The valence band alignment at ultrathin SiO_2/Si interfaces

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High resolution x-ray photoelectron spectroscopy has been used to determine the valence band alignment at ultrathin SiO_2/Si interfaces. In the oxide thickness range 1.6–4.4 nm the constant band-offset values of 4.49 and 4.43 eV have been obtained for the dry SiO_2/Si(100) and the wet SiO_2/Si(100) interfaces, respectively. The valence band alignment of dry SiO_2/Si(111) (4.36 eV) is slightly smaller than the case of the dry SiO_2/Si(100) interface. © *1997 American Institute of Physics.* [S0021-8979(97)00203-X]

Ultralarge scale integration (ULSI) of metal-oxide-semiconductor (MOS) devices will need reliable gate oxides thinner than 5.0 nm in the near future. In order to predict the tunneling leakage current through the ultrathin gate oxides, an accurate description of the energy band profile at the ultrathin SiO_2/Si interfaces or a precise knowledge on the value of the valence band alignment and the conduction band barrier height is required.[1] Although the energy band profile of thick SiO_2/Si interfaces has been determined by an internal photoemission technique,[2] reliable values for the electron or hole barrier height at ultrathin SiO_2/Si interfaces remain an unresolved issue. Among the various attempts that have been made in the past to gain a comprehensive understanding of the barrier height or the energy band profile for ultrathin SiO_2/Si interfaces,[3–8] the consistent picture of the energy band profile has not yet been drawn. Horiguchi and Yoshino[3] have reported that the barrier height for SiO_2/Si(100) decreases when the oxide thickness becomes thinner than 3.1 nm. On the other hand, by using an electron-beam-assisted scanning tunneling microscopy technique, Heike *et al.*[4] have concluded that the barrier height at the SiO_2/Si(100) interfaces keeps a constant value of 2.7 eV in the oxide thickness range 1.8–4.5 nm. Grunthaner and Grunthaner[9] have measured valence band spectra of ~6-nm-thick SiO_2 thermally grown on Si(111) by using x-ray photoelectron spectroscopy and found the valence band offset of 4.5 eV. Also, Himpsel *et al.*[10] have obtained a valence band alignment of 4.3 eV for the SiO_2/Si(100) interface by using the Si $2p$ core level spectrum. Thus well established values of the valence band alignment or the barrier height at ultrathin SiO_2/Si interfaces are not available.

The purpose of our study is to directly determine the magnitude of the valence band alignment or the hole barrier height at the ultrathin SiO_2/Si interface and derive a value for the conduction band barrier height by using a measured SiO_2 band gap, based on the valence band density of states (VBDOS) for ultrathin gate oxides (below 5.0 nm) thermally grown on Si(100) and Si(111) surfaces by employing high-resolution x-ray photoelectron spectroscopy (XPS).

Ultrathin gate oxides were grown at 1000 °C in a 2% dry O_2 gas diluted with N_2 or at 850 °C in wet ambient. Hydrogen-terminated p-type Si(100) substrates (10 Ω cm) were obtained by modified RCA cleaning with a low concentration of NH_4OH followed by a chemical treatment in a 1% HF solution. The high-resolution XPS measurements were performed with an ESCA-300 (Scienta Instruments AB), using monochromatic Al $K\alpha$ radiation (1486.6 eV) with an acceptance angle of 3.3°. The base pressure during the measurements was maintained in the 10^{-10} Torr range. The Si $2p$, O $1s$, and C $1s$ core level peaks were measured at photoelectron take-off angles of θ=35°, 60°, and 90°, and the valence band spectra were acquired at a take-off angle of 35°. The thicknesses of the ultrathin oxides were evaluated from angle-resolved XPS measurements of the Si $2p$ core-level by assuming that the Si $2p$ photoelectron escape depths in Si and SiO_2 are 2.7 and 3.4 nm, respectively.[11]

The deconvolution of the Si $2p$ core-level peak indicates that the Si^{4+} $2p_{3/2}$ peak arising from SiO_2 shifts towards higher binding energies and O $1s$ also exhibits a similar shift when the oxide thickness increases. The observed peak shift of the Si^0 $2p_{3/2}$ signal from bulk Si is at most 40 meV, whereas the maximum energy shift of Si^{4+} $2p_{3/2}$ reaches a value of 333 meV, a factor of 8 larger. A similar result is obtained also for the binding energy of the O $1s$ core level peak where the maximum energy shift is very close to that of the Si^{4+} $2p_{3/2}$ peak. Both dependencies reflect a differential charging effect for core-level peaks originating from the oxide layer and bulk Si. Photoelectrons emitted from the bulk Si are compensated by electrons supplied from the sample holder, while those originated in the ultrathin oxide cannot be fully compensated by tunneling electrons from the substrate. This effect leads to the formation of a positive charge in the oxide layer and the corresponding band bending of SiO_2. Detailed treatment of this effect has been described in Ref. 12. Once the differential-charging-induced shift for each of the Si $2p$ components is identified, it is possible to determine the valence band density of states (VBDOS) with an exact energy scale for ultrathin SiO_2/Si interfaces as a function of the oxide thickness by means of the XPS valence band spectra. The binding energy corresponding to the O $1s$ or Si^{4+} $2p_{3/2}$ peak for the thinnest (1.6 nm) oxide is taken as the energy reference for all other oxides since the charging effect is minimum or negligible for this oxide. Therefore, the

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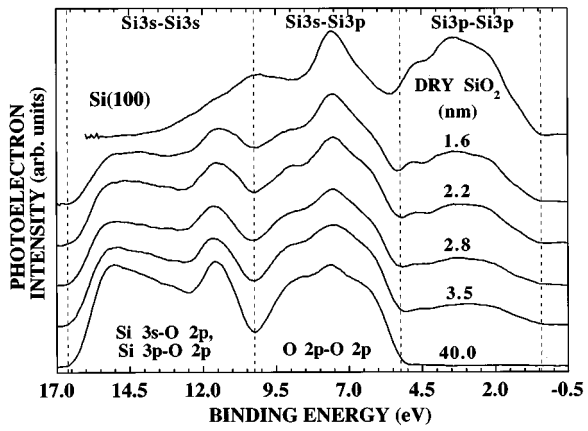

FIG. 1. Valence band density of states for ultrathin dry SiO_2/Si(100) interfaces obtained by high-resolution XPS. The VBDOS for a H-terminated Si surface and a 40.0-nm-thick dry SiO_2 layer are also displayed for comparison. The charging effect has been corrected for all spectra.

oxide valence band edge energies have been corrected by shifting each spectrum by the value given by the difference between the respective O 1*s* or Si^{4+} $2p_{3/2}$ peak position and that of the 1.6 nm oxide to correct the oxide charging contribution.

The VBDOS measured for the 1.6-, 2.2-, 2.8-, and 3.5-nm-thick dry SiO_2/Si(100) are shown in Fig. 1. The VBDOS of the H-terminated Si(100) and a 40-nm-thick dry SiO_2 are also displayed as references in the same figure, showing that the VBDOS of the various ultrathin dry SiO_2/Si(100) can be considered as a linear combination of the Si(100) and SiO_2 VBDOS spectra. The method employed here to obtain the ultrathin SiO_2 VBDOS depicted of any Si substrate influence consists of subtracting the Si substrate VBDOS component, which has been measured from a hydrogen-terminated *p*-Si(100) sample, from the measured SiO_2/Si interface VBDOS.

The ultrathin and thick dry oxide VBDOS show nearly identical spectra as shown in Fig. 2. Note that the top of the valence band of the various ultrathin oxides coincides with that of the thick oxide when the differential charging effect

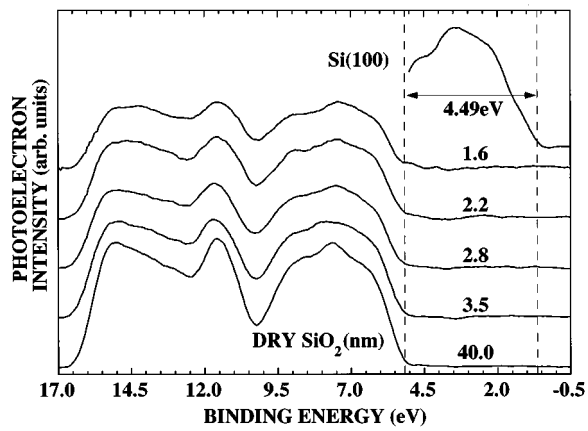

FIG. 2. Valence band density of states for ultrathin dry oxides after having subtracted the Si substrate component. The charging effect has been corrected for all spectra.

TABLE I. Valence band alignment or hole barrier height and electron barrier height for the various ultrathin SiO_2/Si interfaces.

	Valence band alignment (eV)	Conduction band barrier height (eV)
dry SiO_2/Si(100)	4.49	3.29
wet SiO_2/Si(100)	4.43	3.35
dry SiO_2/Si(111)	4.36	3.42

of oxides is carefully corrected. The difference between the energy position of the top of the ultrathin SiO_2 valence band and the top of the Si(100) reference valence band was determined by the method described in Ref. 9, yielding the valence band alignment, which is a constant value of 4.49 eV regardless of the oxide thickness from 1.6 to 3.5 nm. An SiO_2 band gap of 8.90 eV as recently obtained for ultrathin gate oxides by the analysis of the O 1*s* plasmon loss peak[13] can yield the corresponding conduction band barrier height of 3.29 eV for ultrathin dry SiO_2/Si(100) interfaces. In the case of wet oxides we have obtained similar VBDOS with a constant valence band alignment value of 4.43 eV regardless of the oxide thickness from 2.5 to 4.4 nm and a corresponding electron barrier height of 3.35 eV. Thus determined valence band alignment and the conduction band barrier height of dry SiO_2/Si(100) have been used to calculate the tunneling current through 3–5-nm-thick gate oxides. It is demonstrated that the measured tunnel current density versus oxide voltage characteristic agrees well with the calculated results.[1]

The values found for the valence band alignment and the conduction band barrier height are summarized in Table I for the various ultrathin SiO_2/Si interfaces. The reported value of the conduction band barrier height for thick SiO_2/Si(100) is known to be 3.25 eV (see Ref. 14) that is close to the value obtained for ultrathin SiO_2/Si(100). It is interesting to note that the value of the valence band alignment for dry SiO_2/Si(100) is 0.13 eV larger than dry SiO_2/Si(111). Although this difference is not far from the experimental error bar of 0.1 eV, this reproducible result implies that the band alignment depends slightly on the silicon surface orientation. A possible mechanism to explain this might be the existence of strained Si–O–Si bonds near the SiO_2/Si interface. In fact, it is shown that the LO-phonon peak of ultrathin SiO_2 on Si(111) exhibits a larger redshift than that for SiO_2/Si(100).[15] The redshift is largest at the interface and becomes small in the oxide layer within 2 nm from the interface. Since the redshift is explained by compressive stress in the oxide, the higher stress is existing in the SiO_2/Si(111) interface as compared to SiO_2/Si(100). Such orientation dependent stress in the interface might modify the interface dipole moment for the SiO_2/Si(111) and SiO_2/Si(100) boundaries.

In summary, the VBDOS of ultrathin oxides grown on Si is found to be nearly identical to that of thick SiO_2. The valence band alignment of 4.49 eV for the dry SiO_2/Si(100) interfaces is very close to the wet SiO_2/Si(100) value (4.43 eV). The measured values are constant regardless of the oxide thickness from 1.6 to ~5.0 nm. A little difference in the valence band alignment or conduction band barrier height

between SiO_2/Si(100) and SiO_2/Si(111) interfaces could be associated with different built-in strain between SiO_2/Si(100) and SiO_2/Si(111) interfaces.

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