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Accurate determination of SiO₂ film thickness by x-ray photoelectron spectroscopy

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We established the number of Si 2*p* photoelectrons emanating from a Si(100) substrate covered with a silicon-oxide film as a function of azimuthal and polar angles using the oxide film thickness as a parameter. The elastic and inelastic scattering cross sections of Si 2*p* photoelectrons in silicon oxide were deduced by reproducing the experimental results with Monte Carlo simulation for the path of Si 2*p* photoelectrons in silicon oxide. Based on the simulation, we found that the elastic scattering of Si 2*p* photoelectrons in silicon oxide could effectively be neglected in several specific directions. We also found that an emitting direction different to these specific directions is indispensable when precisely determining the thickness using XPS with a large receiving angle.

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Some previous studies on silicon oxide film, such as those on the early stages of Si oxidation and SiO₂/Si interface structures, have been done using Si 2*p* photoelectron spectra measured with x-ray photoelectron spectroscopy (XPS).^{1–5} Analyses of Si 2*p* photoelectron spectra have widely been used to determine the thickness of the silicon oxide film because oxidized Si can be distinguished nondestructively from nonoxidized Si. However, the values reported, such as the photoelectron attenuation length of Si 2*p* photoelectrons in silicon oxide, have varied markedly although this is an essential parameter in determining oxide film thickness with XPS.^{6–9} This is because the Si 2*p* photoelectron intensity has a large angle dependence that is caused by the diffraction or interference between the primary photoelectron wave and the secondary electron wave, elastically scattered by crystal lattices.^{7,10} We recently found that the elastic scattering of Si 2*p* photoelectrons in silicon oxide as well as in crystalline Si must be considered in explaining the dependence of Si 2*p* photoelectron intensity on the azimuthal-angle for a Si(100) or Si(111) substrate covered with a SiO₂ thin film.^{11,12} A methodology to precisely determine oxide film thickness using XPS was proposed by Lu *et al.*⁹ They found through experiments that they could suppress the effects of photoelectron diffraction on photoelectron intensity by using the large receiving angle (28°) of a photoelectron energy analyzer. It is therefore necessary to state the efficiency of the proposed methodology through quantitatively understanding the effects of elastic scattering of Si 2*p* photoelectrons in silicon oxide on the Si 2*p* photoelectron spectral intensity.

Extremely uniform oxide films, which were essential in

our study, were prepared in the following way. First, a 1–9 Ω cm *n*-type Si layer epitaxially grown on a Si(100) surface was treated in 0.5% hydrofluoric acid solution to derive an atomically flat Si surface terminated with hydrogen (H). Second, to preserve the atomic-scale flatness of the H-terminated Si(100) surface, back-bond oxidation was done to form a preoxide with a thickness of 0.3 nm. The back-bond oxidation was done in a dry oxygen ambient at 4 Torr and 300 °C, which prevented the Si–H bonds from being broken.¹³ Through this preoxide, oxidation was done in 1-Torr-dry oxygen at 600–880 °C to form an oxide with a thickness of about 1.8 nm. An area with a diameter of 20 mm in the middle of the Si substrate was optically heated with a halogen lamp, and the center of this heated region was used to measure the photoelectron spectra.

We measured Si 2*p* photoelectron spectra with the ESCA-300, which is a highly sensitive, high-resolution photoelectron spectrometer equipped with a monochromatic Al *Kα* radiation source.¹⁴ We set the electron receiving angle of the electron energy analyzer (γ) at 2°. The direction of photoelectron emission from the surface of crystalline Si into the vacuum is expressed through azimuthal angle (ϕ) and polar angle (θ), both of which are defined as angles with respect to crystal orientation.

The thickness of oxide film (T_{ox}) was determined through the following equation:

$$T_{\text{ox}} = \Lambda_{\text{ox}} \sin \theta \ln \left[\frac{Y_s \Lambda_s n_s}{Y_{\text{ox}} \Lambda_{\text{ox}} n_{\text{ox}}} \times \{ (NO + NI) / NS + 1 \} \right],$$

where NS , NO , and NI represent the respective spectral intensities of Si 2*p* photoelectrons that are emitted from the Si substrate, SiO₂, and the intermediate oxidation states^{15–17} of Si. $n_s(n_{\text{ox}})$, $\Lambda_s(\Lambda_{\text{ox}})$, and $Y_s(Y_{\text{ox}})$ represent the respective

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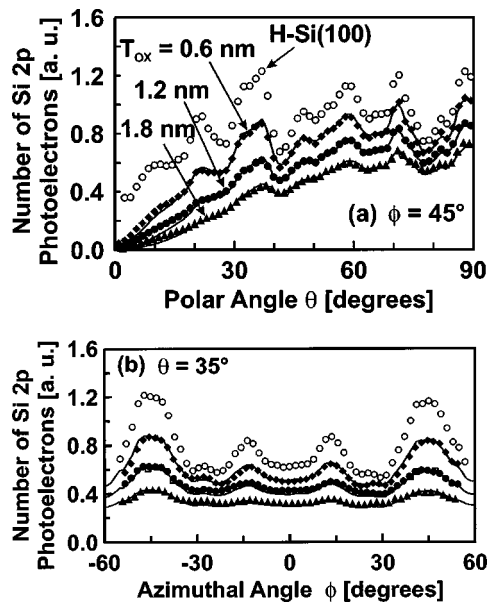


FIG. 1. Number of Si 2*p* photoelectrons emitted from H-terminated Si(100) and from Si substrate covered with 0.6, 1.2, or 1.8 nm thick silicon oxide film: (a) as function of azimuthal angle (ϕ) measured at polar angle (θ) of 35°; (b) as function of polar angle (θ) measured at azimuthal angle (ϕ) of 45°. Solid curves were derived from simulation by considering both elastic and inelastic scattering of photoelectrons in silicon oxide film.

density of Si atoms in the Si substrate (SiO_2), the electron attenuation length of Si 2*p* photoelectrons in Si (SiO_2), and the yield of Si 2*p* photoelectrons in Si (SiO_2). The respective atomic density, electron attenuation length, and photoelectron yield of intermediate oxidation states of Si are assumed to be equal to n_{ox} , Λ_{ox} and Y_{ox} . In the present analyses, we used the following values:

- (1) $5 \times 10^{28} \text{ m}^{-3}$ for n_s and $2.28 \times 10^{28} \text{ m}^{-3}$ for n_{ox} ,¹⁸
- (2) 2.11 nm for Λ_s ,⁹ and
- (3) 0.59 for Y_s and 0.69 for Y_{ox} .⁹

The values for Λ_{ox} (3.80 nm) and θ (52°) will be presented in a later discussion. The other experimental details and analytical procedures for the Si 2*p* photoelectron spectra are described elsewhere.¹⁷

Figure 1 shows the number of Si 2*p* photoelectrons emitted from H-terminated Si(100) and from Si(100) covered with 0.6, 1.2, or 1.8 nm thick silicon oxide films as a function of ϕ varied from -60° to 60° with θ fixed at 35° [Fig. 1(a)], and as a function of θ varied from 0° to 90° with ϕ fixed at 45° [Fig. 1(b)]. The change we observed in the number of Si 2*p* photoelectrons as a function of ϕ or θ is referred to as an interference pattern generated by so-called photoelectron diffraction from Si substrates. Figures 1(a) and 1(b) reveal that Si 2*p* photoelectron spectral intensity decreases as oxide film thickness increases. This is because some of the Si 2*p* photoelectrons emitted from the Si(100) surfaces lose their energy due to inelastic scattering in silicon oxide. We also found that the interference pattern became more indistinguishable as oxide film thickness increased. This is because Si 2*p* photoelectrons emitted from the Si(100) surface changed their directions of travel as they were elastically scattered in the silicon oxide.^{7,19}

Salvat and Parellada revealed elastic and inelastic scat-

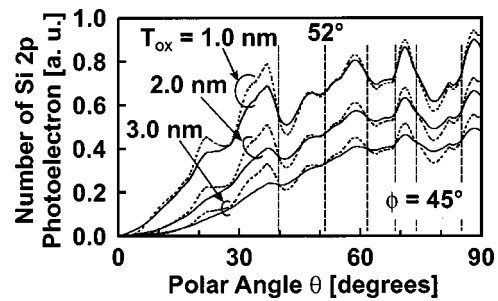


FIG. 2. Dependence of Si 2*p* spectral intensity on the polar angle calculated for samples with 1.0, 2.0, or 3.0 nm thick oxide films. Solid curves were derived from the simulation by considering both elastic and inelastic scattering of photoelectrons in oxide film, while dotted curves were derived from the simulation by only considering inelastic scattering. The elastic scattering of Si 2*p* photoelectrons in silicon oxide can effectively be neglected in some photoelectron emission directions, which are indicated by the vertical dashed lines.

tering processes for photoelectrons in metal through Monte Carlo simulation.²⁰ Applying this model, we will discuss the scattering process of Si 2*p* photoelectrons in silicon oxide to obtain a scattering cross section. The simulations were done, based on the following assumptions, to reveal the path of Si 2*p* photoelectrons in oxide:

(1) The crystal structure of the Si substrate near the SiO_2/Si interface is not changed by oxidation.²¹ Therefore, we used the interference pattern from the H-terminated Si surface as an initial pattern before scattering occurred in silicon oxide film.

(2) Angular deflections due to elastic scattering of Si 2*p* photoelectrons can be calculated using the Wentzel model²² of Coulomb potential $V(r) = (Zq^2/r) \exp(-\beta r/a_0)$, where r is distance from the center of an atom, q is electron charge, Z is the atomic number of the target atom, a_0 is the Bohr radius, and α is the screening constant expressed by the following equation; $\alpha = Z^{1/3}$. Meanwhile β is an adjustable parameter and is equal to 1 in the Wentzel model.

(3) The elastic scattering cross section [$\sigma_{\text{el}}(\pi)$] in silicon oxide is given by the following equation: $\sigma_{\text{el}}(\pi) = (1/3)\sigma_{\text{elSi}}(\pi) + (2/3)\sigma_{\text{elO}}(\pi)$, where $\sigma_{\text{elSi}}(\pi)$ and $\sigma_{\text{elO}}(\pi)$ represent the respective elastic scattering cross section for Si atoms and that for oxygen atoms and denote the integration of the scattering cross section within a scattering angle range of 0 to π .²⁰

(4) The inelastic cross section (σ_{in}) represents the sum of cross sections for all inelastic scatterings of Si 2*p* photoelectrons in silicon oxide. An inner potential^{19,23} of 15.3 eV was used to calculate the emitting direction of photoelectrons from the oxide surface into the vacuum.

The solid curves in Figs. 1(a) and 1(b) were obtained by Monte Carlo simulation with both a $\sigma_{\text{el}}(\pi)$ and σ_{in} of $1.17 \pm 0.07 \times 10^{-20} \text{ m}^2$. They correlated well with the experimental results. Here, the value for $\sigma_{\text{el}}(\pi)$ was obtained with a β of 0.80 ± 0.03 . The inelastic mean free path (L_{ox}) of Si 2*p* photoelectrons in silicon oxide was deduced to be $3.80 \pm 0.22 \text{ nm}$ from a σ_{in} of $1.17 \pm 0.07 \times 10^{-20} \text{ m}^2$ through the following equation; $L_{\text{ox}} = 1/(n_{\text{ox}}\sigma_{\text{in}})$. The value of L_{ox} determined above was in an excellent agreement with the 3.8 nm obtained theoretically by Tanuma *et al.*²⁴

Figure 2 shows the dependence of spectral intensity of

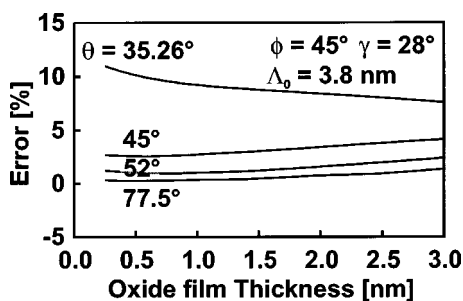


FIG. 3. Errors in oxide film thickness determined from Monte Carlo simulation of path of Si 2*p* photoelectrons in silicon oxide film with receiving angle of 28° and using photoelectron takeoff angle as a parameter.

Si 2*p* photoelectrons on the polar angle calculated for samples with 1, 2, or 3 nm thick silicon oxide films. The solid curves were obtained when photoelectrons were scattered elastically and inelastically in silicon oxide, while the dotted curves were obtained when photoelectrons were only scattered inelastically in silicon oxide. The values of $\sigma_{el}(\pi)$ and σ_{in} used in Fig. 1 were both $1.17 \times 10^{-20} \text{ m}^2$.

We will now discuss the accuracy of measuring oxide film thickness using XPS with a small receiving angle, based on the above discussion on photoelectron diffraction. In measuring silicon–oxide film thickness, it is especially important to measure photoelectrons which enter the vacuum in a direction defined by a ϕ of 45° and a θ of 52° as indicated by the one of the dashed lines in Fig. 2. There are two reasons for selecting this particular direction:

- (1) In this photoelectron-emitting direction, the elastic scattering effect of Si 2*p* photoelectrons in silicon oxide on photoelectron spectral intensity can effectively be neglected and
- (2) errors in aligning the direction of receiving photoelectrons at the detector with respect to the direction of photoelectron emission can be minimized because changes in Si 2*p* spectral intensity are marginal in this latter vicinity.

Next we will discuss the efficiency of Lu and his collaborator's methodology⁹ using XPS with a large receiving angle. In Fig. 3, errors in oxide-film thicknesses were determined from Monte Carlo simulation with a ϕ of 45° and a γ of 28°. We used a Λ_{SiO_2} of 3.8 nm that was determined from simulation. As we can see from the figure, the two photoelectron emission angles (ϕ, θ) of (45°, 35.26°) and (45°, 45°) did not enable us to determine oxide-film thickness as Lu *et al.* pointed out.⁹ Also, photoelectron emission angles (ϕ, θ) of (45°, 52°) could not be used to determine oxide-film thickness with a large receiving angle of 28°, although they were effective with an extremely small acceptance angle (2°) as we can see from Fig. 2. However, the errors in oxide film thicknesses are extremely small (0.3%–1.3%) for photoelectron emission angles (ϕ, θ) of (45°, 77.5°), which correlates well with the experimental results obtained by Lu *et al.*⁹ We can thus conclude that photoelectron measurement with a large receiving angle should be used where photoelectron emission angles (ϕ, θ) = (45°, 77.5°), so that we can precisely determine oxide-film thicknesses.

To summarize, we determined the number of Si 2*p* photoelectrons emanating from a Si(100) substrate covered with silicon oxide film as a function of azimuthal and polar angles using the oxide film thickness as a parameter. The elastic and inelastic scattering cross sections of Si 2*p* photoelectrons in silicon oxide were deduced by reproducing the experimental results with Monte Carlo simulation for the path of Si 2*p* photoelectrons in silicon oxide. Based on the simulation, we found that elastic scattering of Si 2*p* photoelectrons in silicon oxide could effectively be neglected in several specific directions. We demonstrated that an emitting direction different from these directions is indispensable when precisely determining the thickness using XPS with a large receiving angle.

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- ¹T. Hattori, *CRC Crit. Rev. Solid State Mater. Sci.* **20**, 339 (1995).
- ²D.-A. Luh, T. Miller, and T.-C. Chiang, *Phys. Rev. Lett.* **79**, 3014 (1997).
- ³S. Dreiner, M. Schürman, C. Westphal, and H. Zacharias, *Phys. Rev. Lett.* **86**, 4068 (2001).
- ⁴K. Hirose, K. Sakano, H. Nohira, and T. Hattori, *Phys. Rev. B* **64**, 155325 (2001).
- ⁵K. Takahashi, M. B. Seman, K. Hirose, and T. Hattori, *Jpn. J. Appl. Phys., Part 2* **41**, L223 (2002).
- ⁶R. Flitsch and S. I. Raider, *J. Vac. Sci. Technol.* **12**, 305 (1975).
- ⁷J. M. Hill, D. G. Royce, C. S. Fadley, L. F. Wagner, and F. J. Grunthaner, *Chem. Phys. Lett.* **44**, 225 (1976).
- ⁸M. P. Seah and W. A. Dench, *Surf. Interface Anal.* **1**, 2 (1979).
- ⁹Z. H. Lu, J. P. McCaffrey, B. Brar, G. D. Wilk, R. M. Wallace, L. C. Feldman, and S. P. Tay, *Appl. Phys. Lett.* **71**, 2764 (1997).
- ¹⁰C. S. Fadley, *Prog. Solid State Chem.* **11**, 265 (1976).
- ¹¹T. Hattori, K. Hirose, H. Nohira, K. Takahashi, and T. Yagi, *Appl. Surf. Sci.* **144/145**, 297 (1999).
- ¹²H. Nohira, K. Hirose, K. Takahashi, and T. Hattori, *Appl. Surf. Sci.* **162/163**, 304 (2000).
- ¹³M. Fujimura, K. Inoue, H. Nohira, and T. Hattori, *Appl. Surf. Sci.* **162/163**, 62 (2000).
- ¹⁴U. Gelius, B. Wannberg, P. Baltzer, H. Fellner-Feldegg, G. Carlsson, C. G. Johansson, J. Larsson, P. Munger, and G. Vergerfos, *J. Electron Spectrosc. Relat. Phenom.* **52**, 747 (1990).
- ¹⁵T. Hattori and T. Suzuki, *Appl. Phys. Lett.* **43**, 470 (1983).
- ¹⁶G. Hollinger and F. J. Himpsel, *Appl. Phys. Lett.* **44**, 93 (1984).
- ¹⁷K. Ohishi and T. Hattori, *Jpn. J. Appl. Phys., Part 2* **33**, L675 (1994).
- ¹⁸M. F. Hochella, Jr. and A. H. Carim, *Surf. Sci.* **197**, L260 (1988).
- ¹⁹C. S. Fadley, *Prog. Surf. Sci.* **16**, 275 (1984).
- ²⁰F. Salvat and J. Parellada, *J. Phys. D* **17**, 185 (1984).
- ²¹Oxidation-induced changes in the crystalline structure do not occur in the vicinity of the SiO₂/Si interface because no differences could be detected between the diffraction pattern of Si 2*p* photoelectrons emitted through thermally grown silicon oxide and that of Si 2*p* photoelectrons emitted through the deposited silicon oxide, both of which had almost the same thickness.
- ²²G. Wentzel, *Z. Phys.* **40**, 590 (1927).
- ²³T. Miller, A. P. Shapiro, and T.-C. Chiang, *Phys. Rev. B* **31**, 7915 (1985).
- ²⁴S. Tanuma, C. J. Powell, and D. R. Penn, *Surf. Interface Anal.* **17**, 927 (1991).