

Process-dependent band structure changes of transition-metal (Ti,Zr,Hf) oxides on Si (100)

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In this study, we have deposited Ti, Zr, and Hf oxides on ultrathin (~ 0.5 nm) SiO₂ buffer layers and have identified metastable states which give rise to large changes in their band alignments with respect to the Si substrate. This results in a potential across the interfacial SiO₂ layer, significant band bending, and large shifts of the high- k valence band. The magnitude of the shift differs for the three materials and is dependant on both the SiO₂ buffer layer thickness and annealing temperature. We propose a model where excess oxygen accumulates near the high- k -SiO₂ interface providing electronic states, which are available to electrons that tunnel from the substrate. © 2004 American Institute of Physics. [DOI: 10.1063/1.1639944]

The task of identifying a suitable replacement dielectric for high-performance, low-power devices is complex with many difficulties. Transition-metal (Tm) oxides have received much attention for their large dielectric constants and relatively large band gaps. Zirconium and hafnium oxides, in particular, have been considered. Titanium oxides have also received attention but, due to their smaller band gap, they have generally not received the same consideration as potential replacement dielectrics for field effect transistors (FETs).

The primary goal in choosing a replacement for SiO₂ is to reduce the tunneling current through the gate oxide of a FET while maintaining the channel charge density. There are two main parameters that effect tunneling current: (1) the physical thickness of the dielectric and (2) the barrier height or band offset with respect to Si. Choosing a high- k material with a large dielectric constant can solve the tunneling problem by increasing the dielectric thickness, but these materials often have barrier heights smaller than the traditional SiO₂ on Si, sometimes very much smaller. For instance, TiO₂ has essentially no barrier with respect to the Si conduction band, and electrons would be free to move from channel to gate, through the oxide.¹

Understanding barrier heights and how they can be altered by different process conditions is a critical part of choosing a replacement dielectric material. In this letter, we report an effect that can alter barrier heights by as much as 2.0 eV. We determine the circumstances where the effect occurs and propose a model to explain these large shifts in band structure.

All experiments employed n -type 25 mm diameter Si(100) wafers with phosphorous doping of $\sim 4 \times 10^{18}$ cm⁻³. The doping density is calculated from the lowest value in the resistivity range quoted from the manufacturer. All processing and characterization occurred in UHV conditions. The Si wafers were prepared with a SiO₂ buffer layer by either remote plasma oxidation or remote plasma enhanced chemical vapor deposition. In this study, Tm oxides were formed by electron beam evaporation of a

metal (Ti, Zr, or Hf) onto the SiO₂ buffer layer followed by remote plasma oxidation. The electronic states were then characterized with x-ray and ultraviolet photoelectron spectroscopy (XPS,UPS). A more detailed description of this approach has been presented previously.¹

In characterizing the band offsets of the Tm as-deposited oxides on a SiO₂ buffer, we observed a large shift in the valence band turn-on and all of the oxide core levels when the films were annealed to 500 °C. This effect was found to occur in Ti, Zr, and Hf oxides, with ZrO₂ demonstrating the largest shift. Figure 1 shows UPS spectra for all three oxides in their as-grown state (solid lines) and in their annealed state (dotted). With annealing, the ZrO₂ valence-band maximum (VBM) was shown to shift up to ~ 2.0 eV, while the HfO₂ and TiO₂ shifted by ~ 0.8 eV, depending on process conditions. Accounting for changes in band bending, we deduce the Si-high- k valence band offset (VBO) to be 1.65, 0.95, and 2.05 eV for the as-grown Ti, Zr, and Hf oxides, respectively, and after annealing, the VBO increase to 2.55, 3.0, and 2.75 eV for the respective Ti, Zr, and Hf oxides.

We previously reported the VBO of 2.2 eV for TiO₂ which falls between the shifted and annealed values we observe in this study,¹ and Campbell *et al.* found a VBO of 1.0

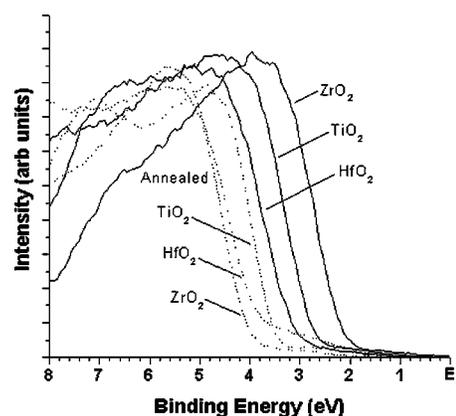


FIG. 1. UPS valence band spectra for Ti, Zr, and Hf oxides with a SiO₂ buffer layer on Si. The solid lines indicate the as-grown state and the dotted lines indicate the annealed state.

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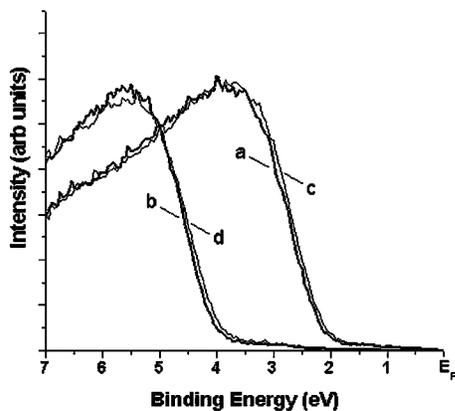


FIG. 2. UPS spectra of a ZrO_2 film with a SiO_2 buffer layer on Si. The spectra were obtained (a) as grown, (b) 500°C anneal, (c) reoxidized, and (d) second 500°C anneal.

eV which is near the value of the as-deposited film.^{2,3} In a study of ZrO_2 on Si (100), Miyazaki *et al.*, utilizing XPS, found a valence band offset of 3.2 eV,^{4–6} which is in reasonable agreement with our measurements of the annealed film. Predictions made by Robertson using the charge neutrality model obtain a VBO of 2.0 and 3.3 eV for TiO_2 and ZrO_2 , respectively.⁷ For HfO_2 Robertson has noted that the charge neutrality model predicts a VBO of 3.4 eV. Sayan *et al.* have used photoemission to measure the VBO of HfO_2 with respect to Si and found values between 3.03 and 3.63 eV,⁸ which is in relative agreement with the predictions and our measurements. However, Yu *et al.* have found that their as-grown HfO_2 films showed a VBO of 2.22 eV,⁹ which is similar to our observations of the as-grown state.

We have explored the origin of this effect through a process of re-exposing the annealed films to the remote plasma oxidation. As shown in Fig. 2 the VBM of the as-grown and reoxidized spectra are essentially identical, as are the two annealed spectra. The core level spectra of the Tm oxide shifted in a similarly consistent way suggesting that the shifts are of electronic, not chemical, origin. Similar films were annealed and characterized in a stepwise fashion at temperatures of 200, 300, 400, and 500°C . The photoelectron spectra shifted gradually at low temperatures and shifted to a greater extent at higher temperatures.

The core levels of the Tm and the Tm oxide-related O 1s core level spectra showed similar shifts to the valence band. An interesting aspect was evident on examination of the SiO_2 related O 1s and Si 2p core levels. The core level spectra associated with the buffer layer shifted to a lesser degree than the Tm oxide core levels and the valence band spectra. Figure 3 shows the O 1s spectra for an as-grown and annealed ZrO_2 film. The strongest spectral feature (at lower binding energy) is associated with the ZrO_2 which, upon annealing, shifted by a magnitude equal to that of the valence band maxima. The weaker feature, at slightly higher binding energy, is associated with the SiO_2 buffer layer, which shifted less than the ZrO_2 component.

We also explored how variations in the thickness of the SiO_2 buffer layer affect the changes in band structure. Buffer layers were prepared with thicknesses of 0.5, 2.0, and 3.5 nm followed by the deposition of 1.2 nm of HfO_2 . Valence band and core level spectra were recorded, and the shift between

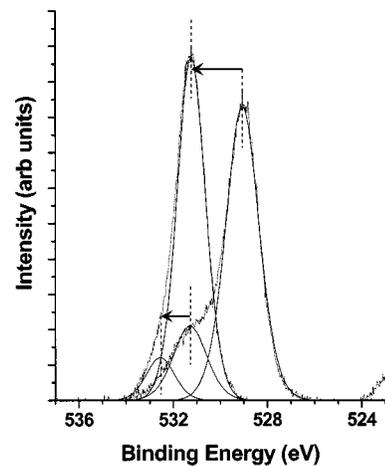


FIG. 3. XPS O 1s core level of an as-grown and annealed ZrO_2 film with a SiO_2 buffer on Si. The larger peaks are associated with the ZrO_2 layer and the smaller peaks with the buried SiO_2 buffer layer. The shifts on annealing (arrows) are larger for the ZrO_2 than the SiO_2 buffer layer.

the as-grown and annealed states was measured. For the 0.5 nm buffer layer, a VB shift of 1.50 eV was measured. The shifts in the core levels and valence band decrease as the buffer layer thickness is increased. Increasing the thickness of the buffer to 2.0 nm resulted in a 1.35 eV shift. A further increase in buffer layer thickness to 3.5 nm resulted in a VB shift of 0.20 eV.

We suggest that the exposure to a remote oxygen plasma (and a high concentration of atomic oxygen) introduces excess oxygen into the high- k material and that this oxygen is in a metastable state where annealing can apparently drive out the excess.

On first examination one might suggest that an interface dipole has formed at the Si-buffer layer interface. However, such a dipole would shift the entire band structure equally, meaning that the SiO_2 and ZrO_2 electronic states would shift by the same magnitude and direction. This was not the observed case; instead the spectra associated with the SiO_2 buffer layer and Tm oxide shifted in the same direction but by a different magnitude, suggesting that there is a potential drop across the buffer layer. We propose that excess negative charge is present near the high- k - SiO_2 interface and that there is consequently a potential across the buffer oxide, between the substrate and the charge layer in the high- k material. Figure 4(a) displays a schematic of the bands of the as-grown film with excess charge at the high- k interface and a potential across the buffer layer, and Fig. 4(b) shows the annealed state with flat bands, no excess charge and no potential over the buffer layer.

Fissel *et al.* have noted similar core level shifts for PrO_2 on Si and have suggested a model, which assumes no interfacial layer of SiO_2 and an epitaxial oxide on the Si substrate.¹⁰ In our case, with the purposeful formation of an interfacial oxide, it is unlikely that our Tm oxides are epitaxial nor is our growth method conducive to forming single crystal oxides. As such, we must explore other possibilities in explaining our observations.

Our results indicate that the total electronic shift falls off as a function of increasing buffer layer thickness; approaching zero as the buffer layer grows past 3.5 nm. If the charge were constant near the interface then the potential difference

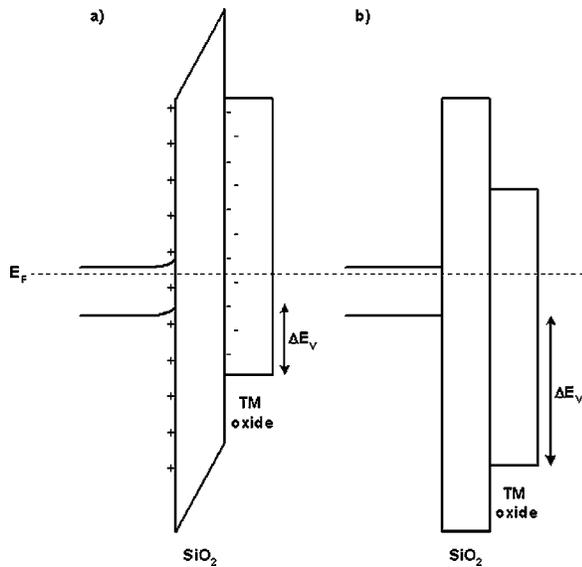


FIG. 4. Schematic diagram of the as-grown (a) and annealed (b) state: (a) excess oxygen near the Tm oxide–SiO₂ interface attracts electrons from the substrate, resulting in a potential across the SiO₂ buffer layer; (b) the oxygen diffuses to vacuum, there are no interface electronic states and the bands become flat. The valence band offset (ΔE_V) can change by up to 2.0 eV with annealing.

across the buffer layer would increase with buffer layer thickness. This is not the observed case, and, in fact, the decreasing potential suggests that the amount of charge decreases with increasing buffer layer thickness. We propose that the charge layer is controlled by a tunneling process from the substrate.

The tunneling probability of an electron through SiO₂ falls off exponentially, with the probability becoming small after 3–4 nm thickness. We suggest that electrons tunnel from the substrate, through the buffer layer, to satisfy the electronic properties of the excess oxygen in the high- k material. The Tm oxides, ZrO₂ in particular, are known to be ionic conductors where the majority ion (oxygen) may move with relative ease.¹¹ We suggest the following as a possible scenario: oxygen diffuses into the high- k dielectric and electrons tunnel from the substrate, through the SiO₂ buffer layer to satisfy the electronic states of the excess oxygen. This results in a potential across the buffer oxide and a shift in the band structure of the high- k material. When the source of oxygen is removed, the oxygen diffuses from the interface and escapes to vacuum. This diffusion of oxygen can be accelerated with annealing.

To estimate the charge needed to produce the measured shifts, we treat the buffer layer as a simple dielectric filled capacitor with thickness of $d=2.0$ nm, a dielectric constant of $k=3.9$ for SiO₂ and a voltage of $V=1.0$ V. From this we determine a charge density of $\sim 1 \times 10^{13}$ cm⁻². We can likewise estimate the positive charge in the Si from the change in band bending at the Si substrate. We use $N_s = \sqrt{2k\epsilon_0 N_D V/q}$ to calculate the charge density, where N_s is the surface charge density, $N_D = \sim 4 \times 10^{18}$ cm⁻³ is the bulk doping density of the Si, q is the charge of an electron, ϵ_0 is the permittivity of free space, $k=12$ is the dielectric constant of Si, and $V=0.3$ V is the change in band bending. This gives a charge density of $N_s = 4 \times 10^{12}$ cm⁻². The charge may not be completely localized at the high- k -SiO₂ interface or other conditions may exist to explain the discrepancy in the two calculations.

This study has demonstrated that the electronic structure of the Tm oxide–SiO₂ interfaces can be significantly influenced by process conditions. The excess oxygen state of this interface is metastable and would certainly lead to time dependent device characteristics. It remains to be seen whether processing approaches could be employed to improve the device characteristics. Correlated interface and device studies are suggested to quantify the effect of the charge layers and internal fields.

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