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Citation: *Appl. Phys. Lett.* **81**, 376 (2002); doi: 10.1063/1.1492024

View online: <http://dx.doi.org/10.1063/1.1492024>

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Energy gap and band alignment for $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ on (100) Si

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(Received 4 March 2002; accepted for publication 14 May 2002)

High-resolution x-ray photoelectron spectroscopy (XPS) was applied to characterize the electronic structures for a series of high- k materials $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ grown on (100) Si substrate with different HfO_2 mole fraction x . Al $2p$, Hf $4f$, O $1s$ core levels spectra, valence band spectra, and O $1s$ energy loss all show continuous changes with x in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$. These data are used to estimate the energy gap (E_g) for $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$, the valence band offset (ΔE_v) and the conduction band offset (ΔE_c) between $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ and the (100) Si substrate. Our XPS results demonstrate that the values of E_g , ΔE_v , and ΔE_c for $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ change linearly with x . © 2002 American Institute of Physics. [DOI: 10.1063/1.1492024]

High- k gate dielectrics as alternates to SiO_2 have received tremendous attention due to the aggressive downscaling of complementary metal–oxide–semiconductor field effect transistor dimensions, which in turn results in increasing levels of tunneling current.¹ HfO_2 has emerged as one of the most promising high- k candidates due to its high dielectric constant, large energy gap, and compatibility with conventional complementary metal–oxide–semiconductor (CMOS) process.^{2–4} However, it may suffer recrystallization at high temperature during postdeposition annealing, which in turn may induce higher leakage current and severe boron penetration issues. On the other hand, Al_2O_3 films grown directly on Si was reported to remain amorphous up to 1000 °C.⁵ Recently Al has been proposed to alloy HfO_2 to raise the dielectric crystallization temperature, and encouraging results were demonstrated.⁶ It was reported that when Al concentration is increased to 31.7%, the corresponding crystallization temperature increases to between 850 and 900 °C, which is about 400 °C higher than that for HfO_2 . In this work, the energy gap (E_g) of $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$, the valence band offset (ΔE_v) and the conduction band offset (ΔE_c) between $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ and the Si substrate as functions of x are obtained based on x-ray photoelectron spectroscopy (XPS) measurement. This information is of vital importance in assessing $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ as a most promising high- k gate dielectric in future CMOS device technology.

The principles of using high-resolution XPS to obtain both E_g and ΔE_v for the dielectrics including SiO_2 and various high- k materials can be found in Refs. 7–9. The conduc-

tion band offset (ΔE_c) can also be derived using the Si energy gap value of 1.12 eV.¹⁰

A total of five $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ samples of various x values prepared by atomic layer deposition (ALD), with low-doped p -type Si (100) wafers as substrates ($P \sim 10^{15} \text{ cm}^{-3}$) were studied in this work. A thin layer of oxide around 10 Å was thermally grown on each Si wafer after the pregate clean using HF last. The wafers were sent to GENUS for ALD and a pre-HF vapor clean to remove the oxide was conducted prior to the deposition of the dielectric films. The deposition temperature for the ALD process is 300 °C. The thicknesses of the $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ films are around 20 nm obtained by a spectroscopic ellipsometer (Woollam Model M-2000). The *ex situ* XPS measurements were carried out using a VG ESCALAB 220i-XL system,¹¹ equipped with a monochromatized Al $K\alpha$ source ($h\nu = 1486.6 \text{ eV}$) for the excitation of photoelectrons. All of the high-resolution scans were taken at a photoelectron take-off angle of 90° and a pass energy of 20 eV. Under such configurations, the full width at half maximum of Si $2p_{5/2}$ core level recorded from H-terminated Si surface was measured as $\sim 0.45 \text{ eV}$, which gives an indication of the instrument energy resolution. Al $2p$, Hf $4f$, C $1s$, O $1s$, valence band maximum, and O $1s$ energy loss spectra were measured and analyzed. The intensities for all the XPS spectra reported here have been normalized for comparison and all of the spectra are calibrated against C $1s$ peak (285.0 eV) of adventitious carbon.

The chemical compositions of various $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ samples [change from HfO_2 ($x=1$) to Al_2O_3 ($x=0$)] can be determined by the intensities of the XPS lines. The five samples are denoted as HAO-1 to HAO-5, respectively, and their corresponding elemental

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TABLE I. Elemental composition of various $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ samples (labeled as from HAO-1 to HAO-5) estimated by XPS. The HfO_2 mole fraction value x as in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ are also given in the table. The Hf at. % = $x/(5-2x)$ and the Al at. % = $2(1-x)/(5-2x)$ are determined by the intensities of XPS lines.

	HAO-1	HAO-2	HAO-3	HAO-4	HAO-5
Hafnium at. %	33.9%	25.8%	18.4%	9.6%	0
Aluminum at. %	0	9.2%	18.2%	27.7%	39.8%
Oxygen at. %	66.1%	65%	63.4%	62.7%	60.2%
HfO_2 mole fraction value x as in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$	1	~0.85	~0.67	~0.41	0

compositions as well as the value of x are given in Table I. All the samples show good stoichiometry and trace amounts of carbon are detected from all of the samples' surfaces.

XPS spectra for Hf 4*f*, Al 2*p*, and O 1*s* core levels are shown in Figs. 1(a), 1(b), and 1(c). It is observed that all the core level peak positions of Hf 4*f*, Al 2*p*, and O 1*s* experience a shift to higher binding energy with the increase of Al_2O_3 concentration in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ system, and these changes are similar to the XPS chemical shifts in ZrSiO_4 vs SiO_2 and ZrO_2 as discussed in Ref. 12. The earlier shift is due to the fact that Hf is a more ionic cation than Al in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$,¹³ and thus the charge transfer contribution changes with the increase of Al concentration.^{12,13}

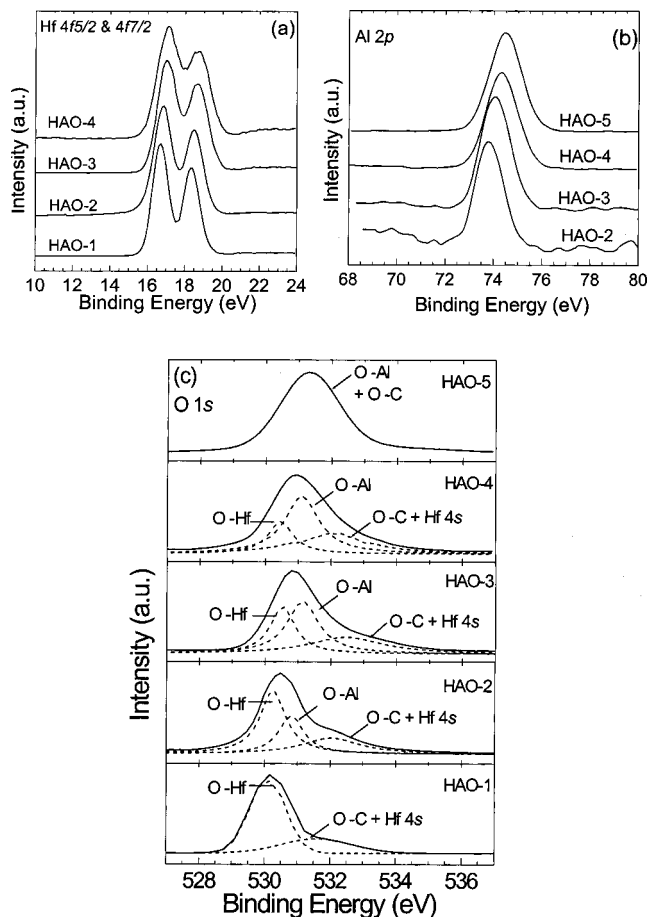


FIG. 1. XPS spectra for (a) Hf 4*f* core levels, (b) Al 2*p* core levels, and (c) O 1*s* core level taken from various $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ samples. The core level peak positions of Hf 4*f*, Al 2*p*, and O 1*s* shift continuously towards greater binding energy with increasing Al components. For O 1*s* spectra, solid lines are experimental data and dashed lines are the curve fitting results. From the curve fitting results, it is clearly shown that the Al–O bond (~531.2 eV) component increases with increasing Al composition.

For the O 1*s* core level spectra (the solid lines), a curve-fitting method (Gaussian fitting; the dashed lines) is applied to analyze the variation in O 1*s* spectra shape. For the samples HAO-2, HAO-3, and HAO-4, three peaks can be clearly resolved. The peak located at ~530.5 eV is attributed to Hf–O bonds, and another peak at ~531.2 eV to Al–O bonds. From the curve-fitting results as well as the O 1*s* spectra collected from HfO_2 (HAO-1) and from Al_2O_3 (HAO-5), it is obvious that Al–O components increase with increasing Al in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$. The shoulder at ~532.3 eV is generally interpreted as due to residual surface contaminants (i.e., C–O bonds)¹⁴ and it is observed that this shoulder decreases with the decrease of Hf component in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$. However, Hf 4*s* photoelectron line is also located around this energy.¹⁵ Therefore, it is suggested that both of the earlier-indicated sources contribute to the peak at ~532.3 eV.

Let us turn to focus on the major topic: energy band alignment for the $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$. Figure 2(a) shows the O 1*s* energy-loss spectra, which are caused by the outgoing photoelectrons suffering inelastic losses to collective oscillations (plasmon) and single particle excitations (band to band transitions).¹⁶ As is well known, the energy gap values for the dielectric materials can be determined by the onsets of energy loss from the energy-loss spectra.^{8,16} By this mean, the energy gap value for HfO_2 (sample HAO-1) is measured as 5.25 ± 0.10 eV, and for Al_2O_3 (sample HAO-5) it is measured as 6.52 ± 0.10 eV. The energy gap value of Al_2O_3 is consistent with those reported by Itokawa *et al.*⁸ (6.55 ± 0.05 eV) and Bender *et al.*⁹ (6.7 ± 0.2 eV). From the results, a linear change of energy gap value with x in the $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ system is also observed.

The determination of valence band alignment of $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ on Si substrate was made by measuring the valence band maximum (VBMax)-difference between the $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ grown on *p*-Si(100) substrate samples and the H-terminated *p*-Si (100) substrate sample with the same substrate doping of $P \sim 10^{15} \text{ cm}^{-3}$, as demonstrated in Fig. 2(b).¹⁷ The VBMax of each sample is determined by extrapolating the leading edge of valence band spectrum to the base line [the cross points in Fig. 2(b)] from its specific spectrum.¹⁶ Thus, ΔE_v values of 3.03 ± 0.05 eV and 2.22 ± 0.05 eV are obtained for Al_2O_3 and HfO_2 , respectively. The ΔE_v value of Al_2O_3 is consistent with the value 2.9 ± 0.2 eV reported by Bender *et al.*⁹ A gradual change of the valence band density of states is also observed from sample HAO-1 to HAO-5, as indicated by the dashed arrow in Fig. 2(b).

With the knowledge of Si energy gap value of 1.12 eV,

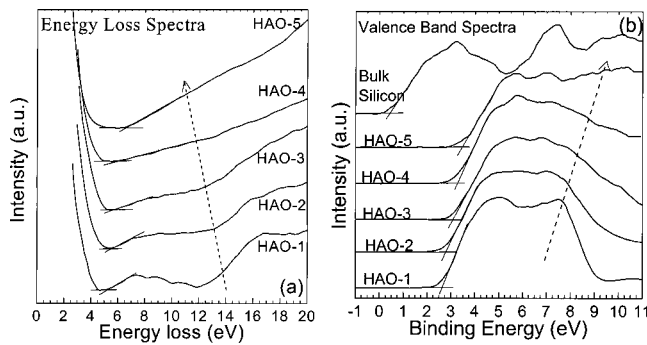


FIG. 2. (a) O $1s$ energy loss spectra for various $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ samples. The cross points (obtained by linearly extrapolating the segment of maximum negative slope to the base line) denote the energy gap E_g values. The dashed arrow shows the continuous change in the energy loss spectra contour from sample HAO-1 to HAO-5. (b) XPS valence band spectra taken from various $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ grown on (100) Si substrate samples and H-terminated (100) Si substrate sample. The cross point from each spectrum denotes the VBMax for that specific sample. The valence band alignment ΔE_v is obtained by the difference of VBMax between the $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ and the H-terminated Si. The dashed arrow indicates the gradual change in the valence band density of states from sample HAO-1 to HAO-5.

the ΔE_c values for $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ can be simply derived by the equation

$$\Delta E_c = E_g - \Delta E_v - 1.12 \text{ (eV)}. \quad (1)$$

Hence ΔE_c for HfO_2 is calculated as 1.91 ± 0.15 eV and for Al_2O_3 , it is calculated as 2.37 ± 0.15 eV. Afanas'ev *et al.* reported 3.23 ± 0.08 eV for the (100) Si valence band to Al_2O_3 conduction band offset, measured by internal photoemission.¹⁸ Using 1.12 eV energy gap for Si, the Si to Al_2O_3 conduction band offset ΔE_c is calculated to be 2.11 ± 0.08 eV, which in turn is in reasonable agreement with our XPS result.

The E_g , ΔE_v , and ΔE_c values obtained by XPS measurements and by Eq. (1) for samples HAO-1 to HAO-5 are plotted in Fig. 3. By linear least square fit, the following

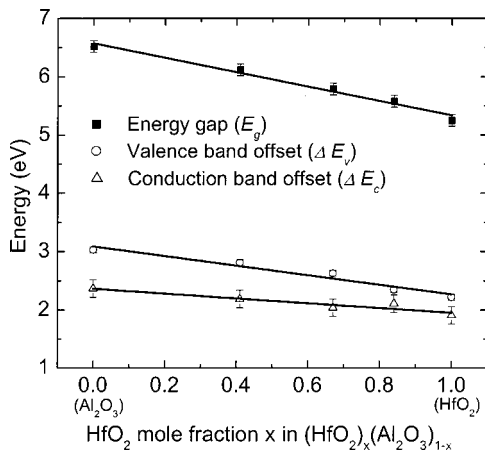


FIG. 3. Dependence of E_g , ΔE_v , and ΔE_c for $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ on HfO_2 mole fraction x . The E_g and ΔE_v data are obtained by XPS measurements. The ΔE_c data are calculated by Eq. (1). The solid lines are obtained by linear least square fits of the data points.

equations are obtained:

$$E_g = 6.52 - 1.27x \text{ (eV)}, \quad (2a)$$

$$\Delta E_v = 3.03 - 0.81x \text{ (eV)}, \quad (2b)$$

$$\Delta E_c = 2.37 - 0.46x \text{ (eV)}, \quad (2c)$$

where x stands for the mole fraction of HfO_2 in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$, as clearly demonstrated in Table I. Accordingly, the electrical properties of $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ gate dielectrics can be tuned by simply changing the HfO_2 mole fraction while keeping the stoichiometry of the materials.

In conclusion, high-resolution XPS measurements were performed to investigate E_g and ΔE_v of $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ high- k materials. Al $2p$, Hf $4f$, O $1s$ core levels spectra, valence band spectra, and O $1s$ energy loss spectra all show continuous changes with the variation of HfO_2 mole fraction x in $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$. E_g , ΔE_v , and ΔE_c values for $(\text{HfO}_2)_x(\text{Al}_2\text{O}_3)_{1-x}$ on Si (100) are determined and can be expressed by $6.52 - 1.27x$ (eV), $3.03 - 0.81x$ (eV), and $2.37 - 0.46x$ (eV), respectively.

This work was supported by the Singapore NSTB/EMT/TP/00/001.2 Grant and the National University of Singapore R263-000-077-112 Grant.

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