

## The Valence Band Alignment at Ultra-Thin SiO<sub>2</sub>/Si(100) Interfaces Determined by High-Resolution X-Ray Photoelectron Spectroscopy

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The valence band alignment at ultra-thin SiO<sub>2</sub>/Si(100) interfaces has been determined by high-resolution x-ray photoelectron spectroscopy. The energy shifts found in the Si2p and O1s core-level peaks induced by differential charging effects between the oxide layer and the Si bulk can reach a maximum value of 330 meV. After correction of the energy scale to account for the charging effects, the valence band density of states for ultra-thin (1.6 - 3.5 nm thick) SiO<sub>2</sub> has been obtained by subtracting the bulk Si contribution from the measured spectrum. Using this method a constant value of  $4.49 \pm 0.10$  eV is obtained for the valence band alignment at ultra-thin SiO<sub>2</sub>/Si(100) interfaces regardless of oxide thickness.

### 1. INTRODUCTION

Thickness and uniformity control of gate oxides are becoming very important for manufacturing advanced MOSFETs. It is especially interesting to obtain the accurate Valence Band Density of States (VB DOS) for ultra-thin SiO<sub>2</sub> grown on Si(100) and the value of the valence band alignment or the conduction band barrier height at the SiO<sub>2</sub>/Si(100) interfaces. Previous studies on ultra-thin SiO<sub>2</sub>/Si barrier heights have led to a variety of results that sometimes are not coincident or even contradictory. Dressendorfer and Barker<sup>1)</sup> obtained a constant barrier height with a value of about 3.0 eV for oxides thicker than 4.0 nm from photoemission measurements. Also Heike et al.<sup>2)</sup> reported a constant value of 2.75 eV for very thin oxides grown on Si(100) substrates irrespective of the oxide thickness by using electron-beam assisted scanning tunneling spectroscopy. However, from tunneling current measurements on oxides grown on Si(100) substrates, Horiguchi and Yoshino<sup>3)</sup> found that the barrier height was oxide thickness dependent, varying from 1.8 to 3.0 eV for oxide thicknesses ranging from 1.5 to 4.0 nm. Our recent high-resolution XPS studies on ultra-thin SiO<sub>2</sub>/Si(111) interfaces have revealed that the structure of the VB DOS including the position of the top of the valence band for ultra-thin oxides (1.8 - 3.7 nm) is almost identical to that of a thick oxide (about 40 nm), and that the valence band alignment has a value of  $4.36 \pm 0.10$  eV regardless of the oxide thickness.<sup>4)</sup>

The purpose of the present study is to determine the VB DOS and the band alignment in the case of ultra-thin oxides thermally grown on Si(100) substrates by using high resolution x-ray photoelectron spectroscopy because of the importance of the SiO<sub>2</sub>/Si(100) system in ULSI technology.

### 2. EXPERIMENTAL

The XPS measurements were performed using a Scienta ESCA-300 instrument with monochromatic AlK $\alpha$  radiation and an acceptance angle of 3.3 deg. The Si2p peak and the valence band region were measured at a take-off angle of 35 deg to enhance signal from the ultra-thin SiO<sub>2</sub>/Si(100) interfaces. Angle resolved XPS measurements were also performed to determine the oxide thicknesses using escape depths of 2.7 and 3.4 nm in Si and SiO<sub>2</sub>, respectively.<sup>5)</sup> The Si2p core-level peaks have been deconvoluted into the Si2p<sub>3/2</sub> and Si2p<sub>1/2</sub> components with an intensity ratio of 0.5 and a separation of 0.61 eV. Ultra-thin oxides were thermally grown on hydrogen-terminated, p-type Si(100) substrates (10  $\Omega$  cm) obtained by RCA cleaning followed by a treatment in a 1% HF solution. The oxidation was carried out at 1000°C in a 2% dry O<sub>2</sub> ambient diluted with N<sub>2</sub>. The oxidation time was varied from 0 to 10 min (40 min in the case of thick reference oxide). Here, 0 min oxidation means simple loading of the wafer into the high temperature zone of the furnace.

### 3. RESULTS AND DISCUSSION

The oxide thickness  $d_{ox}$  as a function of oxidation time  $t$  obeys the following logarithmic law:  $d_{ox}(\text{nm}) = 1.58 + 1.82 \log(t+1)$  as in the case of the SiO<sub>2</sub>/Si(111) system, although the oxidation rate for Si(111) is slightly faster due to the different atomic density between both crystalline orientations (Fig. 1).

The deconvolution of the Si2p core-level peak indicates that the Si<sup>4+</sup>2p<sub>3/2</sub> peak shifts towards higher binding energies and O1s also exhibits a similar shift when the oxide thickness increases as shown in Fig. 2.

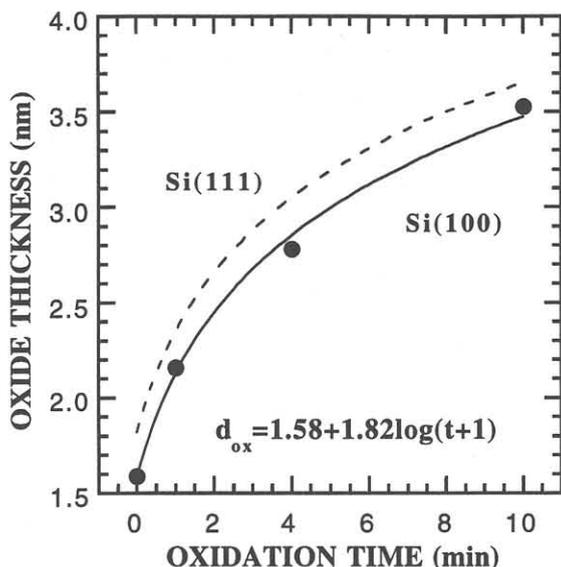


Fig. 1 : Oxide thickness as a function of oxidation time for Si(100).

The  $\text{Si}^{4+}2p_{3/2}$  energy shift is at most 333 meV, while the  $\text{Si}^{0}2p_{3/2}$  shows a much smaller shift of only about 40 meV (Fig. 3). Moreover, the energy shift for the  $\text{Si}^{4+}2p_{3/2}$  peak coincides with the one measured for the O1s peak. This behaviour is a reflection of a differential charging effect between the oxide layer and the Si(100) substrate by which  $\text{SiO}_2$  shows a stronger band bending than Si due to the difficulty to compensate photoelectrons emitted from the oxide. The same effect has been observed in the case of  $\text{SiO}_2/\text{Si}(111)$  and a detailed description of the charging mechanism can be found in Ref. 4.

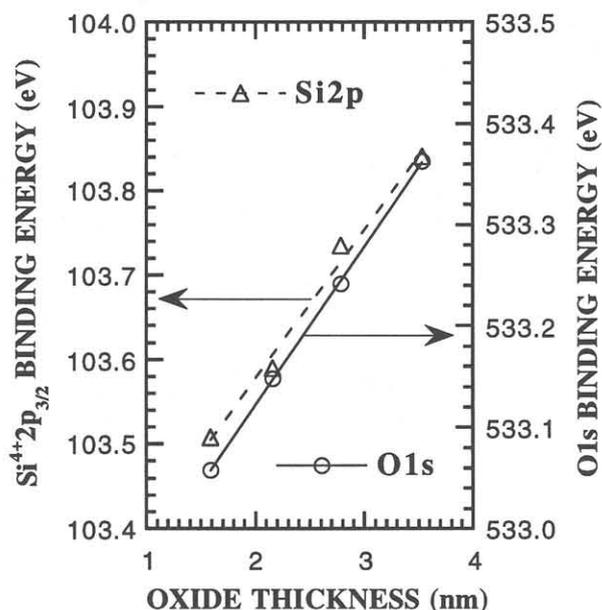


Fig. 2 :  $\text{Si}^{4+}2p_{3/2}$  and O1s core-level binding energy as a function of oxide thickness.

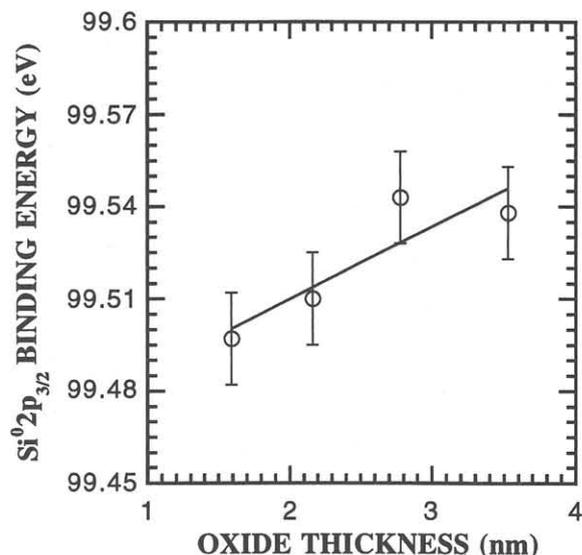


Fig. 3 :  $\text{Si}^0 2p_{3/2}$  core-level binding energy as a function of oxide thickness.

The VBDOS measured for the thin  $\text{SiO}_2/\text{Si}(100)$  interfaces as well as for a thick  $\text{SiO}_2$  (about 40 nm) and H-terminated Si(100) references are compared in Fig. 4, after correcting the energy scale for the above mentioned charging effects by taking the binding energy of Si2p and O1s for the thinnest oxide (1.6 nm) as the energy reference for all oxides. The VBDOS of the  $\text{SiO}_2/\text{Si}(100)$  interface can be described as a linear combination of the H-terminated Si(100) and pure  $\text{SiO}_2$  VBDOS.<sup>6</sup> In the energy region between 0 and 5 eV the ultra-thin  $\text{SiO}_2/\text{Si}(100)$  interface VBDOS only contains the signal arising from substrate Si3p molecular orbitals.

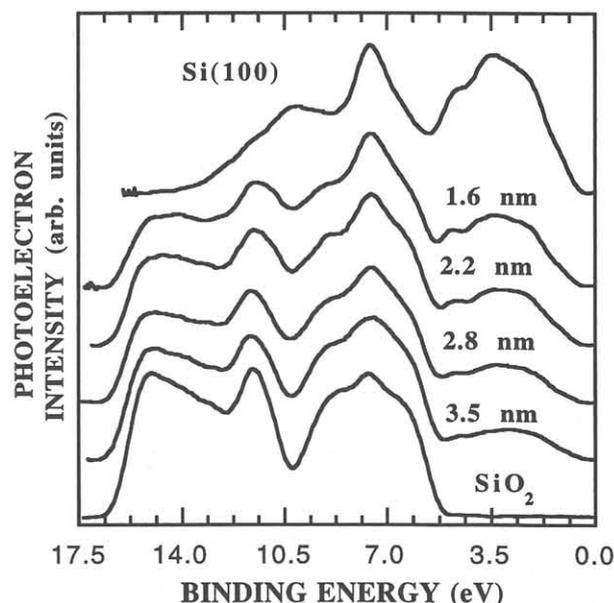


Fig. 4 : VBDOS for various ultra-thin  $\text{SiO}_2/\text{Si}(100)$  interfaces, HF-treated Si(100) reference surface and thick (40 nm) reference  $\text{SiO}_2$  on Si(100).

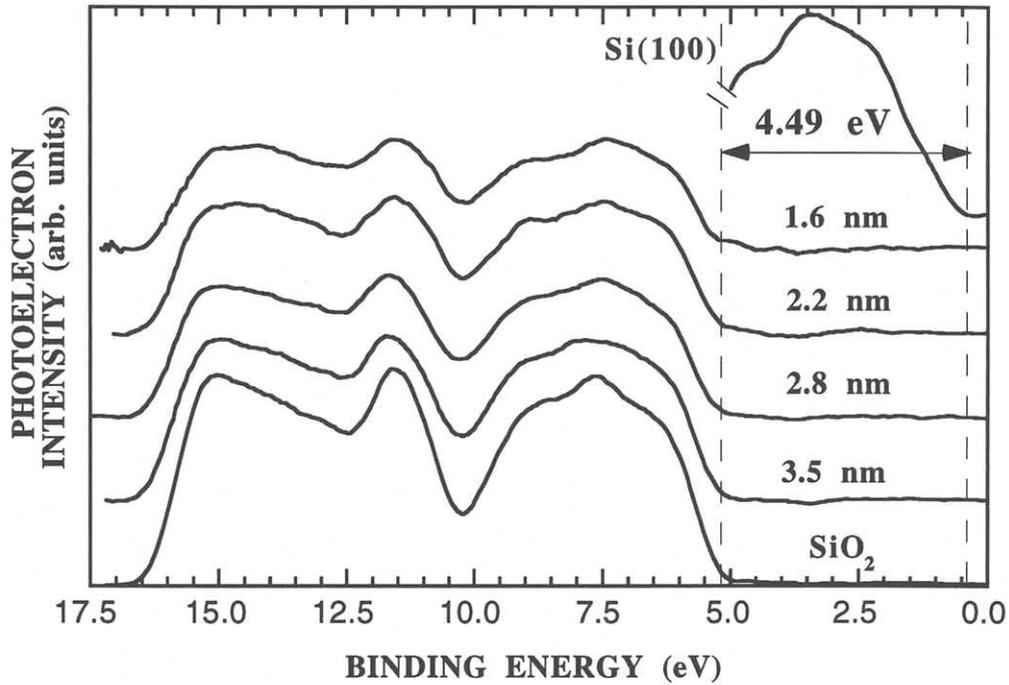


Fig. 5 : VBDOS for various ultra-thin SiO<sub>2</sub> grown on Si(100) substrates.

For energies between 5 and 10 eV the band is dominated by signal from non-bonding O2p and hybrid Si3p-Si3s orbitals. The high energy region from 10 to 17 eV is mostly formed by bonding Si3p- and Si3s-O2p orbitals.

Figure 5 shows the ultra-thin oxide VBDOS after subtracting the Si(100) reference VBDOS from the measured SiO<sub>2</sub>/Si(100) VBDOS. Thus obtained VBDOS profiles for the ultra-thin oxides show no significant difference as compared to the thick SiO<sub>2</sub> reference and are basically identical for all oxide thicknesses. From these VBDOS spectra a value for the ultra-thin SiO<sub>2</sub>/Si(100) valence band alignment of  $4.49 \pm 0.10$  eV is obtained regardless of the oxide thickness. This value is 0.13 eV higher than the one found for the SiO<sub>2</sub>/Si(111) interface. This difference could be partly explained by the different built-in stress at the SiO<sub>2</sub>/Si(100) and SiO<sub>2</sub>/Si(111) interfaces.<sup>7)</sup> Using a reported value of the SiO<sub>2</sub> band gap of 8.80 eV the conduction band barrier height is estimated to be 3.19 eV for the ultra-thin SiO<sub>2</sub>/Si(100) system.

#### 4. CONCLUSIONS

The valence band alignment for ultra-thin SiO<sub>2</sub>/Si(100) interfaces with oxide thicknesses from 1.6 to 3.5 nm has been determined to be 4.49 eV. It is demonstrated that the value of the band alignment is constant regardless of oxide thickness. Also, the VBDOS profile of ultra-thin oxides does not show any significant difference compared with that of a thick oxide.

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