

Interfacial Control and Modulation of Band Alignment of Atomic Layer Deposition-Derived HfO₂/Si Gate Stack by Rapid Thermal Annealing

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ABSTRACT

High-*k* gate dielectric HfO₂ thin films have been deposited on Si substrates by atomic layer deposition. Post-deposition annealing temperature dependent optical properties and band alignment of HfO₂/Si gate stacks are investigated via X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry (SE). XPS measurements have confirmed that annealing from 500 to 700 °C leads to the complete oxidation of the as-deposited film from the adsorption of oxygen in Si substrate and free oxygen in HfO₂. However, the formation of Hf–Si–O layer has been detected after annealing at 800~900 °C. Analysis from SE based on Cauchy mode has indicated that increases in refractive index (*n*) and extinction coefficient (*k*), with increasing annealing temperature, are observed due to the formation of higher packing density and the enhancement of scattering effect in HfO₂ films. Meanwhile, red shift in band gap with the increase in annealing temperature has been observed. Additionally, the annealing temperature dependent valence band and conduction band offset relative to Si have been determined in detail.

KEYWORDS: Atomic Layer Deposition, Annealing Temperature, X-Ray Photoelectron Spectra, Optical Properties, Band Alignment.

1. INTRODUCTION

With the further down-scaling of complementary metal-oxide semiconductor (CMOS), traditional SiO₂-based dielectrics have approached their physical limits due to high leakage current from channel to gate. To address the problem, alternative high-*k* materials have been proposed and investigated extensively. Among them, HfO₂ was considered as one of the most promising candidates due to its high dielectric constants (~25), large band gap (~5.8 eV), suitable band offset relative to Si, and good thermal stability when in contact with Si.^{1–3} However, HfO₂ has poor barrier to oxygen diffusion, which lead to the formation of low-*k* interfacial layer with many defects and high interface state density, which will prohibit its potential application in future device. To avoid the formation of low-*k* interfacial layer, much effort has been devoted

to investigate the evolution of the interfacial chemistry of HfO₂/Si gate stacks.

By far, many deposition methods have been pursued to obtain HfO₂/Si gate stacks with good interface control, such as sputtering, pulsed laser deposition (PLD), electron beam evaporation (EBE), plasma ion assisted deposition (PIAD), metal organic chemical vapor deposition (MOCVD), and so on.^{6,7} However, it is difficult to obtain HfO₂ gate dielectric with high-quality due to the complicated procedure and uncontrollable interfacial layer growth.

Currently, atomic layer deposition (ALD) has been investigated to deposit high-*k* gate dielectric because of its highly controlled deposition parameters, excellent deposition uniformity and consistency.⁸ In this letter, high-*k* HfO₂ gate dielectrics have been obtained on Si substrate by ALD process, following thermal annealing in high-vacuum ambient. Although there exist some report on the electrical and potential dielectric properties, the effect of post deposition annealing on the optical, interfacial chemical

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bonding states, and band alignment of HfO₂/Si gate stacks has not been thoroughly paid more attention. Due to the importance of the determination of optical properties and band alignment to the development of Hf-based microelectronic devices, to understand its evolution of the interfacial chemistry and band alignment related with post deposition process, which are considered as material fundamental properties, is crucial.

In current works, the optical properties, interfacial chemical bonding states, and electrical band structure of the HfO₂/Si gate stack have been determined by characterization from X-ray photoelectron spectroscopy (XPS) and spectroscopy ellipsometry as a function of annealing temperature.

2. EXPERIMENTAL DETAILS

The growth of HfO₂ was carried out by ALD on Si wafers by using tetrakis (ethylmethylamino) hafnium, TEMA and H₂O as the precursors and oxidant, respectively. Prior to loading Si substrates into the ALD growth chamber, six *p*-type Si (100) wafers with resistivity of 10 Ω cm were cleaned in ultrasonic shaking ethanol for 10 min to remove organic contamination and surface impurities, then washed with a mixed chemical solution (NH₃·H₂O:H₂O₂:H₂O = 2:1:7) for 10 min at 75 °C. After that, the wafers were cleaned with a hydrofluoric acid solution for 30 s to remove native oxides, which followed by a rinse in deionized water. The as-cleaned six substrates were put into ALD reactor (LabNano 9100, ENSURE NANOTECH) immediately. The container of the Hf precursor was heated to 75 °C, while H₂O was set at room temperature. Then 3 nm HfO₂ film was deposited on Si wafers by controlling the cycles of the precursor. To investigate the effect of the high temperature annealing on the thermal stability of the HfO₂/Si system, *ex-situ* post-deposition rapid thermal annealing (RTA) was conducted under high vacuum ambient condition with a temperature range of 500–900 °C for 1 minute. *Ex-situ* XPS measurements were performed to investigate the interfacial chemistry and band alignments of HfO₂/Si gate stacks by using (ESCALAB 250Xi) system, equipped with an Al Kα radiation source (1487.6 eV) and hemispherical analyzer with a pass energy of 20 eV. The collected data were corrected for charging effect-induced peak shifts using the binding energy (BE) of Si 2*p* peak of substrate (99.3 eV). Spectral deconvolution was performed by Shirley background subtraction using a Voigt function convoluting the Gaussian and Lorentzian functions. In all the spectra, black solid lines show the measured results, and other color lines show the fitted XPS results. Spectroscopic ellipsometer (SE) measurements were performed using a commercial instrument (Shanghai Sanco Instrument Co., Ltd., SC630) to obtain the optical constant. The incident light was scanned in the range 190~1100 nm at incident angles of 65 and 75°. The instrument measures the complex ratio of the

Fresnel reflection coefficients for *p*- and *s*-polarized light and reports the ratio in terms of the ellipsometric parameters ψ (ψ) and Δ defined by the equation

$$\rho = r_p/r_s = \tan \psi e^{i\Delta}$$

where r_p and r_s are the amplitude reflection coefficients for light polarized in the *p*- and *s*-planes of incidence, respectively. For a layer sample, the measured spectra from it may be analyzed using an appropriate fitting model, which is constructed based on the sample structure. For interpreting the measured pseudodielectric functions, a five-layer model is assumed: the incident medium (air), the surface roughness layer, the HfO₂ layer, SiO₂-like interlayer and the Si substrate. The surface roughness layer is composed of 50% void space and 50% HfO₂, modeled by an effective medium approximation applying the Bruggeman formalism.⁹ Variables in the fitting procedure included all the layer thickness, the volume fraction of air present for the surface rough layer and the dispersion relation describing the optical properties of the HfO₂ thin films themselves. In current SE analysis, the unknown pseudodielectric functions $\epsilon = \epsilon_1 + i\epsilon_2$ of the HfO₂ thin films are described by parameterized Cauchy dispersion relation. The optical constant, refractive index n and the extinction coefficient k are decided as follows:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \quad (1)$$

$$\kappa(\lambda) = \alpha \exp \beta \left(12400 \left(\frac{1}{\lambda} - \frac{1}{\gamma} \right) \right) \quad (2)$$

where the five parameters of the model (A , B and C are the index parameters that specify the index of refraction, and α , β and γ are the extinction coefficient amplitude, the exponent factor, and the band edge γ , respectively) can be defined as a variable fit parameter during the data evaluation. The standard deviations were calculated from the known error bars on the calibration parameters. A least squares-fitting procedure employing the modified Levenberg–Marquardt algorithm, the convergence of which is faster than that of the SIMPLEX algorithm, is used in the fitting.

3. RESULTS AND DISCUSSION

3.1. XPS Analysis

In order to investigate the interfacial chemical states, the profiles of Si 2*p*, O 1*s*, Hf 4*f*, and Al 2*p* chemical states were examined nondestructively using XPS. All the Si 2*p* regions were aligned in binding energy to the Si–Si Si 2*p*_{3/2} peak at 99.3 eV. As shown in Figure 1, the Si 2*p* spectra of the as-deposited and annealed HfO₂/Si system from 500 to 900 °C have been demonstrated. Due to the high resolution of the XPS instrument, the Si 2*p* spectra for the as-deposited sample present two main peaks. One centered at 99.3 eV and the other located at 99.86 eV

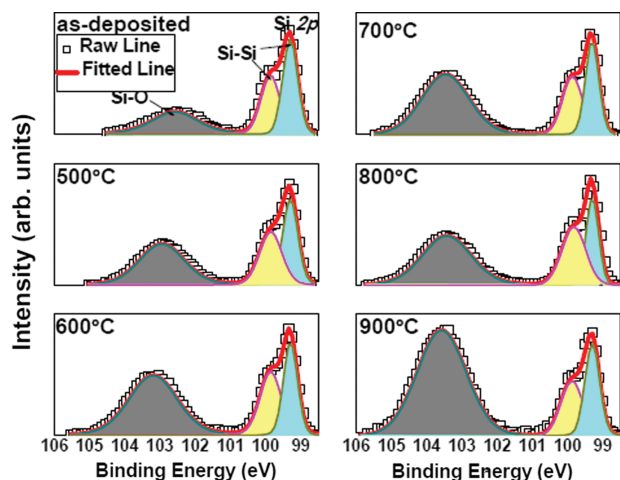


Fig. 1. Si 2*p* core level XPS spectra of HfO₂/Si system for as-deposited and annealed films from 500 to 900 °C for 1 minute in 6.3E−5 mbar vacuum ambient.

are attributed to the Si substrate. Additionally, there is also another peak observed at higher binding energy of 102.57 eV for the as-deposited film. The position and relative intensity of the Si 2*p* spectra indicates the formation of the interfacial SiO_{*x*} (*x* < 2) layer. When annealing at 500 °C, the binding energy of Si–O shifts to 102.94 eV, which is higher 3.64 eV than bulk Si, corresponding to Si⁴⁺ chemical state and consisting with SiO₂.^{10,11} Based on Figure 1, it can be noted that with increasing annealing temperature, Si 2*p* core-level spectra originating from interfacial SiO₂ component shift towards higher binding energy sides and the peak intensity corresponding to SiO₂ increases, resulting from the complete oxidation of the sub-oxides involved in the interfacial layer by diffusion of oxygen from the released oxygen from the adsorption of oxygen in Si substrate and free oxygen in HfO₂ at higher temperature.

In order to further probing of the nature of interface, Hf 4*f* spectra were analyzed. All the Hf 4*f* spectra show two peaks, originating from the Hf 4*f*_{7/2} and Hf 4*f*_{5/2} bonding states, which can be fitted by a spin orbit doublet with an energy splitting of 1.63 (±0.03) eV. For the as-deposited sample, Hf 4*f* spectra are composed of two peaks at binding energy of 17.94 and 19.57 eV, corresponding to the Hf 4*f*_{7/2} and Hf 4*f*_{5/2} peaks of HfO₂, respectively. With the annealing temperature ranging from 500 to 700 °C, Hf 4*f* peaks shifts towards the direction of the higher energy, suggesting the full oxidation of HfO₂ film by the released oxygen in both HfO₂ films and Si substrates. However, the binding energy of Hf 4*f* spectra demonstrates a slight reduction when the annealing temperature rises to 800 degrees, which can be explained as the generation of silicate in the interfacial layer.¹² Therefore, it can be supposed that a thin HfSiO_{*x*} was formed between HfO₂ film and Si substrate after high temperature annealing. Also, the Hf 4*f* spectra of HfO₂ film annealed at 900 °C shows

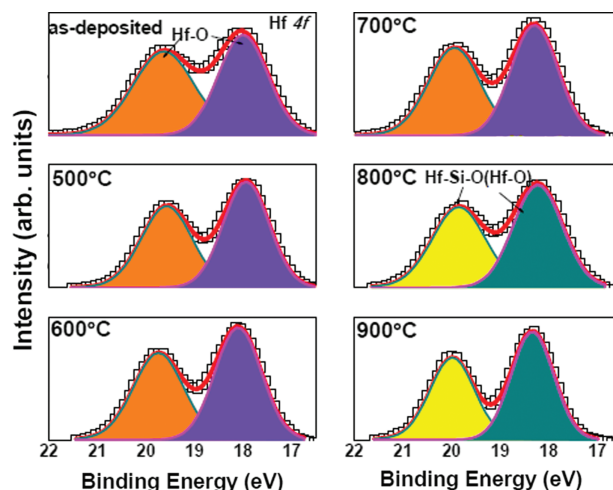


Fig. 2. Hf 4*f* core level XPS spectra of the as-deposited and annealed HfO₂ films on Si.

a slight increase in intensity, indicating the increasing silicate content of HfO₂ films from 800 to 900 °C. Based on Figure 2, it can be noted that an important feature of the as-deposited and annealed sample tested shows no evidence of the Hf 4*f* electron peaks associated with Hf–Si bonds, regardless of annealing temperature. This means that the present sample has no silicide bonds and that the Si and Hf atoms form chemical bonds solely with O atoms. The lack of Hf–Si bonding is expected because deleterious Hf–Si bonding will be energetically unfavorable compared to Si–O bonds at the interface.

Figure 3 presents O 1*s* core-level spectra of the as-deposited and subsequently annealed HfO₂/Si system at 500, 600, 700, 800, and 900 °C, respectively. As for the as-deposited film, the spectra are deconvoluted into two peaks. The low energy state center at 531.56 eV is attributed to oxygen in HfO₂ and the higher binding energy state locates at 532.57 eV comes from the formation of

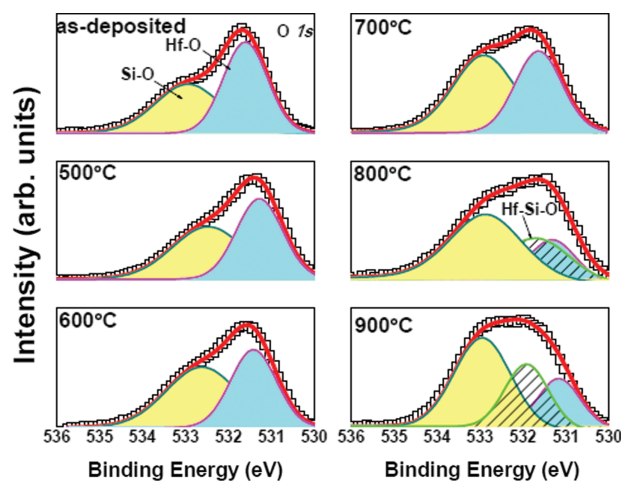


Fig. 3. O 1*s* core level XPS spectra of the as-deposited and annealed HfO₂ films on Si.

Si–O bond. When annealing at 500 °C, the O 1s spectra corresponding to Hf–O bond shifts towards lower binding energy value located at 531.28 eV, which is due to the crystallization of HfO₂.¹³ The bond energy of Si–O shifts higher position from 532.6 to 533 eV with increasing annealing temperature from 500 to 900 °C and this is indicative of increasing silicon dioxide formation, which is in good agreement with previous results shown in Figure 1. However, for the sample annealed at 800 °C, there is another energy peak at 531.9 eV. The fact can be explained as the formation of HfSiO_x. Rapid thermal annealing process make HfO₂, SiO₂ and Si react each other and lead to the formation of silicate layer. For the annealed at higher temperature (900 °C), the intensity of Hf–Si–O increases, suggesting more formation HfSiO_x at 900 °C.

3.2. SE Measurements

To investigate the evolution of the optical constant of the HfO₂ films related with annealing temperature, SE measurements have been carried out. The measured and fitted spectra of a representative HfO₂ film at the incident angle of 65° and 75° are shown in Figure 4. From Figure 4, it can be clearly seen that an excellent agreement between the experimental and fitted spectra for the HfO₂ films has been attained in the entirely measured energy range, suggesting that the structured Cauchy model is reasonable and can describe the structure of the as-deposited sample. Based on the simplified five-layer model, the best-fitted results used in the simulation of measured spectra have been obtained. The variation of the refractive index as a function of annealing temperature has been demonstrated in Figure 5. It has been seen that the values of refractive index for the annealed films are larger than the as-grown one, which is due to the change of structure correlated with the annealing temperatures. It is well known that the refractive index is closely related to the packing density of materials, which is lower at lower density. For the as-deposited HfO₂ film, it has loose arrangement and rough surface, resulting in low values of density packing density

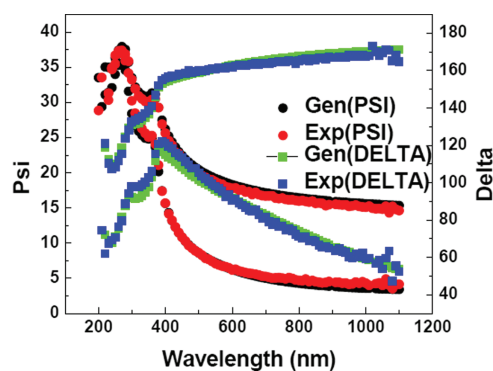


Fig. 4. Experimental and generational (fitted) spectroscopic ellipsometric data psi and delta in the incidents of 65 and 75° (the below lines are measured in 75°, the others are measured in 65°) for the as-deposited HfO₂ film, derived from the result of the Cauchy model fitted.

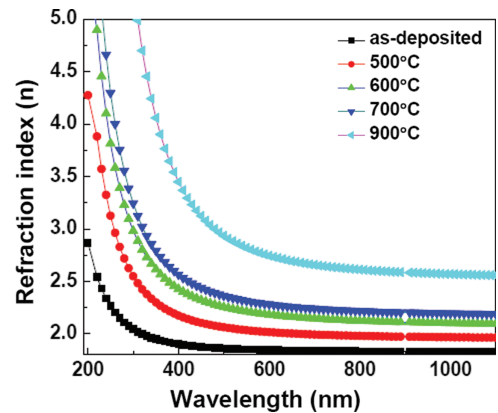


Fig. 5. The calculated refractive index dispersion relation of the HfO₂ films with post-annealing temperature from 500 to 900 °C, derived from the result of the Cauchy model.

and refractive index.¹⁴ After annealing, the molecules of HfO₂ films gain more energy order to migrate and reset on Si substrates, which leads to the increase of packing density and refractive index of HfO₂ films. Additionally, it can be seen that with increasing annealing temperature from 500 to 900 °C, the values of refractive index increase, due to the increasing packing density as well, as a higher temperature of annealing accelerates the mobility of the atoms or molecules of the film and favors the formation of more closely packed thin film. In addition, it is worth noting that the resulting refractive index obtained decreases sharply and then decreases slowly and trends to a horizontal line at an end as the wavelength increases. Based on Figure 6, it can be noted that the as-deposited and annealed at 500, 600, 700 and 900 °C thin HfO₂ films show 1.84, 2.01, 2.17, 2.27 and 2.71 at a wavelength of 632 nm, respectively. It can be seen that the values obtained for as-deposited and 500 °C films are smaller than the literature reported value of 2.1 for bulk HfO₂ and the other values are larger than the reported value, which is due to the films deposited by atomic layer deposition process and rapid thermal annealing at high temperature in

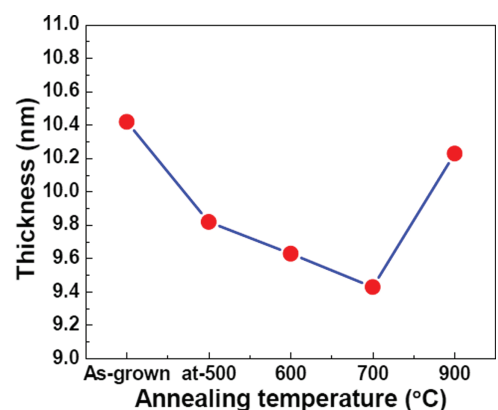


Fig. 6. The thickness of the as-deposited and annealed at 500, 600, 700 and 900 °C films, derived from the result of the Cauchy model fitted.

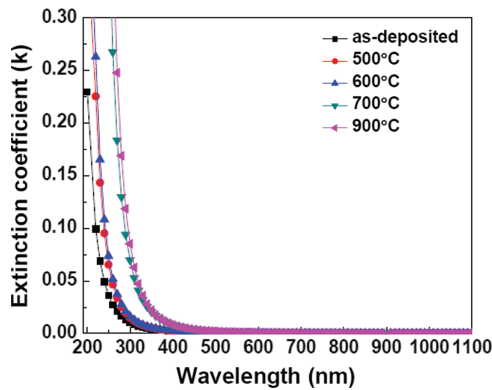


Fig. 7. The calculated extinction coefficient of the as-grown film and annealed films with respect to wavelength.

$6.3E-5$ mbar vacuum ambient have lower defect density and higher packing density than bulk HfO₂.¹⁵

The extinction coefficient is one of the most important optical parameters of the HfO₂ films that it cannot be ignored. Figure 7 presents annealing temperature dependent extinction coefficient of the as-grown film and annealed films. It is obvious that the extinction coefficient of the films is very low and close to zero, indicating a very small optical loss due to absorption in the visible region. The result is consistent with the fact that HfO₂ is a transparent material in the visible and infrared regions, suggesting that a high-quality HfO₂ thin film is obtained in terms of optical properties. As we know, the extinction coefficient is connected with the absorption and the scattering of grains. It can be seen that the k values increase clearly with the increase of annealing temperature, which is due to the enhancement of scattering effect in the nanocrystalline HfO₂ films. Moreover, the extinction coefficient increase is likely due to a phase transition and lack of O₂ incorporation as well.^{16,17} However, the extinction coefficient of the films annealed at 500 and 600 °C are closely overlapped with each other, indicating that there are identical scattering effect between the two films.

Figure 8 shows the resulting dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ of the as-deposited and annealed HfO₂ films calculated

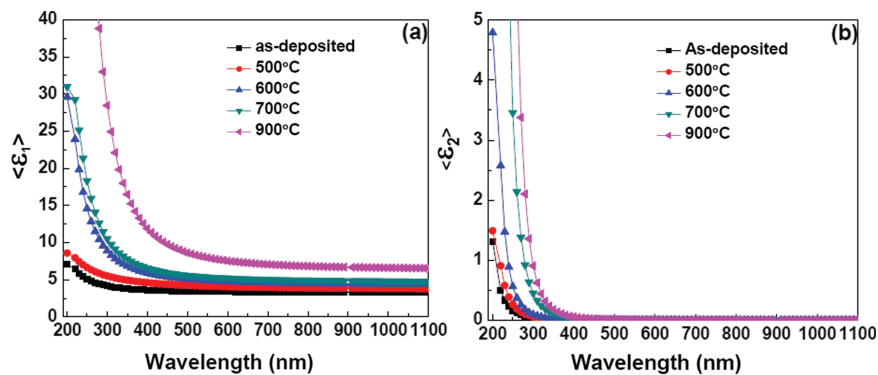


Fig. 8. The real (ε_1) and imaginary (ε_2) dielectric function for the as-deposited and annealed from 500 to 900 °C thin HfO₂ films derived from the results of Cauchy model.

from the measured and the best-fitted spectra. It can be known that the dielectric function of a thin film is strongly related to its microstructure and energy-band structure. After annealing, the structure changes from a disordered to a more ordered crystalline phase and the amplitude of the critical points increases, which lead to higher ε_1 and ε_2 values of annealed film compared to the as-deposited one, as shown in Figure 8. Thus, higher values of both the real and imaginary part of dielectric function indicate higher packing density of the thin HfO₂ films, consisting with previous observations. Additionally, the lines of the ε_1 and ε_2 are in keeping with the change of refractive index and extinction coefficient, due to $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$ in the visible region measured.

3.3. Band Gap Determination and Band Alignment

In order to determine the conduction band offset (ΔE_c) values of the HfO₂/Si under different annealing temperatures, the E_g energies of HfO₂ films will be determined. According to the evolution of the extinction coefficient related with the annealing temperature, it can be concluded that the apparent increase in extinction coefficient may be an effect of the shift of band gap energy, since $\alpha = 4k/\lambda$ and $\alpha E = B(E - E_g)^{1/2}$, where α is the absorption coefficient, λ is the wavelength, B is a constant and $1/2$ depends on the type of transition corresponding to the direct band gap. The band-gap energy can be found by drawing relatively a linear fit line with a maximum negative slope in the curve. The tangent intersects with the horizontal axis and the crossing point gives the band gap value. As can be seen from Figure 9, the band energies of the as-deposited and annealed from 500 to 900 °C are 5.95, 5.86, 5.80, 5.69 and 5.58 eV, respectively. All the energies values are in 5.2~6.0 eV, which is in good agreement with previous reported results.^{18,19} The inset of Figure 9 is the valence band spectra of bulk Si determined by linear extrapolation method. The leading edge of the valence-band spectrum for the p -type Si substrate is found to be located at 0.33 eV from Fermi level, which is close to 0.30 eV obtained by He.²⁰

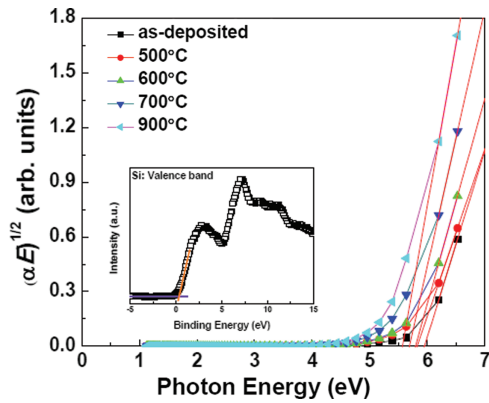


Fig. 9. The band-gap energy of HfO₂ films under various annealing temperature. Inset in Figure 9 is the valence band of bulk Si determined by linear extrapolation method.

Figure 10 demonstrates the valence-band maximum (VBM) of HfO₂ films on Si substrate under various annealing temperature. The VBM position is determined by linearly fitting the leading edge of the valence band and linearly fitting the flat energy distribution and fitting the intersection of the two lines.²¹ According to Kraut's method, the valence band offset (ΔE_v) of HfO₂/Si interface can be described to the formula below²²

$$\Delta E_v = (E_{\text{Si}2p}^{\text{Si}} - E_{\text{VBM}}^{\text{Si}}) - (E_{\text{Si}2p}^{\text{HfO}_2/\text{Si}} - E_{\text{Hf}4f}^{\text{HfO}_2/\text{Si}}) - (E_{\text{Hf}4f}^{\text{HfO}_2} - E_{\text{VBM}}^{\text{HfO}_2})$$

since $E_{\text{Si}2p}^{\text{Si}} - E_{\text{Si}2p}^{\text{HfO}_2/\text{Si}} = E_{\text{Hf}4f}^{\text{HfO}_2/\text{Si}} - E_{\text{Hf}4f}^{\text{HfO}_2} = 0$, thus, $\Delta E_v = E_{\text{VBM}}^{\text{HfO}_2} - E_{\text{VBM}}^{\text{Si}}$, where $E_{\text{VBM}}^{\text{HfO}_2}$ is the valence band maximum of HfO₂, and $E_{\text{VBM}}^{\text{Si}}$ is the valence band maximum of bulk Si. For the as-grown HfO₂ film, its valence-band maximum is located at 3.96 eV. Therefore, the valence band offset at HfO₂/Si interface is 3.63 eV. With increasing the annealing temperature, the results indicate that valence band offset of 3.24, 3.42, 3.50 and 3.42 eV for the annealed samples on Si substrate has been obtained, as shown in Table I.

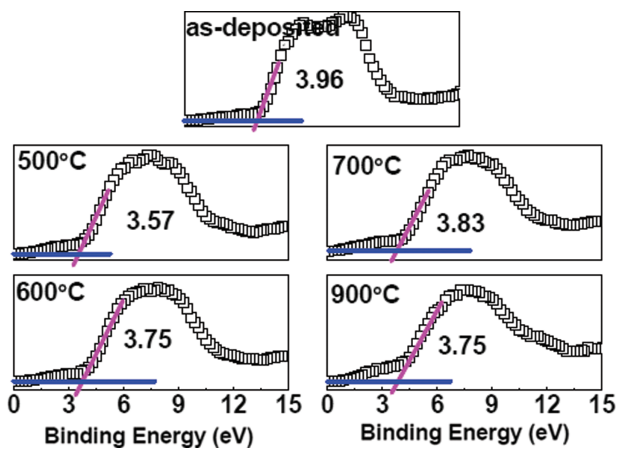


Fig. 10. Valence-band spectra of HfO₂/Si gate stacks determined by extrapolation of the leading edge to the base line.

Table I. The band gap (E_g) of HfO₂, the valence band maximum (VBM) of HfO₂, the valence band offset (ΔE_v), and the conduction band offset (ΔE_c) under different annealing temperature.

	As-deposited	500 °C	600 °C	700 °C	900 °C
E_g	5.95	5.86	5.80	5.69	5.58
VBM	3.96	3.57	3.75	3.83	3.75
ΔE_v	3.63	3.24	3.42	3.5	3.42
ΔE_c	1.2	1.5	1.26	1.07	1.04

As we all know, the valence band maximum of HfO₂ is due to O 2p state.²³ As a result, the shifts toward higher energy at 500–700 °C are on account of the increasing O content in HfO₂. Due to the formation of HfSiO_x in the process of annealing, the valence band offsets of the samples annealed at 900 °C shifts toward lower energy. The conduction band offset (ΔE_c) between HfO₂ and Si can be expressed by

$$\Delta E_c = E_g^{\text{HfO}_2} - E_g^{\text{Si}} - E_v^{\text{HfO}_2/\text{Si}}$$

where $E_g^{\text{HfO}_2}$ is the band gap of HfO₂, $E_v^{\text{HfO}_2/\text{Si}}$ is the valence band offset, and E_g^{Si} is the band gap of the Si wafer. With the knowledge of the Si band gap value of 1.12 eV, ΔE_c values for as-deposited and annealed from 500 to 900 °C samples are calculated to be 1.2, 1.5, 1.26, 1.07 and 1.04 eV, respectively, as shown in Table I. It should be noted that the values of ΔE_c demonstrate a change with increasing annealing temperature. This can be due to nonbonding Hf 5d states and also lies at a fixed energy. All the results indicated that the ΔE_c values of HfO₂/Si are higher the minimum requirement for the barrier height of over 1 eV for future CMOS.

4. CONCLUSIONS

In summary, detailed optical properties and band alignment of HfO₂/Si gate stacks have been investigated by SE and XPS as a function of the annealing temperature. It has been found that the HfO₂/Si gate stacks react more sufficiently with released oxygen and become more intense as the annealing temperature rises from 500 to 700 °C, but there are silicate generating when annealed at 800~900 °C. According to SE measurements based on Cauchy model, increases in the refractive index and extinction coefficient with increasing annealing temperature are observed due to the formation of higher packing density and the enhancement of scattering effect in HfO₂ films. Moreover, the optical band gaps are calculated between 6.0 and 5.5 eV and demonstrate red shift with increasing annealing temperature. The ΔE_v increases from 3.24 to 3.5 eV gradually when annealing the samples at 500–700 °C and decreases to 3.42 eV for the HfO₂ film annealed at 900 °C, due to the change of O 2p content. In addition, the effect of the annealing temperature on the conduction band offset has been investigated. All the

results indicated that the ΔE_c values of HfO₂/Si are higher than the minimum requirement for the barrier height of over 1 eV for future CMOS. The suitable band gap and moderate band offsets relative to Si render ALD-derived HfO₂ films promising candidates for high-*k* gate dielectrics.

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References and Notes

1. J. W. Liu, M. Y. Liao, M. Imura, and Y. Koide, *Appl. Phys. Lett.* 101, 252108 (2012).
2. T. L. Duan, H. Y. Yu, L. Wu, Z. R. Wang, Y. L. Foo, and J. S. Pan, *Appl. Phys. Lett.* 99, 012902 (2011).
3. J. W. Liu, M. Y. Liao, M. Imura, H. Oosato, E. Watanabe, and Y. Koide, 102, 112910 (2013).
4. D. Reicher, P. Black, and K. Jungling, *Appl. Opt.* 39, 1950 (2000).
5. J. M. Khoshmana and M. E. Kordesch, *Surf. Coat. Technol.* 201, 3530 (2006).
6. J. Shim, J. A. Rivera, and R. Bashir, *Nanoscale* 5, 10887 (2013).
7. T. T. Tang, Z. T. Liu, H. C. Lu, W. T. Liu, and H. Tian, *Opt. Mater.* 32, 432 (2010).
8. R. Suri, C. J. Kirkpatrick, and D. J. Lichtenwalner, *Appl. Phys. Lett.* 96, 042903 (2010).
9. D. A. G. Bruggeman, *Ann. Phys.* 24, 636 (1965).
10. A. Deshpande, R. Inman, G. Jursich, and C. Takoudis, *Microelectron. Eng.* 83, 547 (2006).
11. G. He, S. Toyoda, Y. Shimogaki, and M. Oshima, *Appl. Phys. Exp.* 2, 075503 (2009).
12. A. Deshpande, R. Inman, G. Jursich, and C. G. Takoudis, *J. Appl. Phys.* 99, 094102 (2006).
13. P. D. Kirsch, C. S. Kang, J. Lozano, J. C. Lee, and J. G. Ekerdt, *J. Appl. Phys.* 91, 4553 (2002).
14. G. He, L. Q. Zhu, M. Liu, Q. Fang, and L. D. Zhang, *Appl. Surf. Sci.* 253, 3413 (2007).
15. R. Thielsch, A. Gatto, J. Heber, and N. Kaiser, *Thin Solid Films* 410, 86 (2002).
16. Z. W. Zhao, B. K. Tay, L. Huang, S. P. Lau, and J. X. Gao, *Opt. Mater.* 27, 465 (2004).
17. H. B. Bhuvaneshwarib, V. Rajagopal Reddy, R. Chandramani, and G. Mohan Rao, *Appl. Surf. Sci.* 230, 88 (2004).
18. M. Oshima, S. Toyoda, T. Okumura, J. Okabayashi, H. Kumigashira, K. Ono, M. Niwa, K. Usuda, and N. Hirashita, *Appl. Phys. Lett.* 83, 2172 (2003).
19. F. L. Martinez, M. Toledano-Luque, J. J. Gandia, J. Carabe, W. Bohne, J. Rohrich, E. Strub, and I. Martil, *J. Phys. D: Appl. Phys.* 40, 5256 (2007).
20. G. He, G. W. Meng, L. D. Zhang, and M. Liu, *Appl. Phys. Lett.* 91, 232910 (2007).
21. S. A. Chambers, T. Droubay, T. C. Kaspar, and M. Gutowski, *J. Vac. Sci. Technol. B* 22, 2205 (2004).
22. E. Kraut, R. Grant, J. Waldrop, and S. Kowalczyk, *Phys. Rev. Lett.* 44, 1620 (1980).
23. M. Liu, L. D. Zhang, G. He, X. J. Wang, and M. Fang, *J. Appl. Phys.* 108, 024102 (2010).