of nonlinearity as indicated by the fifth order polynomial fits to the experimental data points. The nonlinearity for low $x$ is greatest for the Zr 3$d_{s2}$ data. It is weaker, but clearly evident in the O 1$s$ data, and much weaker in the Si 2$p$ data.

AES measurements on the as-deposited films were performed on-line immediately following film deposition and are displayed in Fig. 8. The kinetic energies shown are derived from the highest energy peak in the derivative spectra. AES chemical shifts of $O_{KVV}$ and $Zr_{MVV}$ transitions as a function of composition in Fig. 9 and also in Table II show nearly identical nonlinear behavior that is different and therefore complementary to the XPS chemical shifts of the Zr 3$d_{s2}$ and Si 2$p$ core levels. These data display a sigmoidal character. The compositional dependence of the peak kinetic energy values displays a similar sigmoidal nonlinear dependence; however, for the $O_{KVV}$ data the spread in energies between the end-member compounds at $x = 0.0$ and $x = 1.0$ is about 1 eV less due to the compositional dependence of the spectral linewidth [see Fig. 9(c)].

Finally, due to spectral overlap between the $Zr_{MVV}$ and Si 2$p$ features in the AES spectra, it was not possible to track the compositional dependence of the AES Si 2$p$ feature.

### IV. DISCUSSION

This section addresses the following issues: (i) the relative XPS binding energy shifts of O, Zr, and Si as a function of alloy composition, as displayed in Figs. 7(a)–(c); (ii) the asymmetry of the O 2$p$ features in as-deposited 300 °C films; (iii) the nonlinearity of the Zr 3$d_{s2}$ and Si 2$p$ XPS binding energy shifts of Figs. 7(b) and 7(c); (iv) the chemical phase separation in the 900 °C annealed films; (v) the origin of the differences between the nonlinear behaviors in the Zr 3$d_{s2}$ and Si 3$p$ XPS features, and the AES Zr 3$d_{s2}$ and

<table>
<thead>
<tr>
<th>Alloy composition $x$ ($\leq 0.03$)</th>
<th>O 1$s$ core level binding energy (eV±0.15)</th>
<th>Zr 3$d$ core level binding energy (eV±0.15)</th>
<th>Si 2$p$ core level binding energy (eV±0.15)</th>
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</thead>
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Based on the bonding in the end-member oxides, ionic in $c$-ZrO$_2$, and covalent in SiO$_2$, the low energy peak is correlated with non-network-bonded O atoms, primarily $O^2-$ ions, and the high energy peak with twofold and threefold coordinated bridging, and/or network-bonded O atoms.
features; and (vi) the compositional dependence of band offset energies between the conduction and valence bands of c-Si and the Zr silicate alloys, including the relationships between these band offset energies, and the band gaps of Zr silicate alloys.

### A. Trends in binding energies with increasing ZrO$_2$ composition (x)

Based on core level chemical shifts measured by XPS in other pseudobinary metal oxide alloys an empirical rule has been developed which describes the relationship between core level energy and the alloy local bonding environments.$^{12,13}$ In general, a pseudobinary $(M_aO_b)_{1-x}(N_mO_n)_{x-1}$ alloy formed by mixing two elemental oxides, $M_aO_b$ and $N_mO_n$, displays M–O, and N–O bonds, and includes $M$–O–N bonding arrangements as well. Note that the existence of $M$–O–N bonding arrangements does not restrict the bonding coordination of O atoms to being twofold. If M and N are metals, or more generally a metal and a semiconductor atom such as Si, the bonding coordinations of O atoms in the alloys can be as high as four- or sixfold.

If the electronegativity of atom N is larger than M, there are M–O alloy bonds that are more ionic, and N–O bonds that are more covalent in the alloys, than in the respective elemental oxide phases. This counterintuitive result is simply a manifestation of the relative charge transfer between the constituent atoms of the alloy as driven by global or local electronegativity equalization,$^{14,15}$ and will addressed quantitatively in an empirical chemical bonding model discussed below. In addition, this aspect of bonding has previously

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**Fig. 3.** XPS core level (a) O 1s, (c) Zr 3d, and (d) Si 2p spectra of end-member oxides, SiO$_2$ and ZrO$_2$ annealed at 900 °C for 60 s. The spectra in (b) are the numerical derivatives of the corresponding spectra in (a). The ZrO$_2$ film is polycrystalline in the monoclinic phase, and the SiO$_2$ film is amorphous.
been investigated theoretically in $c$-ZrSiO$_4$ (zircon), and its crystalline constituent oxides, $c$-SiO$_2$ and $c$-ZrO$_2$. Bonding charges on each atomic species were calculated using density functional theory (DFT) in the local density approximation (LDA). These charges were determined by calculating the net charge contained within a Wigner–Seitz cell centered about the nucleus of each atomic species. Observed core electron binding energy shifts from XPS were consistent with the empirical rule of Refs. 14 and 15, as well as the calculated results of Ref. 6 that also take into account both final state and Coulomb effects.

In this article, another approach to charge transfer in pseudobinary oxides is presented. It is based on a self-consistent, empirical chemical bonding model previously applied to IR active vibrations of Si–H groups in Si suboxide alloys. The method is based on the principle of electronegativity equalization developed by Sanderson that states that an intermediate value of electronegativity results when atoms chemically combine to form a compound, or an alloy. This same concept is implicit in the definition of electronegativity as originally proposed by Pauling as discussed in Ref. 8. The intermediate value of electronegativity is assumed by Sanderson to be the geometric mean of the electronegativities of the individual atoms appropriately weighted for their relative compositions. This model treats each atom in an average way and does not take into account distributions of inequivalent bonding sites of the same atom.

Since there is no way to experimentally determine the exact ionicity of any bond, Sanderson makes the following two assumptions: (i) partial atomic charges vary linearly with average electronegativity and (ii) a specific ionicity of 75% in NaF is assumed to establish the scaling relationship be-

![Image](https://example.com/image.png)

**FIG. 4.** XPS core level spectra: (a) O 1$s$, (b) numerical derivative of O 1$s$, (c) Zr 3$d$, and (d) Si 2$p$. Each of these spectra is for as-deposited (300 °C) Zr silicate alloys with $x=0.23, 0.32, 0.43, 0.52, 0.67,$ and 0.76.
between partial charge and changes in electronegativity due to charge transfer in forming chemical bonds. Based on these two assumptions an empirical model has been developed to calculate partial atomic charges $d_A$:

$$d_A = A \frac{S_A - (S_B + S_C)^{1/(x+y+z)}}{1/(x+y+z)} - \frac{1}{2.08 \cdot S_A},$$

where $A_{x+y+z}$ represents the alloy composition, $S_A$, $S_B$, and $S_C$ are the electronegativities of the constituent atoms, and $(S_A - (S_B + S_C)^{1/(x+y+z)})$ is the compositionally average electronegativity of the alloy or compound. Finally, $2.08 \cdot S_A$ is a electronegativity that corresponds to an effective partial charge of + or − one on atom A. In this model, charge is transferred between the atoms A, B, and C until each atom attains the same value of electronegativity. For example, the electronegativities of Si and Zr (or N and M, respectively) increase, and the electronegativity of O decreases in a pseudobinary alloy. Following the model of Sanderson, partial charges for Si, Zr, and O atoms in $Zr_xSi_{1-x}O_2$ pseudobinary.
binary alloys were calculated using Eq. (1) and are presented in Fig. 10. The magnitude of each partial charge changes linearly with composition (increasing $x$) and decreases for Si and Zr (i.e., it becomes less positive) and increases for O (i.e., it becomes less negative). These variations of partial charge predict that the binding energies of the Si 2$p$, Zr 3$d_{5/2}$, and O 1$s$ features will each decrease with increasing $x$, in agreement with results summarized in Table I, and presented in Figs. 7(a)–7(c). The relative asymmetries in the O 1$s$ spectral features for thermal treatments below 900 °C [see Figs. 4(a) and 4(b)] indicate that bonding coordination as well as average bond chemistry must be taken into account to explain the XPS spectral features and their compositional dependence. For example, as discussed in the Introduction, there are two arrangements in SiO$_2$-rich alloys in which O atoms are threefold coordinated, and be represented schematically by Si$_2$–O–Zr and Si–O–Zr$_2$ and these are assumed to contribute to broadening and asymmetry in the O 1$s$ XPS feature. Similar considerations apply as well to asymmetries in the O 1$s$ line shape in the Zr-rich alloy regime.
TABLE II. Kinetic energies for AES highest energy peak in AES derivative spectra.

<table>
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<tr>
<th>Alloy composition x (±0.03)</th>
<th>AES O KVV kinetic energy (eV ± 0.15)</th>
<th>AES Zr MVV kinetic energy (eV ± 0.15)</th>
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B. Asymmetries in O 1s XPS spectral features in the as-deposited films

Based on the nearly linear scaling of the O 1s feature with alloy composition, the spectral peaks for the alloy samples in Fig. 4(a) are assumed to reflect an average alloy coordination for that composition. Since the O 1s XPS features of the end-members are broad and also show some asymmetry, no attempt has been made to fit the alloy spectra as a simple superposition of spectral peaks associated with the specific bonding arrangements of O that have been displayed in Fig. 1. The respective asymmetries in the spectra of the alloy atom O 1s XPS reflect the details of the distribution of O-atom coordinations, and include final state and Coulomb contributions, as well as bond charge that correlates with coordination.

C. Nonlinearities in Zr 3d5/2, O 1s, and Si 2p XPS binding energies (Fig. 7)

The coordination of Zr has been assumed to be eight independent of alloy composition; however, each of these eight oxygen atoms are not equivalent with respect to bonding neighbor coordination and electronic structure. Based on the results presented in Refs. 4 and 8, the number of ionic Zr-O bonds associated with network disruption increases from four to eight with increasing x for alloys in the SiO2-rich bonding regime. In this alloy regime, each O atom makes at least one Zr–O bond with a bond order of one in a Si–O–Zr arrangement, and there must be at least four of these arrangements. The remainder of the eightfold coordination is made up of donor–acceptor pair bonds with bridging O atoms of the nondisrupted portion of the SiO2 continuous random network. These weaker bonds have been modeled in ab initio calculations as components of a dipolar electrostatic field, and alternatively, and equivalently can also be described as donor–acceptor pair or dative bonds. The donor–acceptor bonds are replaced by Si–O–Zr ionic bonding arrangements as x increases, and the network disruption increases. At a composition of x = 0.5, network disruption is essentially complete, and the O-atom coordination is three, and the bond order of the Zr atoms is formally one-half with all bonds between eightfold coordinated Zr4+ ions and terminal O atoms of silicate ions, SiO44−. Each of the terminal O atoms of a silicate ion makes bonds with two Zr4+ ions.

Figure 11(a) and 11(b) indicate the results of the model ab initio calculation used to identify the effects of the donor–acceptor pair bonds. In this model calculation, the Zr atom has four OH groups in a tetrahedral arrangement to emulate the ionic bonds, and four tetrahedrally grouped water molecules with the O atom nonbonding p electron pair aligned in the direction of the Zr atom to emulate the donor–acceptor pair bonding interaction. Figure 11(a) indicates that bonding is optimized at an effective interatomic spacing of ~0.26 to 0.28 nm between the Zr atoms and the bridging O atoms of the network. The minimum is broad and shallow opening up the possibility of a spread in interatomic spacing where bond-strain and configurational entropy are likely to also be contributing factors in determining a statistical distribution of these bonding arrangements in a noncrystalline solid.

Figure 11(b) indicates a positive shift in the Zr 1s bonding energy as a function of the interatom spacing between Zr and bridging O atoms. The results in Fig. 11(b) also indicate the effects the donor–acceptor pair bond on Zr core levels is equivalent to a dipole field. The effect of the donor–acceptor pair bonds or dipole field is to reduce the binding energy of the Zr 1s core state. Since all of the core states move rigidly with respect to the Zr 1s state, this calculation explains the direction of the nonlinearity of the Zr 3d5/2 core state in Fig. 7(c). A more detailed calculation which substitutes OH-terminated Si–O–Si groups for the water molecules is in progress and will be used to make more quantitative comparisons between shifts in binding energies in Fig. 7(c) and ab initio calculations. However, scaling the values for core shifts in the H–O–H model with the ratio of dielectric constants and relative electronegativities of Si–O–Si groups predicts shifts of the order of 0.15 to 0.2 eV comparable to
Comparing the XPS results in Figs. 4 of the alloy than for Si. This is indeed the case. Involving the Zr and O atoms, it is reasonable to assume that the dipole field or donor–acceptor pair bond energies. Since the dipole field or donor–acceptor pair bond involves the Zr and O atoms, it is reasonable to assume that the dipole field model.

what has been found in the analysis of the XPS results.

Finally, the same ab initio calculations also explain the low concentration nonlinearity differences between the Zr 3d
½, O 1s, and Si 2p core state compositional dependences. Since the dipole field or donor–acceptor pair bond involves the Zr and O atoms, it is reasonable to assume that the nonlinearity will be greater for these two atomic species of the alloy than for Si. This is indeed the case.

**D. Chemical phase separation in the 900 °C annealed films**

A comparison between the spectral dependence of O 1s binding energies and associated derivate spectra of Figs. 4(a) and 4(b) for as-deposited films, and Figs. 5(a) and 5(b) for 900 °C annealing, indicates evidence for chemical phase separation at the alloy compositions displayed, $x=0.35$, 0.45, and 0.60. The separated species have binding energies that are close to, but not exactly equal to, those of SiO$_2$ and ZrO$_2$. Comparing the XPS results in Figs. 4(a) and 4(b) with the IR and XRD results for $x=0.23$ and $x=0.50$ samples of Ref. 6, the XPS study confirms chemical phase separation at the $x=0.23$ and 0.50 concentrations, even though the $x=0.23$ sample does not show any evidence for crystallization of the ZrO$_2$ phase.

**E. Differences between the nonlinear behaviors in the Zr 3d$_{5/2}$ and Si 3p XPS features, and the AES Zr MVV and O KVV features**

The chemical shifts of the Auger electron kinetic energies for O KVV and Zr MVV transitions in the as-deposited films are consistent with changes in the calculated partial charges and their effects on the O and Zr core state energies, i.e., the kinetic energies of the Auger electrons increase with increasing $x$ reflecting the decreases in the negative XPS binding energies, i.e., shifts to less negative values. However, the spectral nonlinearities displayed in Figs. 9(a) and 9(b) are listed in Table II are qualitatively different than the corresponding XPS features in Figs. 7(a) and 7(c). In particular, the compositional dependence of the O 1s in Fig. 7(a) is shows the smallest nonlinearity among the XPS features, whereas the compositional dependence of the O KVV is sigmoidal and markedly nonlinear and similar to that of the Zr MVV feature. Similarly, the compositional nonlinearities of the Zr 3d$_{5/2}$ XPS and Zr MVV AES are also markedly different. The differences between the XPS and AES spectral features derive from differences between the XPS and AES processes. Following Ref. 18, the AES electrons of Fig. 8 originate in the valence band, whereas the XPS electrons of Fig. 6 originate in the respective core states with no valence band participation. This is addressed below where the nonlinear AES behaviors reflect systematic shifts in valence band energy with increasing O-atom coordination.

**V. COMPOSITIONAL DEPENDENCE OF BAND OFFSET ENERGIES BETWEEN THE CONDUCTION AND VALENCE BANDS OF c-Si AND THE Zr SILICATE ALLOYS, INCLUDING RELATIONSHIPS BETWEEN BAND OFFSET ENERGIES AND Zr SILICATE BAND GAPS**

The chemical shifts of Si$_{LVV}$ transitions could not be determined because of an overlap between Si$_{LVV}$ and Zr$_{MVV}$ peaks [see Fig. 8(b)]; therefore, no attempt was made to analyze these transitions by a deconvolution of the AES spectra. As noted above, the AES results for Zr and O are complementary to the XPS results and provide information about valence band structure as well, since the ejected Auger electrons in both cases originate from the highest lying valence band.

The O$_{KVV}$ transition in a-SiO$_2$ has been investigated theoretically and it has been demonstrated that the main peak is associated with two electrons being released from the nonbonding O 2p $\pi$ states at top of the valence band.$^{18}$ Based on this assignment, and combined with the XPS and AES results from this study, a model has been developed in Eq. (2) that provides an estimate of the valence band offsets of the Zr silicate alloys with Si as a function of composition $x$. $E_{\text{Ref}}(O 1s)$ is the magnitude of the XPS binding energy, and $E_{K\ell}(O_{KVV})$ is the average kinetic energy of the Auger elec-
electron at the valence band edge. As noted above, this model assumes that a core hole in the O atom 1s state is filed by an electron near the top of the valence band, and that the Auger electron is also emitted from the top of the valence band as well. Under these conditions,

\[ V_{\text{offset}}(x) \sim -A \cdot 0.5[E_{\text{BE}}(O 1s) - E_{\text{KE}}(O_{KV})] + B, \]

where \( E_{\text{BE}}(O 1s) \) is the binding energy determined from the XPS spectra (see Fig. 7), \( E_{\text{KE}}(O_{KV}) \) is the average kinetic energy near the top of the valence band (e.g., the average of the kinetic energies that correspond to the spectral peak, and highest energy peak in the derivative spectra) and \( A \) and \( B \) are constants, 0.44 and 1.2, respectively, which adjust the respective values of \( V_{\text{offset}}(0) \) and \( V_{\text{offset}}(1) \) to 4.6 eV for SiO\(_2\) and 3.1 eV for ZrO\(_2\). This model is presented in Fig. 12(a). The sigmoidal shape of the polynomial fit in Fig. 12(a) is determined by the relative compositional dependencies of the XPS (O 1s) and AES (O_{KV}) data in Figs. 7 and 9, respectively.

Figure 12(b) applied the same model to the Zr\(_{\text{MLL}}\) AES and Zr 3d XPS results of Figs. 7 and 9, respectively. The Zr\(_{\text{MLL}}\) AES data points are for the kinetic energy defined by the highest energy peak in the derivative spectrum, and therefore include any effects to the compositionally dependent AES linewidth. The model equal corresponding to Eq. (2) becomes

\[ V_{\text{offset}}(x) \sim -A' \cdot 0.5[E_{\text{BE}}(Zr 3d) - E_{\text{KE}}(Zr_{\text{MLL}})] + B', \]

where \( A' = 0.64 \) and \( B' = -4.6 \) eV. The differences between these constants and those applied to Eq. (2) to adjust the end-member values, are related to differences in the intermediate states. For the oxygen atom calculation these are the nonbonding states at the top of the valence band, while for the zirconium atom calculation they are deeper in the valence band (see Ref. 22). However, the important point with respect to the band offset composition dependence derived from the Zr XPS and AES is that the sigmoidal dependence is a manifestation of the differences between the compositional dependence of respective XPS and AES data (see Figs. 7 and 9 and Tables I and II).

The alloy dependence of the band gap of Zr silicate alloys is addressed by combining the XPS results of this article with Eq. (2). The total peak shift for Zr 3d and Si 2p XPS core levels over the alloy Zr silicate alloy regime in Figs. 7(b) and 7(c) is 1.8 eV. The aspect of the core level shifts means that the conduction band offset energies with Si, combined with XAS results in Ref. 21 and 22 are independent of alloy composition.

Since the band gap of a Zr silicate alloy at any composition \( x \) is the sum of the conduction and valence band offset energies with respect to Si, plus the electrical band gap of Si, \( \sim 1.15 \) eV, the sigmoidal dependence in Fig. 12, combined with the XPS results discussed above means that band gap variation is also expected to be sigmoidal. The effective band gaps also correlate with changes in the O-atom bonding coordination. When twofold coordination dominates the band gap, referenced either to the Zr 3d\( ^* \), Zr 4s\( ^* \), or Si 3s\( ^* \) states, is the largest, and these band gaps decrease as the coordination increases from two to three, and then from three to four.

VI. CONCLUSIONS

An empirical bonding model has been presented and partial charges for pseudobinary (ZrO\(_2\)\(_x\)SiO\(_2\)\(_{1-x}\) alloys have been calculated as a function of \( x \). Since core levels are a linear function of partial charge, this model predicts linear shifts in O 1s, Zr 3d, and Si 2p core level binding energies as measured by XPS, and Auger electron kinetic energies of O_{KV} and Zr_{MVV} AES transitions provided that final state and Coulomb effects do not contribute significantly. The direction of the compositional dependence in XPS binding energies, and in AES kinetic energies are in agreement with the model, but significant departures from linearity have been shown to derive from different mechanisms: (i) dipolar field effects in the XPS and (ii) valence band offset energy variations in the AES.
Systematic changes in XPS O 1s core level peak shapes are observed for Zr silicate alloys annealed in Ar at 900 °C for 60 s. These changes are due to a chemical phase separation into a-SiO$_2$ or a low concentration Zr silicate noncrystalline phase ($x<0.1$), and either crystalline or noncrystalline ZrO$_2$. These observations of chemical phase separation are complementary to other characterizations, IR and XRD, which have previously revealed chemical separation after annealing at 900 °C.\(^7\)

Finally, the predictions of XPS and AES results for band gap and band offset energies can be tested by both experiment and theory. The prediction is that the threshold for internal photoemission (IPE) from Si valence band states, or from a given metal electrode should be independent of alloy composition $x$ while, the band gap, as determined by photoconductivity (PC), should vary sigmoidally with alloy composition. IPE and PC determinations indicate that the threshold for IPE from the Si valence band, and PC are consistent with both of these transitions terminating in Zr (or Hf) anti-bonding $d$ states.\(^{21,22}\)

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\(^17\)Y. Zhang, G. Lucovsky, and J. L. Whitten (unpublished).
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