

Dielectric constant of ultrathin SiO₂ film estimated from the Auger parameter

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The dielectric constant ϵ of ultrathin (0.55–7.96 nm) SiO₂ films formed on a Si(001) substrate was characterized in terms of the modified Auger parameter of Si atoms, α'_{Si} . The α'_{Si} was found to be as much as 0.7 eV higher for an ultrathin (0.68 nm) SiO₂ film than for thick SiO₂ films. From the observed oxide thickness dependence of α'_{Si} , the ϵ of ultrathin SiO₂ films was estimated by calculating the change in the polarization energy and the change in the electrostatic screening energy originating from dielectric discontinuity at the SiO₂/Si interface. The ϵ of ultrathin (0.68–2.13 nm) SiO₂ films was identical to that of bulk SiO₂ within $\pm 1\%$.

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I. INTRODUCTION

The atomic and/or electronic structures at SiO₂/Si interfaces, such as intermediate oxidation states and valence-band offsets, have attracted much interest in both scientific and technological fields.^{1,2} However, little attention has been paid to these structures in the ultrathin SiO₂ film formed on the Si substrate. Current device technology demands a dramatic reduction in the size of metal-oxide semiconductor field-effect transistors (MOSFETs), which requires that we develop a fundamental physical understanding of the atomic and/or electronic structures of ultrathin SiO₂ films.

Our group has shed light on the atomic structure by showing experimentally that the ultrathin SiO₂ film is compressively strained due to the lattice mismatch between the SiO₂ layer and the Si substrate.³ Our high-resolution x-ray photoelectron spectroscopy (XPS) measurements showed that the energy difference between bonding states in the valence band and in the O 2s core level is larger in an ultrathin (0.6–1.0 nm: two or three layers of SiO₂ molecules) SiO₂ film than in bulk SiO₂. A comparison of the experimental results with the energy levels calculated for model clusters by a first-principles molecular orbital (MO) calculation showed that the average Si-O-Si bond angle is about 135°; the angle is smaller by about 9° in the ultrathin SiO₂ film than in bulk SiO₂.

We have also shed some light on the electronic structure. Experiments revealed that the valence-band electronic states of Si substrates penetrate into ultrathin SiO₂ films. An energy barrier sufficiently high to prevent this penetration is formed when the SiO₂ film is thicker than 0.61 nm.⁴ The penetration of the valence-band states in conjunction with that of conduction-band states, which was revealed by Muller *et al.*,⁵ indicates that the fundamental limit for SiO₂ gate dielectrics usable for MOSFETs is 0.7 nm.

Another aspect of great interest is the dielectric constant ϵ of a strained ultrathin (0.6–1 nm) SiO₂ film. Using the ϵ of bulk SiO₂ is not justified for an ultrathin SiO₂ film formed on Si substrates.⁶ The use of the ϵ of bulk SiO₂ is

also questionable for a strained SiO₂ film. We have estimated the ϵ of a strained SiO₂ film in terms of the modified Auger parameter, α' ,⁷ which is defined as the sum of the binding energy of the photoelectron and the kinetic energy of the Auger electron for the core levels of an atom. A shift in the modified Auger parameter is twice the shift in the relaxation energy associated with a core-hole for the atom,^{8–10} hence reflecting a change in the ϵ of the material.^{11–13}

II. EXPERIMENT

Device-quality SiO₂ films with thicknesses ranging from 0.55 to 7.96 nm were formed on 6-in. *n*- or *p*-type Si(100) wafers (resistivity 10–20 Ω cm) by oxidizing the substrate at 800 °C under dry oxygen at 1 atm. The thicknesses of the oxide films, T_{ox} , were determined by high-resolution XPS (VG Scientific ESCALAB220i-XL). We used the metrology proposed by Lu *et al.*¹⁴ Briefly, T_{ox} can be precisely determined under certain conditions from the Si 2*p* core-level intensity ratio of the oxidized silicon film, I_{ox} and substrate silicon, I_{el} :

$$T_{\text{ox}} = \lambda_{\text{ox}} \sin \theta \ln [I_{\text{ox}} / (\beta I_{\text{el}}) + 1], \quad (1)$$

where λ_{ox} is the effective attenuation length of the photoelectrons in the oxide film, 2.96 nm, θ is the take-off angle of the photoelectrons, 90°, and β is 0.75. Lu found that the larger the acceptance angle of the analyzer, the lower the scattering effects of the photoelectrons.

The samples were studied using XPS. The Si 2*p* photoelectron and Si *KLL* Auger spectra were measured at a θ of 30° using the bremsstrahlung from an AlK α x-ray source.¹⁵ The modified Auger parameter of Si, α'_{Si} , in the SiO₂ films was determined by measuring the binding energy of the Si 2*p* peak and the kinetic energy of the Si *KLL* peak originating from SiO₂ films (Si_{ox} 2*p* and Si_{ox} *KLL*). Although the modified Auger parameter is independent of the charge-up effect and the referencing method, we must pay special attention to other factors such as the carrier trapping phenomena, which we recently found to be crucial in determining the

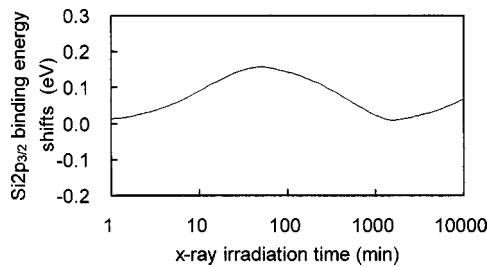


FIG. 1. Dependence of the Si $2p_{3/2}$ peak-energy shift on the measurement time or x-ray irradiation time.

energy levels of the SiO_2/Si samples during XPS measurement.^{16–18} We found that the binding energy of the Si $2p$ core level in Si substrates covered with thin SiO_2 films first increases (0–~50 min), then decreases (~50–~1500 min), and then increases again (~1500–~10 000 min) during XPS measurement or x-ray irradiation, as shown in Fig. 1. A shift toward a higher binding energy indicates that the amount of *positive* charge in the SiO_2 film is increasing, and a shift toward a lower binding energy indicates that the amount of *negative* charge in the SiO_2 film is increasing. This time dependence, caused by the charge trapping phenomena in a SiO_2 film, also changes the peak energies of both the core level and Auger lines from SiO_2 films on the Si substrate. Therefore, we measured the core-level peak and the Auger line for each sample as quickly as possible (within 6 min) at about the same time (~50 min) after x-ray irradiation commenced to minimize errors due to the carrier-trapping-induced shift. We obtained α'_{Si} from the average of three measurements. The reproducibility is shown by the error bars in Fig. 4. The difference between the electron energies for these photoelectrons and the Auger electrons may lead to a difference in escape depth. However, according to the electron energy dependence of the escape depth, the difference in the escape depth is as small as 0.24 nm for Si.¹⁹ Therefore, the α' derived from the energies of the Si $2p$ photoelectrons and Si KLL Auger electrons, both of which come from almost the same escape depth, is a reliable parameter for representing the characteristics of each SiO_2 thickness.

The α'_{Si} for the SiO_2 films was calculated using a first-principles MO method—the Hartree-Fock-Slater method using the discrete variational (DV)- $X\alpha$ code.²⁰ Molecular orbitals were constructed using a linear combination of atomic orbitals, which were generated numerically; the basis functions of Si, O, and H were $1s-3d$ for Si, $1s-3d$ for O, and $1s-2p$ for H. The Auger and photoemission energy levels for the core levels were calculated using the Slater transition state procedure,²¹ which is suitable for studying the binding energy in XPS spectra and the kinetic energy of Auger peaks. We used $\text{Si}_5\text{O}_{16}\text{H}_{12}$ clusters, shown in Fig. 2, to represent the SiO_2 structures. The 12 hydrogen atoms were arranged so as to terminate the dangling bonds of the surrounding 12 oxygen atoms and to make the cluster representative of the bulk SiO_2 , without the surface effects. We used constant interatomic distances of 0.162 nm for Si and O and 0.092 nm for O and H, which are consistent with those used by Edwards.²² In addition, we used a bond angle of $144^\circ-135^\circ$ for the

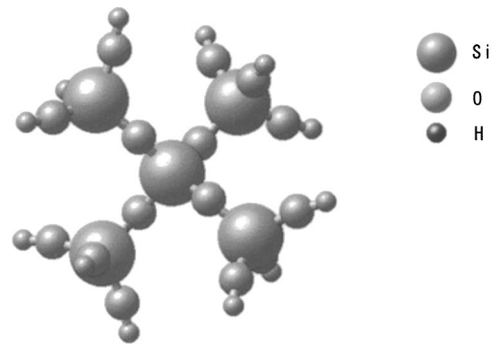


FIG. 2. $\text{Si}_5\text{O}_{16}\text{H}_{12}$ cluster with C_3 point symmetry.

Si-O-Si angle to investigate the effect of strain on α'_{Si} . The validity of the parameter values used in this calculation was previously confirmed by comparing the energy levels calculated for the SiO_2 cluster with the experimental XPS spectrum for bulk SiO_2 and an ultrathin SiO_2 film.^{3,23}

III. RESULTS AND DISCUSSION

Figure 3 shows the wide-region spectrum of the Si-related levels for 0.86-nm-thick SiO_2 film formed on a Si substrate, measured using the bremsstrahlung from an $\text{AlK}\alpha$ x-ray source. It shows the Si $2p$ photoelectron peaks and the Si KLL Auger peaks from the SiO_2 film ($\text{Si}_{\text{ox}} 2p$ and $\text{Si}_{\text{ox}} KLL$) and from the Si substrate underneath ($\text{Si}_{\text{el}} 2p$ and $\text{Si}_{\text{el}} KLL$). The α'_{Si} values were determined precisely from a much narrower region spectrum including $\text{Si}_{\text{ox}} 2p$ and $\text{Si}_{\text{ox}} KLL$. The peak energy of $\text{Si}_{\text{ox}} 2p$ was determined after the spectrum was decomposed into $\text{Si}_{\text{ox}} 2p$ and $\text{Si}_{\text{el}} 2p$ peaks taking into account the intermediate oxidation states, which consisted of Si^+ , Si^{2+} , and Si^{3+} , as defined by Hollinger *et al.*²⁴

Table I shows the α'_{Si} for the 0.55–7.96-nm-thick SiO_2 film. The value for the 7.96-nm-thick SiO_2 film was 1711.48 eV, which agrees well with the value reported for bulk SiO_2 , 1711.5 eV.²⁵ This excellent agreement is due to the fact that the modified Auger parameter is unaffected by changes in the surface Fermi level due to a calibration of the spectrometer and/or to the charge-up effect. The modified Auger parameter shift, $\Delta\alpha'_{\text{Si}}$, was determined with respect to that for 7.96-nm-

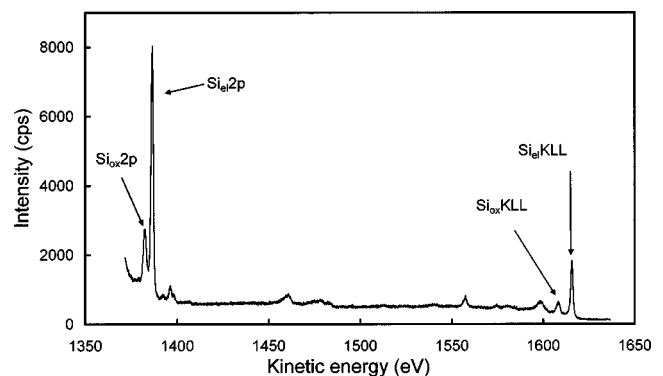


FIG. 3. Wide-region spectrum of Si-related levels of the 0.86-nm-thick SiO_2 film formed on the Si substrate, measured using bremsstrahlung from an $\text{AlK}\alpha$ x-ray source.

TABLE I. Modified Auger parameter α'_{Si} in thermal SiO₂ formed on a Si(001) substrate, and the shift in α'_{Si} with respect to that of 7.96-nm-thick SiO₂ film or of the bulk value, $\Delta\alpha'_{\text{Si}}$.

Substrate type	SiO ₂ film thickness (nm)	Modified Auger parameter (eV)	
		α'_{Si}	$\Delta\alpha'_{\text{Si}}$
<i>p</i>	0.55	1712.02	0.64
<i>p</i>	0.68	1712.04	0.70
<i>n</i>	0.86	1711.94	0.51
<i>p</i>	0.95	1711.93	0.52
<i>p</i>	1.04	1711.99	0.55
<i>p</i>	1.60	1711.72	0.24
<i>p</i>	1.72	1711.81	0.34
<i>p</i>	2.13	1711.77	0.29
<i>n</i>	4.10	1711.55	0.07
<i>n</i>	6.26	1711.50	0.02
<i>n</i>	7.96	1711.48	0.00

thick SiO₂ film or to that for bulk SiO₂. It was 0.34 eV for a 1.72-nm thick SiO₂ film and as high as 0.7 eV for a 0.68-nm-thick SiO₂ film.

The dependence of $\Delta\alpha'_{\text{Si}}$ on film thickness is plotted in Fig. 4. It increased monotonically with decreasing thickness. This observed shift is in contrast with previous reports. Wagner *et al.* did not observe any shift in the modified Auger parameter for oxide thicknesses ranging from 2 to 7 nm even

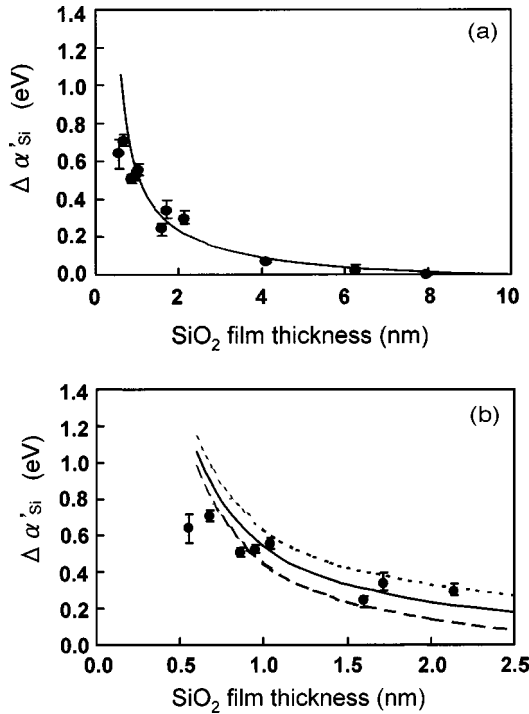


FIG. 4. Shift in the Auger parameter $\Delta\alpha'_{\text{Si}}$ in SiO₂ with respect to that in bulk SiO₂ for SiO₂ film thicknesses of (a) 0–10 nm and (b) 0–2.5 nm. Solid curves are theoretical curves for $\epsilon_{\text{SiO}_2} = 2.1\epsilon_0$, the dotted curve is for $\epsilon_{\text{SiO}_2} = 2.1\epsilon_0 + 1\%$, and the broken curve is for $\epsilon_{\text{SiO}_2} = 2.1\epsilon_0 - 1\%$.

though they expected one near the SiO₂/Si interface.²⁶ Iqbal *et al.* measured the Auger parameter for Si and found that it does not differ between thin SiO₂ film (0.8 to 20 nm) formed on a Si substrate and bulk SiO₂.²⁷ However, a careful analysis of their data reveals a shift of about 0.3 eV for a 1.2–1.3-nm-thick film, but not for a 0.8-nm-thick film. This exception is probably due to the carrier trapping effect, which was not taken into account in their measurement. Note that in our studies, we used device-quality SiO₂/Si samples and paid special attention to the carrier trapping effect to obtain more precise α'_{Si} values.

Now we consider the reason for the observed shift in the modified Auger parameter. To a first order approximation, $\Delta\alpha'_{\text{Si}}$ is given as twice the shift in the relaxation energy R associated with a core-hole accompanying the photoionization of the SiO₂ film.^{8,9}

$$\Delta\alpha'_{\text{Si}} = 2\Delta R, \quad (2)$$

where ΔR is determined with respect to the R for bulk SiO₂.

R of the SiO₂ film formed on the Si substrate is in turn determined by the bulk polarization energy E_{pol} , and by the effect of the boundaries, E_z , such as the SiO₂ surface and the SiO₂/Si interface,⁶

$$R = E_{\text{pol}} + E_z. \quad (3)$$

We can thus estimate $\Delta\alpha'_{\text{Si}}$,

$$\Delta\alpha'_{\text{Si}} = 2(\Delta E_{\text{pol}} + \Delta E_z), \quad (4)$$

where ΔE_{pol} and ΔE_z are the shifts in E_{pol} and E_z with respect to that in bulk SiO₂. The strong spatial variation in the relaxation energy caused by ΔE_z is limited to an interface layer with a thickness of the order of the characteristic screening length, ~ 0.1 nm for the SiO₂/Si system.²⁸ Beyond the interface layer, i.e., film thickness $> \sim 0.2$ nm, ΔE_z is expressed as the electrostatic screening energy, or the classical image potential of a core hole or point charge.^{29,30}

Therefore, we estimated $\Delta\alpha'_{\text{Si}}$ by calculating ΔE_{pol} and ΔE_z . First,

$$\Delta E_{\text{pol}} = -\frac{e^2}{2}(4\pi r)^{-1} \left(\frac{1}{\epsilon_{\text{SiO}_2}} - \frac{1}{\epsilon_{\text{SiO}_2}^b} \right), \quad (5)$$

where ϵ_{SiO_2} and $\epsilon_{\text{SiO}_2}^b$ are the dielectric constants for ultra-thin SiO₂ film and bulk SiO₂, respectively, and where e is the electronic charge. We used 0.14 nm, which is the Si 3*p* orbital radius for the cavity radius, r .^{6,12} Next, ΔE_z can be calculated using the image charge caused by dielectric discontinuity at the vacuum/SiO₂/Si interface using the method proposed by Pasquarello *et al.*³⁰ The image charge at Z in SiO₂ film with a thickness of d is calculated using

$$\Delta E_z = -\frac{e^2}{2}(4\pi\epsilon_{\text{SiO}_2})^{-1} \sum_{n=0}^{\infty} (\eta\xi)^n \left[\frac{\eta}{2Z - 2nd} + \frac{\xi}{(2n+2)d - 2Z} + \frac{2\eta\xi}{(2n+2)d} \right], \quad (6)$$

where

$$\eta = \frac{\epsilon_{\text{SiO}_2} - \epsilon_{\text{Si}}}{\epsilon_{\text{SiO}_2} + \epsilon_{\text{Si}}} \quad \text{and} \quad \xi = \frac{\epsilon_{\text{SiO}_2} - \epsilon_0}{\epsilon_{\text{SiO}_2} + \epsilon_0},$$

and where ϵ_{Si} and ϵ_0 are the dielectric constants of Si and vacuum, respectively.

The Z dependence of ΔE_{pol} and ΔE_z should affect the position of the $\text{Si}_{\text{ox}} 2p$ and $\text{Si}_{\text{ox}} KLL$ peaks. Precise determination by XPS of these peak positions depends on d and the electron escape depth. To take into account these effects, we calculated the average shift for various SiO_2 film thicknesses by taking into account two factors: the Z -dependent ΔE_{pol} and ΔE_z , and a weighting function characterized by an electron escape length, λ_{SiO_2} , of 2.6 nm.

Next, we compare the double shift of the image charge with the measured $\Delta\alpha'_{\text{Si}}$. The theoretical curve in Fig. 4(a), the solid line, was obtained using Eqs. (4)–(6) for $\epsilon_{\text{SiO}_2} = \epsilon_{\text{SiO}_2}^b = 2.1\epsilon_0$, and $\epsilon_{\text{Si}} = 12\epsilon_0$. We assumed that ϵ_{SiO_2} is constant, i.e., ΔE_{pol} is zero, throughout the SiO_2 film thickness. The present data fit surprisingly well on the theoretical curve. Figure 4(b) shows the enlarged figure for SiO_2 film thicknesses from 0 to 2.5 nm. It clearly shows that ϵ for the ultrathin (0.68–2.13 nm) SiO_2 films is virtually identical to that of the bulk SiO_2 ($\pm 1\%$ accuracy). In other words, the oxide-thickness dependence of $\Delta\alpha'_{\text{Si}}$ can be used to estimate ϵ for ultrathin SiO_2 films to within $\pm 1\%$ accuracy. The slight disagreement at an oxide thickness of 0.55 nm might be due to the limit of the image charge approximation, as mentioned above. It should be noted that the oxide-thickness dependence of $\Delta\alpha'_{\text{Si}}$ varied for SiO_2 films with a different ϵ_{SiO_2} due to different screening lengths. This suggests that, in general, the oxide-thickness dependence of $\Delta\alpha'$ can be used to estimate the ϵ for other oxides, including so-called high- k materials, which have a dielectric constant larger than that of SiO_2 and show great potential for advanced large-scale-integrated technology.^{31,32}

From this discussion, we conclude that even an ultrathin (0.6–1 nm) SiO_2 film has the same ϵ as bulk SiO_2 , i.e., a ΔE_{pol} of zero. To reconcile this conclusion with a previous study that found that the ultrathin (0.6–1 nm) SiO_2 film is compressively strained,³ we investigated the effect of strain on the $\Delta\alpha'_{\text{Si}}$ for a SiO_2 film. We calculated the α'_{Si} value for the SiO_2 cluster (Fig. 2) as a function of the Si-O-Si bond angle and obtained the $\Delta\alpha'_{\text{Si}}$ values from the shifts with respect to the $\Delta\alpha'_{\text{Si}}$ for a Si-O-Si bond angle of 144° , which is the most probable average value for bulk SiO_2 .³³ Since the cluster represents bulk SiO_2 , the calculated $\Delta\alpha'_{\text{Si}}$ does not include the contribution of ΔE_z ; it includes only

TABLE II. Calculated shift in the Auger parameter $\Delta\alpha'_{\text{Si}}$ in SiO_2 as a function of the Si-O-Si bond angle. The average bond angle is assumed to be 144° for bulk SiO_2 and 135° for ultrathin SiO_2 films formed on the Si substrate.

Si-O-Si bond angle ($^\circ$)	$\Delta\alpha'_{\text{Si}}$ (eV)
130	1714.52
135	1714.50
144	1714.55
150	1714.52

the contribution of ΔE_{pol} in Eq. (4). The calculated values are shown in Table II. The $\Delta\alpha'_{\text{Si}}$ or ΔE_{pol} value is clearly less than 50 meV for an Si-O-Si bond angle of 135° , which is assumed for a strained ultrathin SiO_2 film on Si substrates.³ These results are quantitatively consistent with a previous study using a first principles calculation, which revealed the absence of a substantial shift (>50 meV) in the relaxation energy for the Si $2p$ core-level energy with a change in the Si-O-Si bond angle.³⁰ Thus, the strained structure assumed for an ultrathin SiO_2 film does not substantially affect the ΔE_{pol} value. This is consistent with the experimental results.

IV. SUMMARY

In summary, we measured the modified Auger parameter α'_{Si} for $\text{SiO}_2/\text{Si}(001)$ interfaces by using x-ray photoelectron spectroscopy and Auger electron spectroscopy. We found that it differs by as much as 0.7 eV between thick SiO_2 films and ultrathin (0.68 nm) SiO_2 films. From the observed oxide-film-thickness dependence of α'_{Si} , we estimated the dielectric constant of an ultrathin SiO_2 film by calculating the change in the polarization energy and the change in the electrostatic screening energy originating from dielectric discontinuity at the SiO_2/Si interface. We found that the dielectric constant for an ultrathin (0.68–2.13 nm) SiO_2 film is identical to that of bulk SiO_2 within $\pm 1\%$. Since the oxide-film-thickness dependence of α' varies among oxides with different dielectric constants, this analysis can also be used for estimating the dielectric constant for other oxides, including those of high- k materials.

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