Band alignment and optical properties of \((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) gate dielectrics thin films on \(p\)-Si (100)

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\((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) dielectric films on \(p\)-Si (100) were grown by atomic layer deposition method, for which the conduction band offsets, valence band offsets and band gaps were obtained by using X-ray photoelectron spectroscopy and reflection electron energy loss spectroscopy. The band gap, valence and conduction band offset values for \((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) dielectric thin film grown on Si substrate were about 5.34, 2.35 and 1.87 eV, respectively. The band alignment is similar to that of \(\text{ZrO}_2\) thin film. In addition, The dielectric function \(\varepsilon(\mathbf{k},\omega)\), index of refraction \(n\) and the extinction coefficient \(k\) for the \((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) thin films were obtained from a quantitative analysis of REELS data by comparison to detailed dielectric response model calculations using the QUEELS-\(\varepsilon(\mathbf{k},\omega)\)-REELS software package. These optical properties for \((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) thin films are similar to that of \(\text{ZrO}_2\) dielectric thin films.

1. Introduction

High-\(k\) dielectric materials have been intensively investigated as alternative gate dielectrics to \(\text{SiO}_2\) for application in advanced semiconductor devices in recent years [1]. Among the prominent candidates in high-\(k\) materials, amorphous Zr and Hf based complex oxides have been largely studied due to their composition-tunable structure and electrical properties [2,3]. In contrast to the transition metal (TM) and rare-earth (RE) silicates and aluminates, the binary alloy between TM and RE oxide or two different TM or RE oxides had also been investigated to improve properties. Both terminated oxides have high-\(k\) and suitable wide band gap [4,5]. The \((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) dielectrics also attracted some attention and were frequently explored [6]. It has been reported that HfO\(_2\) addition into \(\text{ZrO}_2\) thin film exhibited improved electrical properties. There are some benefits of Hf addition into \(\text{ZrO}_2\), e.g., HfO\(_2\) has a chemical structure similar to that of \(\text{ZrO}_2\) and completely miscible in \(\text{ZrO}_2\) [7]. The primary goal of using high-\(k\) dielectrics as alternatives to \(\text{SiO}_2\) is to reduce tunneling currents through the gate oxides. Hence, band alignment is one of the fundamental physical properties in characterizing the gate dielectrics. An adequate large band gap and sufficient barrier height are necessary for any alternative high-\(k\) material [8]. Asymmetry in the barrier heights between holes and electrons is a potentially significant limitation in the operation of CMOS devices and their reliability. We need to identify the band gap and band offsets for the dielectrics on a nanometer scale special resolution. How the energy band structure of Zr compounds aligns with Si is of fundamental importance because it affects the performance of transistors, e.g., electrical properties. In addition, quantitative optical properties are playing increasingly important roles in electronic structure studies of materials. The study of optical properties for the nano-scale dielectrics is also necessary.

In this paper, we investigated Zr based dielectrics with the thickness in nanometer range. We compared the band gap and band alignment of \((\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}\) thin film with \(\text{ZrO}_2\) thin film by combining reflection electron energy loss spectroscopy (REELS) and X-ray photoelectron spectroscopy (XPS) measurement to gain more insight into the band alignments for these dielectrics.
Furthermore, we obtained the dielectric function and optical properties of (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ and ZrO$_2$ thin films for comparison by a quantitative analysis of REELS spectra.

2. Experiment

(ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film was grown on p-Si (100) substrate by atomic layer deposition (ALD) method. Prior to growing a mixed oxide film, a p-type Si substrate was cleaned by using the Radio Corporation of America (RCA) method. Hf[N(CH$_3$)(C$_2$H$_5$)]$_4$ and Zr[N(CH$_3$)(C$_2$H$_5$)]$_4$ were used as precursors, and O$_3$ vapor served as oxygen source. The film was grown in N$_2$ ambience, which was supplied as the purge and carrier gas. The growing temperature was below 300 $^\circ$C. The physical thickness of deposition was 7 nm.

XPS and REELS spectra were obtained by using the VG ESCALAB 210 spectroscopy. Spectra were measured using Mg K$\alpha$ source and with the pass energy of 20 eV. XPS binding energies were referenced to C 1$s$ peak of hydrocarbon contamination at 285 eV. The composition of compounds was determined via XPS analysis using the relative sensitivity factor, 1.084, of the ratio of (ZrO$_2$)$_2$ to (HfO$_2$)$_2$, which was obtained from standard (ZrO$_2$) and (HfO$_2$) thin films. REELS were measured with the primary electron energy of 1.0, 1.5 and 1.8 keV for excitation and with the constant analyzer pass energy of 20 eV. The full width at half maximum (FWHM) of the elastic peak was 0.8 eV.

3. Results and discussion

Figure 1(a) shows the Zr 3$d$ photoelectron spectra, whereas Fig. 1(b) shows the valence band spectra for (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film and the ZrO$_2$ thin film spectra were included for comparison. One of Zr 3$d$ spectra was characteristic of the fully oxidized state of Zr$^{4+}$ for ZrO$_2$. It has the binding energies of Zr 3$d$$_{5/2}$ and Zr 3$d$$_{3/2}$ peaks measured at 182.4 and 184.8 eV, respectively. Two peaks have the spin-orbital splitting of 2.4 eV [9]. For the (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film, the Zr 3$d$$_{5/2}$ peak located at 182.1 eV was at a lower energy relative to that of ZrO$_2$. Since the electronegativity difference between Hf (1.30eV) and O (3.44eV) is larger than that between Zr (1.33eV) and O (3.44eV) [10], the formation of Hf-O bonds would be preferred rather than the formation of Zr-O bonds for (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film. This resulted in the shift of the Zr 3$d$ core level in (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film to a lower binding energy relative to ZrO$_2$ thin film.

To obtain the valence band offset at the dielectric and Si interface, the valence band spectra were measured to determine the valence band maximum (VBM). The valence band spectra are shown in Figure 1 (b). The VBM was determined by using the same method described in our previous work [9,11]. From the energy difference between the VBM of the gate dielectric and Si, the valence band offset was obtained. Valence band maximum of p-Si bulk is positioned at 0.24 eV. Here we do not take into account any possible band bending in the silicon with the oxide grown on top of the Si. The valence band offset of (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film shows the same valence band offset as that of ZrO$_2$ thin film with an accuracy of 0.05 eV.
For (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film, the conduction band offset was 1.87 eV, which is similar to that of ZrO$_2$ thin film. A sufficiently large barrier height for the electrons was obtained in (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ thin film. The band alignment for this dielectric was shown in figure 3. We also showed the band alignment of ZrO$_2$ and HfO$_2$ thin films for comparison [9,11]. Through the identification of band alignment for these gate dielectrics, we noticed that the barrier heights for electrons and holes were more symmetric for (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ and ZrO$_2$ thin films on Si. Adequate large barrier heights for (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric thin film suggests it could be a better alternative to SiO$_2$ thin film. The band alignment of (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric was similar to that of ZrO$_2$ dielectrics. A roughly symmetrical offsets at the valence and conduction bands were found for (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric, which is desirable for an idea gate dielectric.

We have also studied the optical properties of the (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric thin film by quantitative analysis of the REELS spectrum by using the Tougaard-Yubero QUEELS-$\varepsilon$(k,\omega) - REELS software package [13]. The experimental inelastic scattering cross section from the measured REELS spectra was obtained from the QUASES-XS-REELS software. Comparison of the theoretical inelastic cross section to that of experimental inelastic scattering cross section allows us to determine the dielectric function of the (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric thin films. The theoretical inelastic-scattering cross section was calculated from the dielectric response theory [14]. In this model, the response of the material to a moving electron is described by the dielectric function $\varepsilon$, which is conveniently described by the energy loss function (ELF) $\varepsilon(k,\omega)$. To evaluate the ELF, we parameterized it as a sum of Drude-Lindhard type oscillators, [14,15] given by

$$\varepsilon(k,\omega) = \theta(\hbar\omega - E_g) \sum_{i} \frac{A_i \gamma_i \hbar \omega}{(\hbar^2 \alpha_{i0}^2 - \hbar^2 \omega^2)^2 + \gamma_i^2 \hbar^2 \omega^2},$$

where the dispersion relation is given in the form

$$\alpha_{i0}^2 = \hbar^2 \omega_{i0}^2 + \frac{\hbar^2 k_i^2}{2m}.$$ Here, $A_i$, $\gamma_i$, $\hbar \omega_{i0}$ and $\alpha_i$ are the oscillator strength, damping coefficient, excitation energy and momentum dispersion coefficient of the $i$th oscillator, respectively. The step function $\theta(h\omega - E_g)$ is included to simulate a possible energy gap, $E_g$, which was estimated from the onset of energy loss in the REELS data (Figure 2). The parameters in the ELF were determined via a trial-and-error procedure, until a satisfactory quantitative agreement between the experimental and theoretical inelastic scattering cross section was reached. The parameters were determined from the REELS spectra for primary energies of 1.0, 1.5 and 1.8 keV.

Figure 4. shows the experimental $\lambda K_{exp}$ (line) from REELS spectra, which is compared with the theoretical $\lambda K_{te}$ (dot) by using the QUEELS-$\varepsilon(k,\omega)$ - REELS software. The parameters in the ELF were determined via a trial-and-error procedure, until a satisfactory quantitative agreement is reached. Note that in all the calculation, the same ELF was used for all energies. The dielectric loss functions for (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric thin films were obtained from REELS spectra for the primary electron energies of 1.0, 1.5 and 1.8 keV.
Figure 4. Experimental inelastic cross section $\lambda K_{\exp}$ (solid line) obtained from REELS data compared to theoretical inelastic cross section $\lambda K_{\text{sc}}$ (dotted line with empty circles) evaluated using the simulated energy loss function.

Table 1. Parameters in the model energy loss functions of $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ and ZrO$_2$ thin films on p-Si (100) substrates that give the best fit overall to the experimental cross sections at 1.0, 1.5, and 1.8 keV.

The resulting oscillator parameters of ELF for the $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ and ZrO$_2$ dielectric thin films are similar [12, 16]. However, there is a shift for $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ dielectric at energy lower than 40 eV as indicated by the peak overlapping with the ELF of HfO$_2$ thin films. From this analysis, we conclude that the electronic structure of $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ dielectric is mainly contributed from that of ZrO$_2$ even though we cannot rule out the effect of HfO$_2$ dielectric. The loss function $\text{Im}\{1/\varepsilon\}$ allows us to perform a Kramers-Kronig transformation to obtain the real part $\text{Re}\{1/\varepsilon\}$ of the reciprocal of complex dielectric functions. We can also obtain the real part $\varepsilon_1$ and imaginary part $\varepsilon_2$ from $\text{Im}\{1/\varepsilon\}$ and $\text{Re}\{1/\varepsilon\}$ [15]. The real and imaginary parts of the dielectric function are as follows:

$$
\varepsilon_1 = \frac{\text{Re}\{1/\varepsilon\}}{\left(\text{Re}\{1/\varepsilon\}\right)^2 + \left(\text{Im}\{1/\varepsilon\}\right)^2}
$$

and

$$
\varepsilon_2 = \frac{\text{Im}\{1/\varepsilon\}}{\left(\text{Re}\{1/\varepsilon\}\right)^2 + \left(\text{Im}\{1/\varepsilon\}\right)^2}.
$$

Figure 5(b) shows the real part $\varepsilon_1$ and imaginary part $\varepsilon_2$ (corresponding to the absorption spectrum) of dielectric functions. As can be seen in the inset of Fig. 5(b), the main peak position of dielectric function of $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ dielectric is the same as that of ZrO$_2$ dielectric. In the absorption spectrum $\varepsilon_2$, the strong absorption below 9 eV was associated with a transition of the valence band electrons into the unoccupied $d$ states in the conduction bands [17].

As can be seen in Figure 5(a) and (b), there are no difference in the energy loss of the peaks in $\varepsilon_1$ and $\varepsilon_2$ for $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ dielectric compared with that of ZrO$_2$ dielectric. These results lead to the conclusion that ZrO$_2$ have a strong effect on the dielectric function and optical properties of $(\text{ZrO}_2)_{0.66}(\text{HfO}_2)_{0.34}$ dielectric thin films.
4. Conclusion

We have investigated the band alignments and optical properties for ZrO$_2$ and (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectrics. The band alignments were investigated by using REELS and XPS analysis. The results showed that the (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric has almost the same barrier heights as those of ZrO$_2$ dielectric. (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric should exhibit good electronic properties with these optimal barrier heights. Through a quantitative analysis of REELS spectra of (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric thin films, we found that the optical properties of (ZrO$_2$)$_{0.66}$(HfO$_2$)$_{0.34}$ dielectric thin films obtained by analyzing the ELF with Kramer-Kronig relations are similar to that of ZrO$_2$ dielectric thin films. Hence, a quantitative analysis of REELS provides us with a straightforward way to determine the electronic and optical properties of high- $k$ dielectrics materials.

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6. References