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Interface instabilities and electronic properties of ZrO$_2$ on silicon (100)

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The interface stability of Zr-based high-$k$ dielectrics with an oxide buffer layer was explored with x-ray ($h\nu=1254$ eV) and ultraviolet ($h\nu=21.2$ eV) photoemission spectroscopy. Zirconium oxide films were grown and characterized in situ in a stepwise sequence to explore their chemical stability and electronic properties as a function of film thickness and processing conditions. The buffer layers serve to lower the interface state density and to address the high temperature instabilities of ZrO$_2$ in direct contact with Si. This research addresses three issues: (1) the development of the band offsets and electronic structure during the low temperature ($T<300$°C) growth processes, (2) variations in the band structure as affected by process conditions and annealing ($T<700$°C), and (3) the interface stability of Zr oxide films at high temperatures ($T>700$°C). Annealing the as-grown films to 600°C results in an $\sim 2$ eV shift of the ZrO$_2$-Si band alignment, giving a band offset that is, favorable to devices, in agreement with predictions and in agreement with other experiments. We propose that the as-grown films contain excess oxygen resulting in a charge transfer from the Si substrate to the internal (ZrO$_2$-SiO$_2$) interface and that annealing to 600°C is sufficient to drive off this oxygen. Further annealing to 900°C, in the presence of excess Si at the surface, results in decomposition of the oxide to form ZrSi$_2$. © 2004 American Institute of Physics.

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I. INTRODUCTION

The planned scaling of integrated circuit devices involves a reduction of the gate insulator thickness to obtain the targeted capacitance and sheet charge density in the channel. As the gate dielectric thickness is reduced below 2 nm, direct tunneling between the gate and channel becomes significant, leading to increased power consumption and device failures. As an alternative to reducing the physical thickness of the gate oxide the dielectric constant could be increased. This would allow the desired increase in capacitance with a physically thicker layer, resulting in both a reduced tunneling current and an increase in sheet charge density. With conventional thermal oxides and oxynitrides approaching their physical limits, the exploration of alternative materials has gained significant momentum.

The fundamental criteria for a gate dielectric include band offsets that will block both electrons and holes, chemical stability in contact with both the silicon substrate and the gate material, and a low density of interface electronic states. Zirconium oxides and silicates, with their large band gap of $\sim 5.8$ eV and dielectric constants of 15–25, are of particular interest. Moreover, the ZrO$_2$-Si band offsets have been predicted to be favorable for blocking both holes and electrons.

A typical complimentary metal oxide semiconductor process includes a 900–1000°C dopant activation anneal during which the gate dielectric must not undergo significant chemical changes or interfacial reactions. Previous studies of Zr oxides and silicates on Si have noted several instabilities. The interface between Zr oxides and Si has been reported to be chemically unstable at high temperatures by Chang and Lin, Copel et al., and Stemmer et al., among others. Results indicate that the temperature at which the interface decomposes during vacuum annealing is in the range of 880–1000°C. Chang and Lin noted the instability and suggested possible reaction paths for converting ZrO$_2$ and ZrSiO$_4$ into gaseous SiO. They have also calculated free energies for these reactions at different temperatures and equilibrium pressures, showing that at low overpressures of SiO and ZrO the decomposition reaction is energetically favorable.

Stemmer et al. showed that annealing in an oxygen partial pressure $<10^{-7}$ Torr yielded ZrSi$_2$ precipitates and that greater partial pressures of oxygen can suppress the decomposition reaction. They also found that at high oxygen partial pressures, SiO$_2$ formation occurs at the dielectric-Si interface.

Other studies have explored the electronic structure of Zr dielectrics on Si. Miyazaki et al. found a band gap of 5.5 eV and a valence band offset (VBO) of 3.15 eV for evaporated ZrO$_2$ on Si(100). Their results also indicated that annealing these films to 500°C in $10^{-5}$ Torr dry O$_2$ does not significantly effect either the band gap or the VBO.

In this study, we have spectroscopically explored the chemical and electronic instabilities of Zr oxide on a Si substrate with SiO$_2$ and Si$_3$N$_4$ buffer layers. Using ultrahigh vacuum (UHV) transfer between processing and characterization chambers we were able to perform measurements at various points during film processing and explore the evolution of the Zr oxide films from both a chemical and an electronic perspective.

II. EXPERIMENT

All experiments were performed on 25 mm diameter, $n$ type, 0.05 to 1 Ω cm ($1 \times 10^{18}$ to $5 \times 10^{15}$ cm$^{-3}$ phosphor-
ous), Si(100) wafers. Prior to loading into UHV the wafers were cleaned with a wet chemical dip in JT Baker 100 for 15 min. at room temperature, a 1 min rinse in deionized water, and a 10:1 HF:H₂O spin etch.

After chemical cleaning the wafer was loaded into a UHV integrated growth and analysis system which includes a linear UHV transfer system interconnecting 13 different process and characterization chambers. Five of these chambers were employed in this study, including plasma oxidation, electron beam deposition of zirconium, solid source molecular beam epitaxy (MBE) deposition of Si, x-ray photoemission spectroscopy (XPS), and ultraviolet photoemission spectroscopy (UPS).

An initial oxygen plasma exposure was employed to remove residual hydrocarbon contamination and to form the thin (0.5 nm) oxide buffer layer. Zirconium oxide thin film growth involved successive steps of zirconium metal deposition followed by plasma oxidation with annealing steps to relax the oxide structure and to explore film stability. After each process step the films were analyzed with XPS and UPS to observe trends in chemical and electronic properties.

The initial O₂ plasma clean/buffer layer formation and subsequent oxidations were performed in a remote plasmahd-enhanced chemical vapor deposition (RPECVD) chamber with a base pressure of 3 × 10⁻⁹ Torr. Plasma exposures took place with a wafer surface temperature of 300°C, a gas flow of ten standard cubic centimeters per minute (sccm) O₂ and 50 sccm H₂, and an operating pressure of 60 mTorr H₂/O₂. Twenty watts of inductively coupled rf power were used to excite the plasma.

Zirconium metal depositions were completed with the substrate at room temperature in a UHV chamber with a base pressure of 5 × 10⁻¹⁰ Torr. The deposited Zr thicknesses of 0.2, 0.4, and 0.8 nm were obtained at rates of 0.04 nm/s where the deposition rate and thickness were measured with a quartz crystal oscillator.

Annealing steps were performed in UHV, with wafers radiatively heated by a coiled tungsten filament and temperatures measured by a thermocouple held behind the center of the wafer. For temperatures of 600°C and above, the wafer surface temperature was measured with an optical pyrometer; for lower temperatures, the thermocouple reading has been calibrated based on a linear extrapolation from higher temperatures measured by a thermocouple held behind the center of the wafer. For temperatures of 600°C and above, the wafer surface was measured with an optical pyrometer.

The deposition rate and thickness were measured with a quartz crystal oscillator.

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The deposition rate and thickness were measured with a quartz crystal oscillator.
0.9±0.1 eV above the VBM. These results are consistent with flat band conditions after the initial oxidation.

The XPS of the initial plasma oxidized Si(100) surface displayed the bulk Si 2p core level at 99.65 eV binding energy and an oxide related peak at 103.3 eV (Table I). These results were essentially identical to our prior report which indicated flat bands at the interface of the SiO2 buffer layer and the Si. Analysis of the UPS data obtained after the formation of the SiO2 buffer indicated a VBO of 4.3 eV, in agreement with our previous results and other reports.

After the first 0.2 nm Zr deposition and oxidation, the O 1s core level spectrum, shown in Fig. 1, indicated a large shift in binding energy. We found that the core level from the as-prepared SiO2 buffer layer was at 532.5 eV and that after the formation of 0.3 nm of ZrO2, the strongest peak was then observed at 531.6 eV, with a noticeable shoulder at 529.9 eV. Further growth resulted in the ~529 eV peak becoming more intense, while the peak in the 531 eV range became relatively less intense. Both peaks tended to shift to lower binding energy during the process. At 1.2 nm film thickness, the peaks were of approximately equal intensity and were centered at 531.4 and 529.5 eV, respectively. After the final growth step (3.5 nm film thickness), the more intense peak was at 529.1 eV with a shoulder at 531.3 eV.

The oxide-related Si 2p core level, shown in Fig. 2, displayed similar trends, shifting from 103.3 to 102.2 eV after the formation of 0.3 nm ZrO2. After the deposition of 1.2 and 3.5 nm films, the oxide related Si 2p peak was observed at 101.7 and 101.5 eV, respectively. Shifts in the Si 2p substrate peak were much smaller, with the peak initially observed at 99.65 eV for the SiO2 buffer layer, shifting to 99.45 eV for the 0.3 nm film, and finally to 99.30 eV after 3.5 nm had been deposited. We ascribe the shifts in the ~99 eV peak to changes in band bending of the Si substrate.

The Zr 3d core level (Fig. 3) displayed an increase in intensity with film thickness, and, like the O 1s core level, shifted to lower binding energy with each processing step. The peak position shifted from 182.4 eV for the 0.3 nm Zr oxide to 181.4 eV for the 3.5 nm film.

The UPS spectra of the oxidized films indicated the VBM to be at 3.4 eV binding energy (relative to the bulk Fermi level), after the first 0.3 nm of oxide growth. The VBM shifted progressively toward 1.9 eV with each additional deposition step (Fig. 4). Table I contains a summary of the XPS core level binding energies and the UPS VBM observed during low temperature growth.
B. High temperature instability

To explore thermal stability, the stepwise grown film was annealed to 600, 750, and 900° C. The 600° C annealing resulted in a large shift in the oxide valence band (Fig. 5), shifting from a binding energy (BE) of 1.9 eV for the as-grown 3.5 nm film to a BE of 4.6 eV for the postannealed film. Further annealing to 750° C resulted in a 0.2 eV shift of the VBM back toward the Fermi level to a BE of 4.4 eV (Table I).

The core level spectra underwent similar large shifts after annealing to 600° C (Fig. 6). The O 1s spectrum of the as-grown film initially displayed a 529.1 eV peak with a 531.3 eV shoulder, that, after annealing, had shifted to 531.2 eV with a shoulder at 532.5 eV. The Zr 3d peak shifted from 181.4 to 183.8 eV. The oxide-related Si 2p shifted from 101.5 to 103.1 eV, and the bulk-related Si 2p shifted from 99.30 to 99.50 eV. After annealing, the oxide-related Si 2p core level showed an increase in intensity and a decrease in peak width compared to the as-deposited state.

Similar to the changes in the VBM the core level spectra indicated small changes with further annealing to 750° C. The Zr 3d core level was shifted 0.1 eV lower in binding energy, the O 1s core levels were unchanged, and the Si 2p core levels were both higher in binding energy by 0.2 and 0.05 eV for the oxide- and bulk-related features, respectively.

After annealing to 900° C the O 1s core level was reduced to an almost undetectable level, and the Zr 3d peak was shifted to 179.1 eV, a position representative of Zr metal or Zr silicide. The oxide-related Si 2p was not observable and the bulk-related Si 2p was observed at 99.45 eV, having become much more intense. The UPS spectrum showed emission extending to the Fermi level, indicating a film with a metallic character, and atomic force microscopy (AFM) revealed a high density of islands with radii of ~500 nm.

C. Stability with alternate buffer layers

To explore the conditions of high temperature stability ZrO$_2$ films were prepared with both a 30 nm SiO$_2$ buffer layer and a 1 nm Si$_3$N$_4$ buffer layer. The 3 nm Zr oxide film was characterized in the as-grown state, annealed, and then characterized again.

After formation of the Zr oxide on the 30 nm SiO$_2$ buffer, the O 1s spectrum displayed peaks at 533.5 and 531.6 eV (Table II). Annealing in UHV to 600° C resulted in a shift of the 533.5 eV peak to 533.2 eV while the other peak remained unchanged at 531.6 eV (Fig. 7). Annealing to 750° C found the O 1s peaks were at 533.1 eV and 531.5 eV, respectively, and a subsequent 900° C anneal had shifted them to 533.2 and 531.3 eV. After annealing to 900° C, the 533.2 eV peak was slightly increased in intensity relative to the peak at 531.3 eV. The oxide-related Si 2p core level remained fixed at 104.0 eV through the annealing steps (Fig. 7), and the Zr 3d core levels showed small shifts similar to the O 1s spectra.
A 2.0 nm thick Si layer was deposited by MBE on the annealed Zr oxide film to explore the effect of excess Si on the decomposition process. After Si deposition the Si 2p core level showed a Si bulk peak at 99.55 eV as well as the oxide-related peak at 103.6 eV (Fig. 8). The SiO₂ related O 1s peak was unchanged at 533.2 eV, but the ZrO₂ related peak was shifted slightly to 531.5 eV. The Zr 3d core level was reduced in intensity due to the Si layer and was shifted to 183.8 eV.

Annealing to 600°C and subsequently 750°C (Fig. 8) resulted in a decreased intensity of the Si 2p bulk-related core level, and the oxide-related peak shifted back to 104.0 eV. The two peaks of the O 1s spectra were at 533.2 and 531.6 eV after both the 600 and 750°C annealing steps. These peaks also changed in relative intensity with annealing, with the 533.2 eV peak increasing with respect to the 531.6 eV peak.

When annealed to 900°C the film underwent significant changes. The intensity of the O 1s core level was reduced to a level only slightly above the system noise, the oxide-related Si 2p core level was not observed, and the Zr 3d peak was shifted to a position characteristic of Zr metal or Zr silicide.

To further evaluate the effect of the buffer layer on high temperature stability we deposited a 1 nm Si₃N₄ buffer layer, 3 nm of ZrO₂, and then repeated the annealing experiment, with and without excess Si. The as-grown film as characterized by XPS, displayed core level positions of 99.55 V for the Si 2p bulk peak, 101.5 for the Si 2p nitride related peak, 529.2 for the O 1s peak, and 181.5 eV for the Zr 3d core level (Table III). On annealing to 600°C all of the core level spectra shifted to higher binding energy. The Si 2p core levels shifted to 99.70 and 102.3 eV, respectively, the O 1s shifted to 530.9, and the Zr 3d shifted to 183.2. The films was further annealed to 750 and 900°C after which the bulk Si 2p was observed at 99.80 eV, the nitride bonded Si 2p shifted slightly to 102.4 eV, and the O 1s and Zr 3d were unchanged at 530.9 and 183.2 eV, respectively.

After a 2 nm thick Si layer was deposited via MBE, the bulk Si 2p core level was found to be at 99.50 eV, the nitride bonded Si 2p was no longer visible, and the O 1s and Zr 3d core levels had shifted to 531.3 and 183.5 eV, respectively. After annealing to 600°C the nitride bonded Si 2p was once again visible at 102.8 eV, alongside the bulk peak at 99.60 eV. Annealing to 750°C and finally 900°C resulted in the emergence of a metallic or silicidilike Zr 3d core level at 179.6 eV and a reduction in the oxide-related component at 182.9 eV. After 900°C the VB spectra was of metallic character, with intensity extending to the Fermi level. The nitride bonded Si 2p was detected at 102.2 eV, a position similar to the original Si₃N₄ buffer layer. Tables II and III contain a summary of the data for ZrO₂ films on alternate buffer layers.

### Table II. Tabulated XPS peak positions and UPS valence band data in binding energy relative to the Si E₉ for ZrO₂ deposited on an ~30 nm SiO₂ buffer layer.

<table>
<thead>
<tr>
<th>Process step</th>
<th>Si 2p(bulk)</th>
<th>Si 2p(SiO₂)</th>
<th>O 1s(SiO₂)</th>
<th>O 1s(ZrO₂)</th>
<th>Zr 3d(oxide)</th>
<th>Zr 3d(metallic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>N/a</td>
<td>104.8</td>
<td>533.9</td>
<td>N/a</td>
<td>N/a</td>
<td>N/a</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>N/a</td>
<td>104.3</td>
<td>533.5</td>
<td>531.6</td>
<td>183.9</td>
<td>N/a</td>
</tr>
<tr>
<td>600°C</td>
<td>N/a</td>
<td>104.0</td>
<td>533.2</td>
<td>531.6</td>
<td>183.8</td>
<td>N/a</td>
</tr>
<tr>
<td>750°C</td>
<td>N/a</td>
<td>104.0</td>
<td>533.1</td>
<td>531.5</td>
<td>183.7</td>
<td>N/a</td>
</tr>
<tr>
<td>900°C</td>
<td>N/a</td>
<td>104.0</td>
<td>533.2</td>
<td>531.3</td>
<td>184.0</td>
<td>N/a</td>
</tr>
<tr>
<td>Si</td>
<td>95.55</td>
<td>103.6</td>
<td>533.2</td>
<td>531.5</td>
<td>183.8</td>
<td>N/a</td>
</tr>
<tr>
<td>600°C</td>
<td>99.45</td>
<td>104.0</td>
<td>533.2</td>
<td>531.6</td>
<td>184.0</td>
<td>N/a</td>
</tr>
<tr>
<td>750°C</td>
<td>99.60</td>
<td>104.1</td>
<td>533.2</td>
<td>531.6</td>
<td>183.9</td>
<td>N/a</td>
</tr>
<tr>
<td>99.55</td>
<td>99.35</td>
<td>N/a</td>
<td>533.5</td>
<td>N/a</td>
<td>N/a</td>
<td>179.2</td>
</tr>
</tbody>
</table>
D. Low temperature instability

The large shifts of the VBM and core levels, observed after annealing to 600°C, were explored thoroughly in another study that also measured a similar effect observed in Ti and HF oxides. Our observations of ZrO₂ thin films indicated that when annealed at low temperatures, (T<600°C) the VBM and core levels shift up to 2 eV. Shifts in the valence band and core levels were observed for annealing temperatures as low as 200°C. Exposing the annealed film to an oxygen plasma was found to shift the VBM and core levels back to their respective as-grown binding energy positions. Subsequent annealing and oxidation steps consistently shift the band structure and, to within experimental error, give identical results.

These shifts were observed for ZrO₂ deposited on the 0.5 nm SiO₂ and the 1 nm Si₃N₄ buffer layers but not the 30 nm SiO₂ buffer. To explore this, a series of 3 nm ZrO₂ films were deposited on SiO₂ buffer layers of different thicknesses (0.5, 2.0, and 3.5 nm) and the shifts in the electronic structure were measured. Findings from this series of films indicate that the magnitude of the VB and core level shifts decreases with increasing buffer layer thickness, approaching zero as the buffer layer thickness increases beyond 3.5 nm.

IV. DISCUSSION

We divide this section into three parts giving the details of (a) the integrity of the SiO₂ buffer layer during low temperature ZrO₂ deposition, (b) the high temperature instability and oxide decomposition, and (c) the low temperature instability and changes in electronic structure.

A. Integrity of the SiO₂ buffer layer

The relative intensity of the bulk and oxide bonded Si 2p core level remained unchanged during film growth, indicating that, to our detection sensitivity, there was no diffusion of Si into the ZrO₂ layer. Nor were any core level shifts observed that would indicate the formation of a Zr silicate. It was also observed that, with annealing to 600°C, the positions of the Si 2p and the SiO₂ related component of the O 1s core level return to that of the as-prepared buffer layer. This further suggests that there has been no chemical change of the SiO₂ in the buffer layer. Stemmer et al. and Ramanathan et al. have shown that the formation of a silicate is thermodynamically unfavorable and that over a wide range of compositions the films will spontaneously phase separate in the amorphous phase. Based on this analysis we sug-
suggest that the low temperature growth process allows us to deposit ZrO₂ on an ultrathin SiO₂ buffer layer while maintaining the integrity of the two layers.

**B. High temperature instability**

Previous work on Zr oxides has found them to be stable on Si, but only in the limit of temperatures less than ~850°C.⁵,⁶,¹⁷,¹⁸ There has, however, been some disagreement about the particular temperature where this instability appears. Copel et al. find that 900°C annealing for 2 min does not lead to decomposition of their ZrO₂ films but that a 30 s flash to 1000°C does result in decomposition.⁶ Chang et al. find that 880°C is sufficient to drive the decomposition reaction at low oxygen partial pressures, and they also propose likely reaction paths, all of which involve excess Si as a reactant (Table IV).⁵

Our results indicate that ZrO₂ films on thin (0.5 nm) SiO₂ buffer layers are unstable at ~900°C, decomposing into a metallic film, which is most likely ZrSi₂. Atomic force microscopy images of the decomposed films display a high density of ~500 nm diameter islands. Stemmer et al. have also reported the formation of ZrSi₂ islands during vacuum annealing of Zr oxide films on Si.⁷

In contrast to the results for the thin buffer layer, we find that two different buffer layers, a 30 nm SiO₂ layer and a 1 nm Si₃N₄ layer, can both suppress the decomposition reaction during annealing at up to ~900°C. Moreover, the deposition of a top, 2 nm, Si layer and a second annealing to 900°C, result in the decomposition of the ZrO₂ film and the formation of Zr silicide. These results indicate that the availability of excess Si leads to the decomposition of the ZrO₂. We suggest that the 0.5 nm SiO₂ layer allows Si to diffuse from the substrate to the high- k interface leading to the decomposition reaction. We further suggest that the 30 nm SiO₂ and the 1 nm Si₃N₄ buffer layers inhibit this diffusion and thus prevent the decomposition of the ZrO₂.

Reaction probabilities from a free energy perspective have been calculated by Chang et al. and a summary of that work is contained in Table IV.⁵ Ramanathan et al. have reported that HF and Zr-silicate films tend to phase separate into zirconia and silica during high-temperature anneals, indicating that the first three reaction paths in Table IV are unlikely to occur.¹⁶ Consequently, we expect that the most likely reaction path for the decomposition of our films is the last reaction path given in Table IV, 2ZrO₂ + 5Si → ZrO₂(δ) + 3SiO₂(δ) + ZrSi₂. Stemmer et al. have demonstrated that annealing films in an oxygen ambient rather than in vacuum can improve stability at 900°C, but these annealing conditions will likely result in SiO₂ growth at the Si interface.⁷

**C. Low temperature instability**

The large shifts in electronic structure observed with annealing have been explored in another publication, which also includes findings for other transition metal oxides (TiO₂ and HfO₂).¹³ The following presents a summary of those results as they apply to ZrO₂.

We suggest that exposure to a remote oxygen plasma (and a high concentration of excited oxygen) introduces excess oxygen into the ZrO₂ film. We further suggest that this excess oxygen is a source of electronic states near the buffer layer—high- k interface. Electrons tunnel from the substrate to populate these states, giving rise to a potential across the SiO₂ buffer layer. Annealing removes the excess oxygen and

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**TABLE IV. Chemical reduction of ZrSiO₄ and ZrO₂ involving SiO₂(δ) and ZrO₂(δ) formation.** The equilibrium pressures of SiO₂(δ) and ZrO₂(δ) are set at 0.01 Torr at all temperatures, and that ΔG° = ΔG°₀ + RT ln P is used for the gaseous species. Values for ΔG° are given in kcal/mol for ZrO₂ and ZrSiO₄ decomposition.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>25°C</th>
<th>527°C</th>
<th>727°C</th>
<th>927°C</th>
<th>1127°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrSiO₄ + 5Si → 4SiO + ZrSi₂</td>
<td>272</td>
<td>141</td>
<td>90</td>
<td>39</td>
<td>−10</td>
</tr>
<tr>
<td>2ZrSiO₄ + 7Si → ZrO + 7SiO + ZrSi₂</td>
<td>620</td>
<td>358</td>
<td>256</td>
<td>155</td>
<td>54</td>
</tr>
<tr>
<td>ZrSiO₄ → ZrO₂ + ZrSi₂</td>
<td>5</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>SiO₂ + Si → 2SiO</td>
<td>130</td>
<td>65</td>
<td>40</td>
<td>15</td>
<td>−9</td>
</tr>
<tr>
<td>2ZrO₂ + 5Si → ZrO + 3SiO + ZrSi₂</td>
<td>349</td>
<td>219</td>
<td>168</td>
<td>118</td>
<td>69</td>
</tr>
</tbody>
</table>

See Ref. 5.
the associated electronic states, leading to flat bands with no potential across the SiO$_2$ buffer layer. Figure 9 schematically shows the band structure of the as-grown and annealed ZrO$_2$ films.

As discussed in Ref. 13, the magnitude of the band structure shift decreases as the buffer layer thickness is increased. With our model, the probability of an electron tunneling through the buffer layer would be expected to decrease as the buffer layer thickness increased. This tunneling dependence would explain the lack of band structure shifts in the ZrO$_2$ film prepared on a 30 nm SiO$_2$ buffer layer.

To estimate the charge needed to produce the measured shifts we can treat the buffer layer as a simple dielectric with permittivity of free space, $k$, and the surface charge density, $\sigma$. The change in band bending at the Si substrate is $\Delta E_b = \frac{k \sigma}{\varepsilon_0}$, where $\varepsilon_0$ is the permittivity of free space and $\Delta E_b$ is the change in band bending. This gives a charge density of $\sigma = \frac{2 \varepsilon_0 \varepsilon_r N_F}{q}$. We can calculate the charge density, where $N_F$ is the surface charge density, $N_D = \frac{1}{10^{12}} \text{cm}^{-2}$ is the bulk doping density of the Si, $q$ is the charge of an electron, $e_0$ is the permittivity of free space, $k = 12$ is the dielectric constant of Si, and $V = 0.5$ V is the change in band bending. This gives a charge density of $N_F = 2 \times 10^{12} \text{cm}^{-2}$ and, thus, the two calculations are in relative agreement. The excess charge may not be completely localized at the high-k-SiO$_2$ interface or other conditions may exist to explain the discrepancy in the two different charge density estimates.

Other studies have reported relatively high values of negative fixed charge, $\sim 10^{12} \text{cm}^{-2}$, at internal interfaces between SiO$_2$ and ZrO$_2$. There have also been reports of positive fixed charge at approximately the same density.

Annealing has also been shown to reduce the fixed charge density in films that exhibit either positive or negative fixed charge. The magnitude of the fixed charge density agrees relatively well among the published studies, even for films that have been prepared by different techniques. The sign of the fixed charge, on the other hand, is not well understood, and the conflicting results may suggest that multiple processes are involved. It is evident that further study is needed to correlate processing conditions with the electronic properties of these interfaces.

V. CONCLUSIONS

We have used x-ray and ultraviolet electron spectroscopy to study the chemistry and interface electronic states during the stepwise growth and annealing of ZrO$_2$ on Si. An interfacial buffer layer of SiO$_2$ or Si$_3$N$_4$ was formed to reduce the number of interface states and improve interface stability. The low temperature deposition technique allowed the formation of ZrO$_2$ on the buffer layer without mixing, and the two layers remain distinct. Annealing the films to 600°C resulted in large changes in the band alignment that are attributed to the presence of excess oxygen in the as-grown films. These large shifts of up to 2 eV are consistent and repeatable for multiple oxidation and annealing steps. Annealing at 900°C resulted in film decomposition into ZrSi$_2$, and a high density of silicide islands was observed with AFM.

The stability of the film at 900°C was improved by both a thick (30 nm) SiO$_2$ buffer layer and a 1 nm Si$_3$N$_4$ buffer layer. Zirconium oxide films grown on these alternate buffer layers showed little change with annealing at high temperatures. However, a similar 900°C annealing step after the addition of a 2 nm Si cap led to decomposition of the ZrO$_2$. These results demonstrate that the presence of excess Si leads to a decomposition reaction of the ZrO$_2$ thin films and that a thin Si$_3$N$_4$ buffer layer may improve thermal stability.

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