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Determination of electron escape depth in ultrathin silicon oxide

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Using the high-brilliance synchrotron radiation at SPring-8, we determined the electron escape depths in approximately 1-nm-thick low-temperature oxide layers, which were formed on Si(100) at 300 °C using three kinds of atomic oxygen and that in approximately 1-nm-thick thermally grown oxide layer formed in 1 Torr dry oxygen at 900 °C by measuring angle-resolved Si 2*p* photoelectron spectra at the photon energy of 1050 eV. The results indicated that the electron escape depths in the three kinds of low-temperature oxide layers were 18%–24% smaller than that in the thermally grown oxide layer. Furthermore, the electron escape depth in the thermally grown oxide layer, whose thickness was close to that of the structural transition layer, was 7% smaller than that in bulk SiO_2. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1868066]

The electron escape depth in silicon oxide layer and that in silicon used for the determination of silicon oxide thickness by x-ray photoelectron spectroscopy have been determined by measuring the number of x-ray excited photoelectrons arising from silicon oxide layer and that arising from silicon as a function of thickness of silicon oxide layer.[1,2] However, such method cannot be applied to the oxide layer with the thickness on the order of 1 nm, which mostly determines the quality of a SiO_2/Si interfacial transition layer. One of our goals is to establish a low-temperature oxidation process for the gate insulator of thin-film transistors on glass or plastic substrates. Radical oxidation is one of the most effective ways to conduct an oxidation reaction at low temperature. We evaluated three approaches for effectively generating oxygen radicals. Photo-oxidation uses a xenon excimer lamp producing 172 nm wavelength light, which has a photon energy sufficient to selectively obtain O(1D) radicals and lower than the SiO_2 band gap in order to suppress defect production at the SiO_2/Si interface. Plasma-enhanced oxidation, which is further enhanced by adding a rare gas such as Kr, is also effective for obtaining high-density oxygen radicals. In the present letter the method of determining the electron escape depths in ultrathin silicon oxide layers by measuring angle-resolved Si 2*p* photoelectron spectra is proposed and the electron escape depths in low-temperature oxides formed at 300 °C using three kinds of atomic oxygen are found to be clearly different from that in thermally grown oxide layer formed at 900 °C using molecular oxygen.

On a vicinal Si(100) 0.01° surface, a 0.72-nm-thick oxide layer was formed at 300 °C by using atomic oxygen produced in a krypton-mixed oxygen ($Kr:O_2=97:3$) plasma excited by microwave radiation (2.45 GHz); this layer is referred to as Kr/O_2 plasma oxide hereafter.[3] On the same kind of surface, a 0.86-nm-thick oxide layer was formed at 300 °C by using atomic oxygen produced in an oxygen plasma excited by microwave radiation (2.45 GHz); this layer is referred to as O_2 plasma oxide hereafter.[3] Finally, on a third sample with the same kind of surface, a 0.85-nm-thick oxide layer, referred to as photo-oxide hereafter, was formed at 300 °C by using atomic oxygen produced by exciting molecular oxygen with a xenon excimer lamp. As a reference, a high-quality 1.25-nm-thick silicon oxide layer, referred to as thermal oxide hereafter, was formed in dry oxygen at 900 °C on another vicinal Si(100) 0.01° surface covered with a 0.3-nm-thick pre-oxide layer formed in dry oxygen at 300 °C.[4] The thicknesses of SiO_2 layers were evaluated from the angle-resolved Si 2*p* photoelectron spectra discussed and the thicknesses of compositional transition layers were evaluated from the measurement of Si 2*p* photoelectron spectra at photoelectron take-off angle of 55°, where the effect of elastic scattering can be effectively neglected.[5] Using electron energy analyzer ESCA-200 angle-resolved 1050 eV photons' excited Si 2*p* photoelectron spectra were measured with energy resolution of 100 meV at soft-x ray undulator beam line (BL27SU) of the Super Photon Ring 8 GeV (SPring-8).

Figure 1 shows 1050 eV photons' excited Si $2p_{3/2}$ photoelectron spectra arising from Kr/O_2 plasma oxide, O_2 plasma oxide, photo-oxide and thermal oxide with photo-

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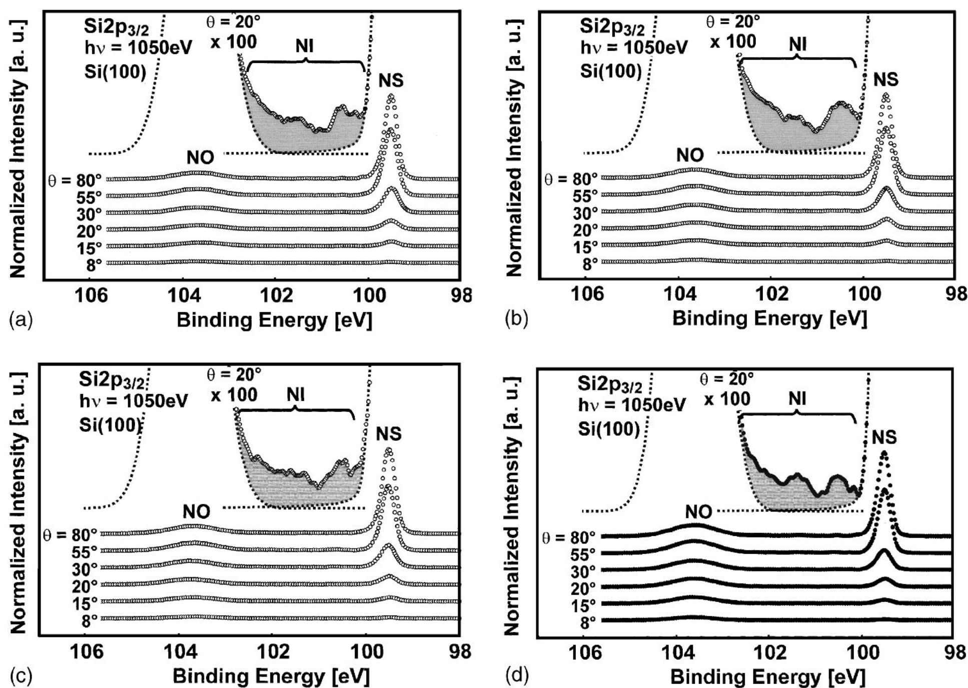

FIG. 1. 1050 eV photons' excited Si $2p_{3/2}$ photoelectron spectra with photoelectron take-off angle θ as a parameter measured for (a) the Kr/O_2 plasma oxide, (b) the O_2 plasma oxide, (c) the photo-oxide, and (d) the thermal oxide, which were formed on Si(100) surfaces.

electron take-off angle θ as a parameter. Here, the refraction of the electron wave at vacuum/SiO_2 interface was taken into account.[6] With decreasing θ, the Si $2p$ photoelectron spectral intensities arising from the Si substrate decreased. This confirmed that the Si substrates were, in fact, covered with silicon oxide layers. Furthermore, the Si $2p_{3/2}$ spectral intensity, NI, arising from the compositional transition layer consisting of intermediate oxidation states of Si measured at photoelectron take-off angle of 20° is indicated by the shaded region in each graph. The amounts of NI are 0.759 ML for Kr/O_2 plasma oxide, 0.865 ML for O_2 plasma oxide, 0.881 ML for photo-oxide, and 0.835 ML for thermal oxide, respectively. Here, 1 ML expresses 6.80×10^{14} cm^{-2}.

The dependencies of NI/NO on θ measured for three kinds of low-temperature oxide layers formed on Si(100) are compared with that measured for thermal oxide in Fig. 2. Here, NO represents the Si $2p$ spectral intensity arising from SiO_2. The dependence of NI/NO on θ can be expressed as a function of the electron escape depth Λ_O in the SiO_2 layer by the following equation. Here, it should be noted that the effect of photoelectron diffraction on the dependence of NI/NO on θ does not have to be taken into account, because the oxide layers are in amorphous states,

$$\frac{\mathrm{NI}}{\mathrm{NO}} = \frac{n_t\Lambda_t \sin\theta\left\{1-\exp\left(-\dfrac{t}{\Lambda_t\sin\theta}\right)\right\}}{n_o\Lambda_o\sin\theta\left\{\exp\left(\dfrac{d}{\Lambda_o\sin\theta}\right)-1\right\}}. \quad (1)$$

Here, n_O and n_t, d and t, and Λ_t denote the densities of silicon atoms in the SiO_2 layer and the compositional transition layer, the thicknesses of the SiO_2 layer and the compositional transition layer, and the electron escape depth in the compositional transition layer, respectively. The following relation between Λ_O and d should be satisfied.

$$\frac{\mathrm{NO}}{\mathrm{NS}} = \frac{n_o\Lambda_o\left\{\exp\left(\dfrac{d}{\Lambda_o\sin\theta}\right)-1\right\}}{n_s\Lambda_s\exp\left(-\dfrac{t}{\Lambda_t\sin\theta}\right)}. \quad (2)$$

Here, Λ_s represents the electron escape depth in the silicon substrate. The value of Λ_s (1.59 nm) was calculated from the escape depth (2.11 nm) of Si $2p$ photoelectrons in silicon excited by Al $K\alpha$ radiation,[2] by considering the dependence of the electron escape depth on the kinetic energy of the electrons.[7] The following relation between Λ_t and t should also be satisfied,

$$\frac{\mathrm{NI}}{\mathrm{NS}} = \frac{n_t\Lambda_t\left\{\exp\left(\dfrac{t}{\Lambda_t\sin\theta}\right)-1\right\}}{n_s\Lambda_s}. \quad (3)$$

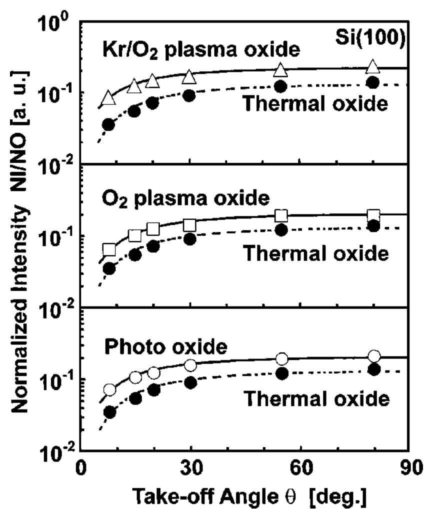

FIG. 2. Dependence of NI/NO on θ for (a) Kr/O_2 plasma oxide, (b) O_2 plasma oxide, and (c) photo-oxide. As a reference, the dependence of NI/NO on θ for the thermal oxide is also shown.

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TABLE I. Electron escape depths in low-temperature oxides.

	Kr/O_2 plasma oxide	O_2 plasma oxide	Photo-oxide	Thermal oxide
Λ_O (nm)	2.04	2.06	2.19	2.67

The values of Λ_0 for the four kinds of oxides were determined by least-squares fitting, shown by the solid and dashed curves in Fig. 2, which were calculated using Eq. (1), with the experimental data. Here, we assumed that n_O was the value for bulk SiO_2, and that $n_t=(n_s+n_O)/2$ and $\Lambda_t=(\Lambda_s+\Lambda_O)/2$. We used values of 5×10^{28} cm^{-2} for n_s and 2.28×10^{28} cm^{-2} for n_O.[8] The resulting values of Λ_0 are listed in Table I. As shown in Table I, the electron escape depth (2.67 nm) in thermal oxide, whose thickness (1.25 nm) was comparable to the thickness of the structural transition layer consisting of SiO_2,[9] was smaller than 2.86 nm, whose value calculated from the escape depth (3.80 nm)[10] of Si 2p photoelectrons excited by Al $K\alpha$ radiation in thermally grown bulk SiO_2 by considering the dependence of the electron escape depth on the kinetic energy of the electrons.[7] This must be correlated with the observation that the density of the structural transition layer is approximately 5% larger than that of bulk SiO_2.[11] The electron escape depths in three kinds of low temperature oxides listed in Table I are 18%–24% smaller than that in thermal oxide. Because the difference between the densities of low-temperature oxide and thermal oxide is nearly 5%, the difference between the electron escape depths in each type of oxide cannot be ascribed to the density difference; rather, it may be ascribed to the difference in the electron scattering mechanisms. Specifically, because the fraction of oxygen atoms that are not incorporated in the oxide network may be larger in low-temperature oxide than in thermal oxide, the scattering frequency of electrons may be larger in the low-temperature oxide, resulting in a smaller electron escape depth as compared to that in the thermal oxide. Furthermore, it should be noted that the electron escape depth in the Kr/O_2 plasma oxide and in the O_2 plasma oxide was 6% smaller than that in the photo-oxide.

In conclusion, the electron escape depths in three kinds of ultrathin low-temperature-oxide and that in ultrathin thermal oxide were determined from angle-resolved Si 2p photoelectron spectra. We found that the electron escape depths in the low-temperature oxide layers were 18%–24% smaller than that in the thermal oxide. The results also indicated that the electron escape depth in the thermal oxide, whose thickness was close to that of the structural transition layer, was 7% smaller than that in bulk SiO_2.

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