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# Oxide thickness dependence of energy shifts in the Si 2p levels for the SiO<sub>2</sub>/Si structure, and its elimination by a palladium overlayer

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The energy difference between the oxide and substrate Si 2p peaks for silicon oxide/Si structures increases with the oxide thickness. The dependence of the energy shift on the oxide thickness almost disappears with the deposition of a thin palladium overlayer, because of the avoidance of the surface charging effect due to photoemission and because of the nearly constant energy shift resulting from extra atomic relaxation. The true chemical shift of silicon oxide layers thicker than 2 nm is determined to be  $\sim$  3.8 eV. For the thickness dependence of the oxide Si 2p energy, the extra atomic relaxation and charging effect are dominant for oxide layers thinner than  $\sim 2$  nm and thicker than  $\sim$ 4 nm, respectively. In the intermediate thickness region, both the effects are important. © 1998 American Institute of Physics. [S0003-6951(98)03133-7]

The silicon oxide/Si structure is one of the most extensively studied systems mainly because of its importance to metal-oxide-semiconductor devices. Photoelectron spectroscopy is often employed to elucidate the electronic structure of thin silicon oxide layers. It is often reported that the energy difference between the oxide and substrate Si 2ppeaks ( $\Delta E_{si}$ ) increases with the oxide thickness.<sup>1–8</sup> The following three effects may contribute to the shifts: (i) changes in the chemical bonds<sup>1</sup> (i.e., the initial state change), (ii) changes in the extra atomic relaxation energy $^{2-4}$  (i.e., the final state change), and (iii) the charging effects of silicon oxide layers due to photoemission.<sup>3,5,6</sup> Grunthaner et al.<sup>1</sup> attributed the dependence of  $\Delta E_{Si}$  on the oxide thickness to the changes in the Si-O-Si bond angle on which the charge transfer from silicon to oxygen depends, i.e., the larger the bond angle, the larger the energy shift. Hollinger<sup>2</sup> observed the energy separation between the Si 2p peak and the Si KLL Auger peak (i.e., the Auger parameter) and attributed the thickness dependence of  $\Delta E_{Si}$  to the variation in the extra atomic relaxation energy. Zhang et al.3 reported that the thickness dependence of  $\Delta E_{Si}$  for oxide layers thinner than 3 nm is due to the change in the final state screening energy, while the further energy shift for thicker oxide layers is due to the charging issue. On the other hand, Iwata and Ishizaka<sup>5</sup> concluded that the change in oxide Si 2p energy with oxide thickness is due to the charging effect.

In the present study, the charging issue is avoided by depositing a grounded thin palladium (Pd) layer on the silicon oxide surface. By the deposition of Pd, the strong dependence of the final state screening energy on the oxide thickness is also avoided.

Phosphorus-doped *n*-type Si(100) wafers with a  $\sim 10 \ \Omega$  cm resistivity were cleaned chemically. Silicon oxide layers of thicknesses ranging between  $\sim 1$  and  $\sim 10$  nm were formed by heat treatments in dry oxygen. For some specimens, a  $\sim$ 3 nm thick Pd layer was deposited on the oxide surface.

X-ray photoelectron spectra (XPS) were recorded using a VG SCIENTIFIC ESCALAB 220i-XL spectrometer with a monochromatized Al  $K\alpha$  radiation source. During the XPS measurements, the rear Si surface and the Pd film were grounded, and photoelectrons were collected in the surfacenormal direction.

Figure 1 shows the XPS spectra in the Si 2p region for the oxide-covered Si(100) substrate without [spectrum (a)]



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FIG. 2. Energy difference between the oxide and substrate Si  $2p_{3/2}$  peaks  $(\Delta E_{\rm Si})$  [plots (a) and (b)], that between the O 1*s* and oxide Si  $2p_{3/2}$  peaks  $(\Delta E_{\rm O-Si})$  [plot (c)], and binding energy of the substrate Si  $2p_{3/2}$  peak [plot (d)] as a function of the oxide thickness: (a), (c), and (d) with no Pd overlayer; and (b) with the Pd overlayer.

and with [spectrum (b)] a Pd overlayer. The doublet peaks are due to the Si  $2p_{3/2}$  and  $2p_{1/2}$  levels of the substrate and the broad peak is due to the oxide layer. The deposition of a Pd overlayer caused the oxide peak to be shifted greatly and the substrate peaks slightly in the lower energy direction.

Figure 2 shows the energy difference between the oxide and substrate Si  $2p_{3/2}$  peaks ( $\Delta E_{Si}$ ) [plots (a) and (b)], that between the O 1*s* and oxide Si  $2p_{3/2}$  peaks ( $\Delta E_{O-Si}$ ) [plot (c)], and the energy of the substrate Si  $2p_{3/2}$  peak [plot (d)] as a function of the oxide thickness. The energy of the oxide Si  $2p_{3/2}$  level was determined by the curve resolution of the broad oxide peak (cf. Fig. 1). With no Pd overlayer,  $\Delta E_{Si}$ increased rapidly with the oxide thickness ( $d_{ox}$ ) when  $d_{ox}$ was below ~2.5 nm and for the thicker oxide layers,  $\Delta E_{Si}$ 



FIG. 3. Band diagrams for the oxide/Si structure under x-ray irradiation: (a) with no Pd overlayer; (b) with a Pd overlayer. (c) shows the image charge potential for the extra atomic final state relaxation.

increased almost linearly with  $d_{ox}$  [plot (a)]. On the other hand,  $\Delta E_{O-Si}$  was nearly constant [plot (c)]. The constant  $\Delta E_{O-Si}$  indicates that  $\Delta E_{Si}$  is not due to a change in the initial bonding states. The substrate Si  $2p_{3/2}$  peak showed small higher energy shifts with the oxide thickness in the thickness range below ~2.5 nm and for the thicker oxide layers, the energy became constant [plot (d)]. With the Pd overlayer,  $\Delta E_{Si}$  increased only slightly with the oxide thickness [plot (b)].

Figure 3 shows the expected band diagrams for the silicon oxide/Si structures under x-ray irradiation without [Fig. 3(a)] and with [Fig. 3(b)] a Pd overlayer. In the absence of the Pd overlayer, positive charges ( $Q_S$ ) are accumulated on the oxide surface due to photoemission. Holes in the oxide valence band can easily transfer to the Si. Holes are likely to be trapped in the gap states present at the oxide surface, i.e., surface states probably arising from unsatisfied bonds. Counter negative charges are induced in the Si surface region, causing a downward band bending in Si. Due to the oxide surface charges ( $Q_S$ ), a downward potential drop is induced across the oxide layer with the magnitude given by

$$\Delta V_{\rm ox} = Q_S / C_{\rm ox} = Q_S d_{\rm ox} / \epsilon_{\rm ox}, \qquad (1)$$

where  $C_{ox}$  is the capacitance of the oxide layer, and  $d_{ox}$  and  $\epsilon_{ox}$  are the thickness and the permittivity of the oxide layer, respectively.  $\Delta V_{ox}$  leads to a higher energy shift of the oxide Si 2p peak with respect to the substrate Si 2p peak ( $\Delta E_{Si}$ ).  $\Delta V_{ox}$  can be calculated easily from  $\Delta E_{Si}$  as described below. In the calculation, it is assumed that the potential (*E*) in the oxide layer changes linearly with the distance (*x*) from the oxide surface [cf. Fig. 3(a)]:

$$E = \Delta V_{\rm ox} x / d_{\rm ox} \,. \tag{2}$$

This assumption is valid in cases where all photogenerated holes are present at the oxide surface, due to a very low gap state density in the oxide bulk. In this case, the oxide Si  $2p_{3/2}$  intensity (*I*) as a function of energy *E* is given by<sup>9</sup>

$$I(E) = C_1 \int_0^{e\Delta V_{\text{ox}}} \exp\left(\frac{-E_x d_{\text{ox}}}{e\Delta V_{\text{ox}}\lambda}\right) \\ \times \left[\exp\left\{\frac{-(E-E_0-E_x)^2}{W^2}\right\}\right] dE_x, \qquad (3)$$

where  $E_0$  is the energy at the intensity maximum of the oxide Si  $2p_{3/2}$  peak,  $\lambda$  is the photoelectron mean-free path in the oxide layer, *W* is a constant related to the peak width, and  $C_1$  is a constant. By deviating Eq. (3),  $\Delta E_{\text{Si}}$  caused by  $\Delta V_{\text{ox}}$  can be estimated. From this calculation, the following simple relation is obtained:

$$\Delta E_{\rm Si} = C(d_{\rm ox}) \Delta V_{\rm ox}, \tag{4}$$

where  $C(d_{\text{ox}})$  is a constant which was found to depend weakly on  $d_{\text{ox}}$  [i.e., C(2.5 nm) = 0.58 and C(10 nm) = 0.76].

The thickness dependence of  $\Delta E_{\rm Si}$  caused by the charging effect is shown by the dotted line in Fig. 2(a). It is seen that the experimental plots in the thickness range larger than ~4 nm is well represented by the charging effect. From the plot in this region, the surface charge density ( $Q_s$ ) is estimated to be ~1×10<sup>12</sup> cm<sup>-2</sup>.

In the presence of the Pd overlayer, charging due to photoemission does not occur. However, because of the difference in the work function between *n*-Si and Pd, electron transfer from *n*-Si to Pd occurs, resulting in the upward band bending in *n*-Si [cf. Fig. 3(b)], thus shifting the substrate Si 2p peak toward a lower energy (cf. Fig. 1). Because of the low depletion layer charge density ( $\sim 5 \times 10^{14}$  cm<sup>-3</sup> for the 10  $\Omega$  cm Si), the potential drop across the oxide layer is calculated to be negligibly small (i.e., less than scores of ten millivolts), leading to the smaller  $\Delta E_{Si}$ .

In the absence of the Pd overlayer, the oxide Si 2p peak is also shifted by a change in the energy of the extra atomic screening of photogenerated hole states by the Si substrate, which is in approximately inverse proportion to the distance from the oxide/Si interface assuming simple image charges,<sup>10</sup> as shown in Fig. 3(c). In this case, the photoelectron intensity (*I*) is given by

$$I(E) = C_2 \int_{-A/d_{\rm im}}^{-A/2d_{\rm ox}} \exp\left(\frac{A}{2\lambda E_x}\right) \\ \times \left[\exp\left\{\frac{-(E-E_0-E_x)^2}{W^2}\right\}\right] dE_x,$$
(5)

where  $d_{\rm im}$  is the distance between the photogenerated hole in the oxide first layer and its image charge (which distance is assumed to be 0.235 nm, i.e., the Si–Si bond length) and where A and  $C_2$  are constants. It is found that the calculation of the oxide Si 2p shift using Eq. (5) well represents the experimental plot [Fig. 2(a)] in the region of thickness smaller than ~2 nm, as shown by the dashed line.

In the intermediate thickness region (i.e., the region between  $\sim 2$  and  $\sim 4$  nm), both the charging and screening effects should be included to express the experimental  $\Delta E_{Si}$ . The calculated thickness dependence of  $\Delta E_{Si}$  (including both the effects) are shown by the solid line in Fig. 2(a), and it is seen that the observed plot in the whole thickness region is well represented by the calculation.

In the calculation of the energy shift due to the charging, the amount of the oxide surface charge  $(Q_S)$  is assumed to be independent of the oxide thickness. The unchanged substrate Si 2p energy with  $d_{ox}$  in the thickness range larger than ~2.5 nm [Fig. 2(d)] indicates a constant  $Q_S$ . The small energy shift of the substrate Si  $2p_{3/2}$  peak in the thickness region below ~2.5 nm is caused by a decrease in the counter negative charge of  $Q_S$  due to an increase in the tunneling probability of  $Q_S$  through the oxide layer.<sup>11</sup> The decrease in  $Q_S$  results in a decrease in  $\Delta V_{ox}$  and thus in a decrease in  $\Delta E_{Si}$ .

In the presence of the Pd overlayer, on the other hand, the photogenerated holes are screened by the electrons in the Pd layer. Since the oxide/Pd interface is present above the oxide layer, the energy shift of the oxide Si 2p peak due to the extra atomic screening effect becomes much smaller than that in the absence of the Pd layer, as is evident from the calculated curve shown by the solid line in Fig. 2(b). Due to the avoidance of the charging effect and the nearly constant extra atomic screening energy,  $\Delta E_{Si}$  depends only weakly on the oxide thickness.

Zhang *et al.*<sup>3</sup> simulated the SiO<sub>2</sub>/Si system by depositing Si<sub>8</sub>H<sub>8</sub>O<sub>12</sub> clusters on the Si(100) surface, by which they avoided a change in the initial bonding state. From measurements of the x-ray exposure time dependence, x-ray flux dependence, and incident photon energy dependence of the oxide and substrate Si 2*p* energies, they concluded that the shift of the oxide Si 2*p* peak by 0.6 eV caused by changing the oxide thickness from 0.6 to 3 nm is due to a change in the extra atomic relaxation energy, while the further shift for thicker oxide is due to the charging effect. The present result agrees well with their result.

In summary, the dependence of the energy difference between the oxide and substrate Si 2p peaks ( $\Delta E_{Si}$ ) on the oxide thickness ( $d_{ox}$ ) is well represented by the charging and screening effects, showing that the initial bonding states do not depend on  $d_{ox}$ .

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