Temperature Dependence of Band Alignment in Ultra-thin HfO$_2$ /Si Interface

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The thermal stability and band alignment of HfO$_2$ thin film grown by atomic layer deposition (ALD) were studied by using X-ray photoelectron spectroscopy (XPS) and reflection electron energy loss spectroscopy (REELS). Band gaps and valence band offsets for HfO$_2$ thin film were estimated from the onset energy of REELS and valence band spectra of XPS. The changes in conduction band offset, valence band offset and band gap were obtained as a function of annealing temperature. HfO$_2$ thin film is found to have asymmetric barrier for electrons and holes and there is a little increase in band gap values after annealing treatment.

INTRODUCTION

For the last three decades, we witnessed the tremendous progress in the semiconductor industry owing to the continued scale reduction achieved in all devices. When the dimension of a semiconductor device is less than 50 nm with the equivalent thickness of gate oxide layer being less then 1.3 nm, SiO$_2$ faces a formidable challenge in further scale reduction because it will soon arrive the fundamental limit, which originated from quantum tunneling phenomena.[1,2] To avoid quantum tunneling, high-*k* (high dielectric constant) gate dielectric layer, which can reduce leakage currents while improving device properties,[3] is needed. Transition metal oxides such as HfO$_2$, ZrO$_2$ and their compounds with either SiO$_2$ or Al$_2$O$_3$ have been proposed as alternative high-*k* gate dielectrics.[2,3] As a candidate material, it should also have proper band gap and band alignment. To reduce direct tunneling currents, we should clearly know about the band offsets between the oxide thin film and Si, which define the barrier height for electrons and holes. In semiconductor device fabrication process, there is a necessity for high temperature annealing treatment. So we needs to understand the band profile change trend related to annealing temperature. Thus, in this paper, XPS and REELS measurement were used to determine the band gap and the band alignment as a function of annealing temperature.

EXPERIMENT

HfO$_2$ thin film was grown by atomic layer deposition (ALD). Prior to high-*k* film deposition, a *p*-type Si substrate with a resistivity of 2-5Ωcm was cleaned using Radio Corporation of America method [4]. HfCl$_4$ was used as a precursors and H$_2$O vapor served as the oxygen source. The film was grown in N$_2$ ambient, which was supplied as the purge and carrier gas. The growing temperature was below 300°C. The physical thickness of deposition was 30 Å. Thin films were in-situ annealed from 600°C to 950°C in 100°C steps for 5 minutes in the analysis chamber. XPS analysis was employed using Mg *Kα* source (1253.6 eV) and REELS was obtained using 500 eV primary electron beam.
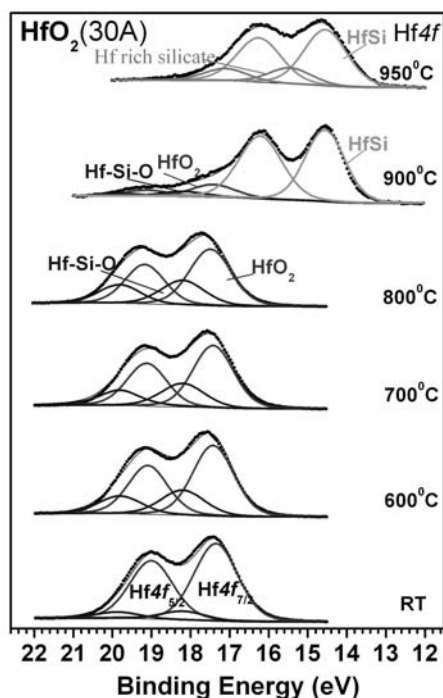
Fig. 1 Hf *4f* fitting results for HfO$_2$ film before and after various annealing temperatures
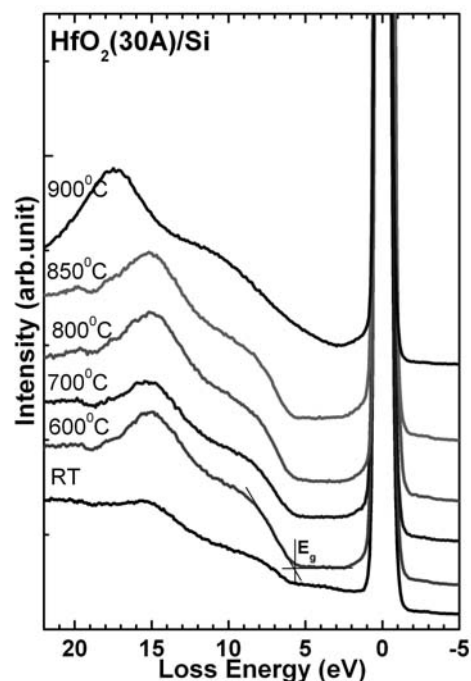

Fig.2 Reflection electron energy loss spectra for HfO$_2$ as a function of annealing temperature

RESULTS AND DISCUSSION

Figure 1 shows Hf *4f* spectra for HfO$_2$ (30 Å) thin film as a function of annealing temperature. Hf *4f* spectra were deconvoluted into two Gaussian-Lorentzian features corresponding to HfO$_2$ ($4f_{7/2}$: ~17 eV) and Hf silicate ($4f_{7/2}$: ~18.2eV). After 600°C annealing, the peak position shifted to the higher binding energy, due to interfacial reaction produced by the formation of more Hf silicate. After 900°C annealing, HfO$_2$ degraded into HfSi, which is located at ~14.5 eV. We observed here the coexistence of Hf-Si-O, Hf-O and Hf-Si. The peak center moved toward lower binding energy, because of Hf-Si-O bond breaking and increasing Hf-Si bonding with consuming Hf-silicate phase. Corresponding to these chemical state changes, it is meaningful to evaluate the temperature dependence of the band gap for HfO$_2$ thin film.

In oxide thin films, the energy loss spectrum of O *1s* photoelectrons has been commonly used to estimate the band gap energy, but it can not be used for HfO$_2$ thin film because Hf *4s* core level is located at the vicinity of O *1s* loss energy region, which may interferes the band gap determination from O *1s*

energy-loss spectra [5]. In this work, the reflection energy loss spectra [6] were used to obtain the band gap.

Figure 2 gives the reflection energy loss spectra for HfO$_2$ film as a function of annealing temperature. Here, the broad peak at about 15 eV is due to plasmon loss, and the onset of loss spectrum is due to an electron-hole excitation. The band gap energy can be defined by drawing a line with a maximum negative slope from the onset of loss spectrum to the background level, then the cross point indicates the band gap value [5]. The band gap for the as-deposited HfO$_2$ was estimated to be 5.52 eV, which was consistent with the values reported in other literatures [7]. After 600°C annealing, the band gap value increased to 5.78 eV. It is known that the crystallization of HfO$_2$ started at the low temperature of 500°C [8]. So the change in the band gap can be related to the phase transition. As was mentioned in XPS data, there was the formation of Hf-Si-O after annealing. So the changes in the band gap value may also be due to the formation of Hf-O and Hf-Si-O in this film. Two different bonds of Hf-O in film and Hf-Si-O existed at the interface. The variation in
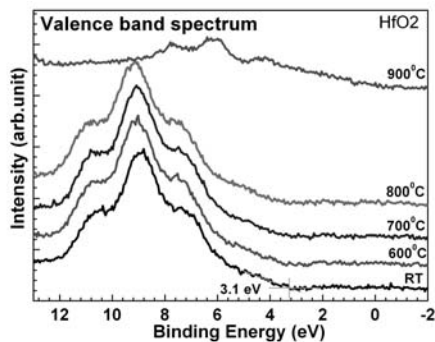
Fig.3 Valence band spectra for HfO_2 (30 Å)/Si thin film before and after annealing

bond length and bond angle would affect electronic structure, which lead to band gap change. Generally, the band gap of transition metal oxide is between the O *2p* valence band states and the conduction band of metal *d* state [9]. From the temperature dependence of loss spectrum, the band gap of annealed HfO_2 was determined. After annealing at the temperature of 600°C, 700°C and 800°C, the estimates of the band gap energy E_g are 5.78, 5.82 and 5.85 eV, respectively. As shown in Fig.1, the interfacial reaction occurred at 600°C and Hf-Si-O content also increased with increasing annealing temperature. The formation of Hf-Si-O will change the O coordination of Hf atom. Therefore it changes the O *2p* energy level, which may induce the variation in the band gap. In addition, the lattice mismatch strain was also regarded as one of the reasons [10]. The strain at the interface is more important in ultra-thin film than in thick film. The present results show that the band gap of Hf silicate is larger than that of HfO_2.

The valence band spectra were also measured to obtain valence band offsets. The valence band maximum is determined by extrapolating the leading edge of valence band spectrum to the base line. The crossing point is taken to be the valence band minimum (VBM) [5]. Figure 3 shows the valence band spectra of HfO_2 on Si substrate. From the energy difference between the VBM of HfO_2 and Si, the valence band offset ΔE_v can be obtained. The VBM of Si was obtained by measuring the valence band spectrum of *p*-Si bulk. The valence band energy E_v(Si) is expected to be 0.24 eV. From the spectrum for as-deposited HfO_2, E_v(HfO_2) is 3.1 eV. So the valence band offset, between HfO_2 and Si, ΔE_v is

2.86 eV. This value is also consistent with other reported value. When the annealing temperature increases from 600°C to 800°C, ΔE_v increased a little bit from 3.26 eV to 3.36 eV. The valence band spectrum contains several regions, but VBM of this oxide is defined as the onset of O *2p* bond. So the O change will affect ΔE_v value. So the formation Hf-Si-O produces the O-O separation, which differs from that in Hf-O bond. The change in O-O separation will induce the overlap between the O *2p* orbital changes and hence changes the valence band. In addition, the shift of VBM derived from O *2p* state may be related to the change in oxygen coordination in HfO_2 film after annealing. In practice, the local bonding at the interface could add an extra interfacial dipole, which will also modify the band offset.

Combining the results of the band gap and valence band offset values, the electron barrier heights (conduction band offset) can be obtained. The conduction band offsets ΔE_c can be calculated through the following expression: $\Delta E_c = E_g(oxide)-E_g(Si)-\Delta E_v(oxide/Si)$. The conduction band offset was estimated to be 1.50 eV, 1.54 eV, 1.44 eV, 1.37 eV at room temperature, at the annealing temperature of 600°C, 700°C, 800°C, respectively. The electronic band structures for as-deposited and 800°C annealed HfO_2 thin films are shown in Fig. 4. Up to 800°C, carrier barrier heights over 1 eV satisfy the requirement for a device. Nevertheless, it showed the asymmetric barrier for electrons and holes.

CONCLUSION

The chemical state changes and band offsets in HfO_2 thin films have been studied as a function of annealing temperature. The band gap was estimated from the reflection electron energy loss spectrum. After annealing up to 800°C, HfO_2 showed a little increase in E_g values. In addition, valence band offset was obtained from the valence band spectra of XPS. The conduction and valence band offsets were observed as a function of temperature. After annealing at 800°C, the band offset for HfO_2 film is asymmetric and barrier height for electron remained over 1 eV, which satisfy the basic requirement for a device. But it is somewhat asymmetric. Perhaps, we
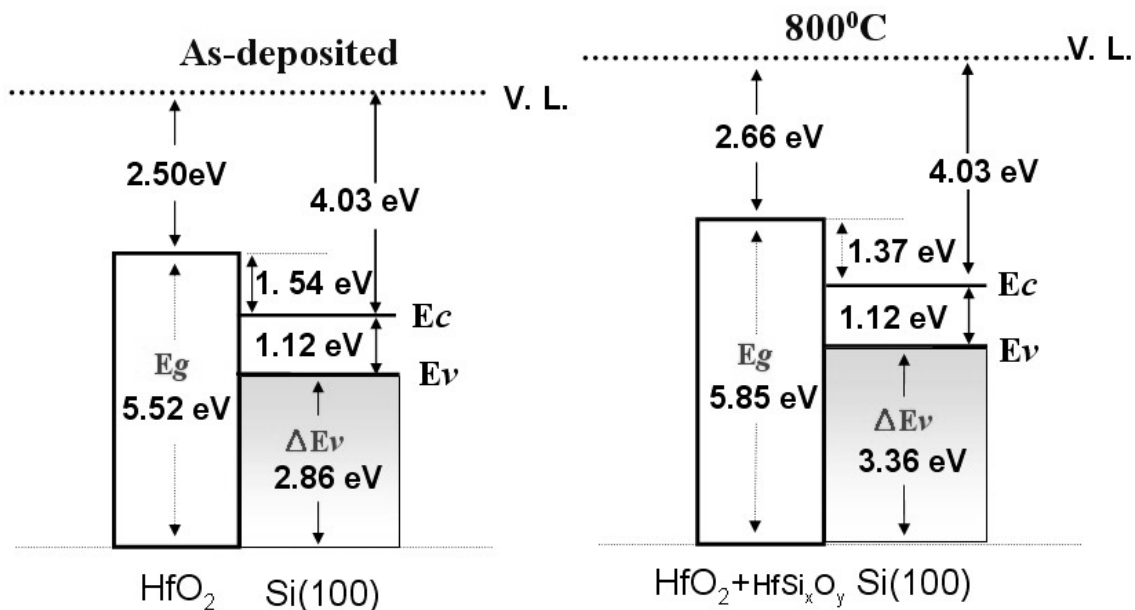
Fig. 4 Band profile for HfO$_2$ as-deposited and after 800°C annealing

can improve this asymmetric barrier height by other method, such as compounding other metal oxide in the near future.

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