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Band gap and band offsets for ultrathin $(HfO_2)_x(SiO_2)_{1-x}$ dielectric films on Si (100)

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Energy band profile of ultrathin Hf silicate dielectrics, grown by atomic layer deposition, was studied by using x-ray photoelectron spectroscopy and reflection electron energy loss spectroscopy. The band gap energy only slightly increases from 5.52 eV for $(HfO_2)_{0.75}(SiO_2)_{0.25}$ to 6.10 eV for $(HfO_2)_{0.25}(SiO_2)_{0.75}$, which is much smaller than 8.90 eV for SiO_2. For ultrathin Hf silicate dielectrics, the band gap is mainly determined by the Hf 5*d* conduction band state and the O 2*p* valence band state. The corresponding conduction band offsets are in the vicinity of 1 eV, which satisfies the minimum requirement for the carrier barrier heights. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2355453]

Rapid progress in complementary metal-oxide semiconductor integrated circuit technology demands for greater integrated circuit functionality and performance, which in turn requires an increased circuit density. This rapid shrinkage of transistor feature size has forced the size of gate oxides to be less than subnanometers. Nevertheless, SiO_2 as gate dielectric will soon reach its fundamental limit owing to an unacceptably high leakage current,[1,2] which implies that SiO_2 should be replaced by other high-*k* gate dielectrics eventually. Among the numerous alternative high-*k* materials, HfO_2, ZrO_2, and their silicates[3–5] have received much attention as viable candidate materials. Especially, high-*k* alloys are proposed as promising gate dielectrics. The oxygen in Hf silicate is covalently bonded and it does not have high ion diffusivity, whereas oxygen ion diffusivity in transition metal oxides is high because of their ionic bond nature.[1] By considering all of the requirements, Hf silicate seems to be a reasonable candidate material, and, in fact, Hf silicate has a variety of desirable properties, which includes reasonable stability against crystallization and phase separation, superior interface thermal stability in contact with either a Si substrate or a poly-Si gate electrode, and excellent electrical properties.[1,6,7]

In this letter, we made Hf silicate $(HfO_2)_x(SiO_2)_{(1-x)}$ thin films with various hafnium contents via atomic layer deposition (ALD), and focused on determining the band gap and band offsets for 3 nm $(HfO_2)_x(SiO_2)_{(1-x)}$ dielectric thin films on Si (100).

Reflection energy electron loss spectroscopy (REELS) was shown to be a good tool for us to investigate the band gap for ultrathin dielectric films,[8] because the low energy electron energy loss spectrum reflects the valence and conduction band structures of the samples. Hence, we make use of REELS analysis to investigate the band gap of Hf silicate films with differing compositions. In order to interpret the composition dependence of the band alignment in a Hf silicate dielectric layer, we combined REELS analysis with x-ray photoelectron spectroscopy (XPS) analysis. XPS analysis can provide us important information on the valence band offset.

Hf silicate gate dielectric thin films, whose stoichiometry was given by $(HfO_2)_x$ $(SiO_2)_{(1-x)}$, were deposited by atomic layer deposition. Prior to thin film deposition, *p*-type Si(100) substrate was cleaned chemically by the Radio Corporation of America (RCA) method.[9] SiO_2 and HfO_2 films were grown at temperatures below 280 °C using tris(dimethylamido)silane and tetrakis(ethylmethylamido)hafnium, respectively, as precursors. O_3 vapor served as the oxygen source and N_2 was supplied as the purge and carrier gas.[10] The SiO_2-incorporated Hf–Si–O was grown by the alternating ALD process, repeating many cycles for HfO_2 and SiO_2 to mix SiO_2 content in a controlled manner. HfO_2 mole fraction was varied by amounts of $x=0.75$, 0.5, and 0.25. The thickness of $(HfO_2)_x(SiO_2)_{1-x}$ films was 3 nm. The film composition was determined by utilizing XPS. Subtracting the Shirley background to correct for effects of inelastic electron scattering[11] and considering the sensitivity factor, corresponding ratios of Hf/Si are found to be 3:1, 1:1, and 1:3. According to Auger depth profile, not shown here, the thin film is distributed uniformly. XPS and REELS measurements were performed with a VG ESCALAB 210 equipment. The chemical states of thin silicate films were obtained using monochromatic Al *Kα* x-ray source (1486.6 eV). The binding energies of the spectra were calibrated by the position of the substrate Si 2*p* peak at 99.3 eV.[12] REELS was measured with the primary electron energy of 1000 eV for excitation and with the constant analyzer pass energy of 20 eV. The full width at half maximum of the elastic peak was 0.8 eV.

Figure 1(a) shows the Hf 4*f* photoelectron spectra obtained from the as-deposited films with the ratio of Hf to Si given by 3:1, 1:1, and 1:3. The comparison of the peak intensity shows the change of the Hf contents in films. Hf $4f_{7/2}$ peaks in Hf silicates are located at 17.9, 18.1, and 18.3 eV, on the binding energy scale for the three different composition films. Wilk *et al.* reported Hf 4*f* peaks in Hf silicate appearing at ~18.2 eV,[13] which is about 1.0 eV higher than that in HfO_2. It is due to the fact that the charge transfer out

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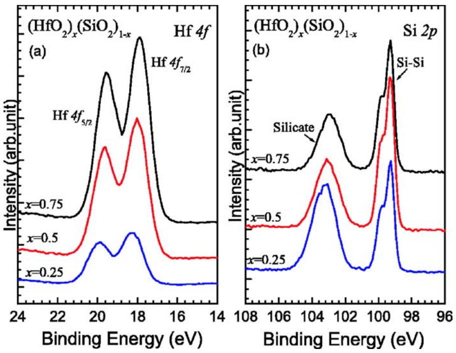

FIG. 1. (Color online) Hf 4*f* (a) and Si 2*p* (b) photoelectron spectra for 3 nm Hf silicate: $(HfO_2)_x(SiO_2)_{1-x}$ with x equal to 0.75, 0.5, and 0.25.

of Hf is larger in Hf silicate than in HfO_2 because the electronegativities of both Si and O are larger than that of Hf. So these spectra indeed indicate the existence of silicate structure. It is observed that the Hf 4*f* doublet is somewhat broader with more SiO_2 incorporated, while Hf silicate with $x=0.75$, having high HfO_2 fractions, shows sharper Hf peaks.

The Si 2*p* photoelectron spectra also reveal the formation of a silicate film. In Fig. 1(b), the Si 2*p* electron peak shifted to a higher binding energy with reduced Hf content. The Si 2*p* peak located at 99.3 eV originates from the Si substrate. Other peaks, centered around 102–102.7 eV,[12] originate from the Hf silicate film, and they are associated with Hf–O–Si bond. Hf silicate peak position is located at a lower energy compared with Si–O bond at 103.3 eV. The shift to low binding energy moving from Si^{4+} in SiO_2 to Si^* in silicate oxidation state should be due to the change of Si's second-nearest neighbor from Si to Hf by introducing more Hf atoms.[14] In addition, since Hf has a lower Pauling's electronegativity compared to that of Si, there is an enhanced charge transfer from Hf atom to silicate Si–O bond as compared to the O–Si–O situation. This results in a shift of the Si 2*p* core level in Si–O–Hf to a lower binding energy relative to SiO_2 and the shift increasing with the number of Hf second-nearest neighbors. All this chemical information, obtained via the XPS analysis, shows the composition dependence of bond states and assures the deposition of Hf silicate.

This excessive energy shift caused by the incorporation of HfO_2 into SiO_2 indicates that charge changes, induced by incorporation of HfO_2, make SiO_2 with different covalences. From the XPS peak energy shift, we can argue that the level of the Hf *d* state depends sensitively on the charge transfer to the surrounding O atom.

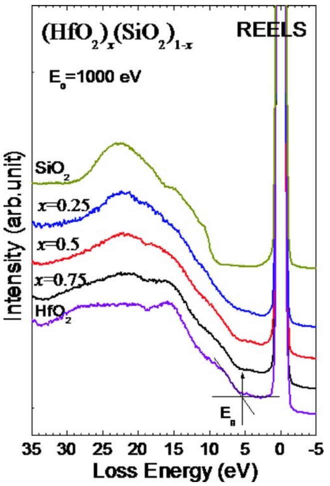

FIG. 2. (Color online) REELS spectra for 3 nm HfO_2, SiO_2, and Hf silicate thin films, using primary electron energy of 1000 eV. The band gap energy E_g is defined as the threshold energy of band-to-band excitation.

In order to investigate the change in the band gap, owing to composition variation in ultrathin Hf silicate films, we have made use of the REELS and found the electronic structure near the band gap at the atomic level.[15] We can determine the band gap values of dielectric films from an energy loss signal, which is obtained by drawing a linear fit line with a maximum negative slope from a point near the onset of a loss signal spectrum to the background level. The crossing point gives the band gap value.[16]

Figure 2 shows the REELS spectra for Hf silicate as a function of composition. For comparison, REELS spectra for ultrathin HfO_2 and SiO_2 dielectric films were shown. The E_g values are 5.50 (Ref. 17) and 8.90 eV for the ultrathin HfO_2 and SiO_2 dielectric films, respectively, and they show a slight change with increasing Hf content. The obtained band gap values are shown in Table I. Here we marked the E_g values of HfO_2 and SiO_2 for comparison. For HfO_2 thin film, we can see the bulk plasmon peak at 16 eV and the surface plasma peak at 9 eV, whereas for SiO_2 the bulk plasmon appears at 23 eV with a shoulder at 15 eV. With decreasing Hf composition, the plasmon peak shape becomes more SiO_2-like. In addition, the intensity for the HfO_2 characteristic loss peak also decreases upon decreasing Hf composition. Thereby, from the energy loss spectra, we can observe the phase change for the films with different compositions. The variation of composition changes the electronic structure, which in turn affects the band gap value. So the change in E_g for these Hf silicate films mainly originates from the slight difference in electronic structure.

It is well known for SiO_2 that the conduction band minimum (CBM) states are formed from the Si extended *s* states, whereas the valence band maximum (VBM) states are formed from the nonbonding O 2*p* state.[18] For the transition metal HfO_2, the CBM states are mostly composed of Hf localized 5*d* state,[19] and the VBM states are mostly composed of O 2*p* states. In Hf silicate dielectric films, when an extended *s* state in SiO_2 is compared to localized *d* states in HfO_2, their energy will be affected by the energy level of the lowest conduction band state. It is also known that the coordination-based mechanism[20] plays an important role in electronic structure. When introducing HfO_2 into SiO_2, the

TABLE I. Band gap and band offset values for the ultrathin gate oxide films.

Energy (eV)	HfO_2	$Hf_{0.75}Si_{0.25}O_2$	$Hf_{0.5}Si_{0.5}O_2$	$Hf_{0.25}Si_{0.75}O_2$	SiO_2
E_g	5.50	5.52	5.70	6.10	8.90
ΔE_v	2.86	3.38	3.42	3.81	4.36
ΔE_c	1.54	1.04	1.18	1.19	3.44

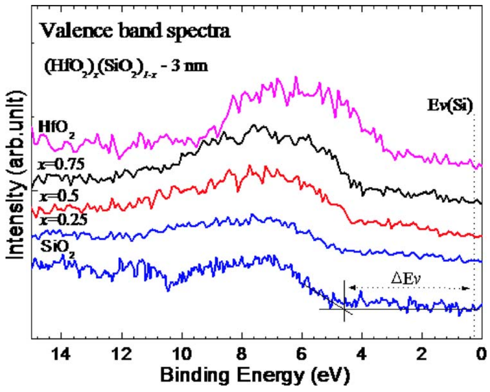

FIG. 3. (Color online) Valence band spectra for 3 nm HfO_2, SiO_2, and Hf silicate thin films. The dotted line denotes the top of the Si valence band energy E_v(Si). The valence band offset energy ΔE_v is defined as the energy difference between the valence band maximum of the dielectrics and that of Si.

Hf–Si–O bonds are formed by breaking up of the continuous covalent network. It is clear that the nonbonding O 2*p* state is on the top of the valence band, and thus the contribution of Hf and Si to the density of states for the conduction band is proportional to their composition. For Hf-rich silicate film, the band gap value is smaller than that for SiO_2 and is similar to HfO_2. It means that the energy level of the *d* electron is lower than the *s* electron energy level, and then, as more and more Hf atoms are added to the SiO_2, the Hf induced states would fill in and broaden to become the lowest conduction band of Hf silicate. The E_g in $(HfO_2)_{0.75}(SiO_2)_{0.25}$ is dominated by the O 2*p* and Hf 5*d* states. The slight increase in E_g for $(HfO_2)_{0.25}(SiO_2)_{0.75}$ could be due to the low density of Hf 5*d* electronic states in the film and the overlap of the Si 3*s* state and the localized Hf 5*d* state, which was caused by O coordination changes within the alloy.

As shown in Table I, E_g slightly increases as the Hf composition decreases. In Hf silicate, it also indicates that the CBM states are formed from the Hf 5*d* state or Si 3*s* state, whereas the VBM states are still from the O 2*p* state. We propose that the CBM energy level would be slightly changed by the coordination number change in the Hf atom. The Si *s* state may mix with the Hf 5*d* state to form a conduction band. When the *x* value is higher than 0.75, the band gap is nearly unchanged and the same as that of HfO_2. We can assume that the CBM is completely determined by Hf 5*d* states. Our analysis suggests that E_g of the Hf silicate film is mainly dominated by the transition metal electron level, and thus the silicate band gap can be adjusted by Hf composition.

To determine the valence band offset at the ultrathin $(HfO_2)_x(SiO_2)_{1-x}$/Si interface, the valence band spectra of Hf silicate together with HfO_2 and SiO_2 films are shown in Fig. 3. The valence band maximum is determined by extrapolating the leading edge of the valence band spectrum to the base line. The crossing point is taken to be the valence band maximum. From the energy difference between the top of the ultrathin oxide valence band and the top of Si(100), the valence band offset ΔE_v can be obtained.[21] The valence band offsets (ΔE_v) are 3.38, 3.42, and 3.81 eV for $(HfO_2)_{0.75}(SiO_2)_{0.25}$, $(HfO_2)_{0.5}(SiO_2)_{0.5}$, and $(HfO_2)_{0.25}(SiO_2)_{0.75}$, respectively. A little shift in the valence band spectra can be related to the O coordination number change in the oxide films with composition variation. In addition, the corresponding conduction band offsets (ΔE_c) are also obtained by the method described in the reference.[21] Values for the band alignment are summarized in Table I for these ultrathin gate oxide films. ΔE_c for these Hf silicate films are in the vicinity of 1 eV. It satisfies the minimum requirement for the barrier heights of over 1 eV in devices. We note that the conduction band offsets for Hf silicate films have nothing to do with the composition change, even though there is a slight increase in the band gap with the increasing of SiO_2 contents. This implies that the increase in the band gap is counteracted by the increase in the valence band offset. The barrier heights for electrons and holes are asymmetric in these $(HfO_2)_x(SiO_2)_{1-x}$ dielectrics.

In summary, the band alignment evolution of Hf silicates as a function of composition was demonstrated by REELS and XPS analyses. It shows slight dependence on the compound composition and increases slightly with decreasing Hf contents. It was found that the band gap slightly increases from 5.52 eV for $(HfO_2)_{0.75}(SiO_2)_{0.25}$ dielectric thin film to 6.10 eV for $(HfO_2)_{0.25}(SiO_2)_{0.75}$ dielectric thin film. For the Hf-rich silicate film, E_g is mainly determined by the Hf 5*f* states and O 2*p* states. The band gap values can be controlled with appropriate Hf metal composition to have the optimum value. REELS analysis turns out to be a powerful and convenient method to obtain information on electronic structure near the band gap of a film. We found that the Hf silicates are promising candidates for alternative gate dielectric materials because they have adequate band gaps to ensure a sufficient conduction band offset to Si. Thus we anticipate that the Hf silicates will be used as alternative gate dielectrics for advanced Si devices in the near future.

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