

## Quantum Confinement Effect in Self-Assembled, Nanometer Silicon Dots

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The first subband energy at the valence band of self-assembled silicon quantum dots grown by low pressure chemical vapor deposition on ultrathin  $\text{SiO}_2/\text{Si}$  substrates has been measured as an energy shift at the top of the valence band density of states by using high resolution X-ray photoelectron spectroscopy. The systematic shift of the valence band maximum towards higher binding energy with decreasing the dot size is shown to be consistent with theoretical prediction. The charging effects of the silicon dots and the  $\text{SiO}_2$  layer by photoelectron emission during the measurements have been taken into account in determining the valence-band edge energy.

### 1. Introduction

The observations of negative conductance associated with the resonant tunneling through  $\text{SiO}_2/\text{Si}$  quantum dot/ $\text{SiO}_2$  double barrier structures[1] and the visible photoluminescence from nanometer Si quantum dots at room temperature[2] have been recently reported. The subband formation in nanometer Si dots has been suggested by a blue shift of the optical absorption edge with decreasing the average dot size[2-3]. However, the dot size dependence of the energy band gap as determined by the onset of absorption spectrum has not been well explained by theories[4-7]. Recently self-assembling of silicon quantum dots with a fairly uniform size distribution and a high areal density has been achieved by controlling the early stages of LPCVD on  $\text{SiO}_2/\text{Si}$  substrates[8].

In this paper, we report on the size dependence of the valence band maximum for self-assembled Si quantum dots on  $\text{SiO}_2$  by using high resolution X-ray photoelectron spectroscopy (XPS).

### 2. Experimental

Chemically cleaned p-type Si(100) wafers ( $10 \Omega\text{cm}$ ) were oxidized at  $1000^\circ\text{C}$  in a 2% dry oxygen diluted with nitrogen to grow 3.2-5.5 nm thick  $\text{SiO}_2$  layers on the Si(100) surfaces. The  $\text{SiO}_2$  surface was subsequently treated by a 0.1% HF solution for 1 min to form surface Si-OH bonds which enhance the dot density and improve the uniformity of dot size[8]. Si quantum dots were self-assembled on the  $\text{SiO}_2$  surfaces at  $565-580^\circ\text{C}$  using LPCVD of pure silane at 0.1 Torr. The dot shape was hemispherical and the size was controlled by the deposition temperature and time as already reported elsewhere[8]. The dot height was accurately measured by atomic force microscopy (AFM) images, while the diameter determined from AFM was a little larger than the real size because of the diameter of AFM tip apex. Therefore, high-resolution scanning electron microscopy was used to calibrate the average dot diameter which was by about 30% overestimated in the case of AFM. High resolution transmission electron microscopy was also used to confirm the formation of single crystalline Si dot with a hemispherical shape[8].

### 3. Results and Discussion

Measured valence band and  $\text{Si}2p$  core level spectra for a Si-dots/5.5 nm  $\text{SiO}_2/\text{Si}(100)$  structure and a hydrogen-terminated bulk-Si(100) surface are compared in Fig. 1. The valence band spectrum for a 5.5 nm  $\text{SiO}_2/\text{Si}$  structure (denoted by VBS-O) is also shown in Fig. 1(a). By comparing the valence band spectra for the Si-dots/ $\text{SiO}_2/\text{Si}$  structure (denoted by VBS-D) with the VBS-O, the feature of the VBS-D below 5 eV is referred to the energy band arising from  $\text{Si}3p$  states of

Si dots. The Si substrate signal through 5.5 nm  $\text{SiO}_2$  is negligible at a photoelectron take-off angle of  $10^\circ$ . The valence band edge of the Si-dots exhibits a shift of about 0.6 eV to the higher binding energy from that of bulk-Si. This shift arises not only from the dot charging effect but also from the subband formation in the dot. It should be noted that the VBS-O and VBS-D in the energy range from 11 to 17 eV originate from the  $\text{Si}3p-\text{O}2p$  and  $\text{Si}3s-\text{O}2p$  bonding orbitals in the oxide layer[9]. A relative shift of the valence band peak positions at about 12 eV for the VBS-D appears to be less positively charged than the VBS-O as indicated by the arrows near 12 eV. The  $\text{Si}2p$  spectrum shown in Fig. 1(b) for the Si-dots/ $\text{SiO}_2/\text{Si}$  structure is composed of the two strong components for the chemically shifted  $\text{Si}^{4+}$  signal from the  $\text{SiO}_2$  layer and for metallic  $\text{Si}^0$  signal from the dots. Note that a contribution to the  $\text{Si}^0$  peak from the Si substrate through the 5.5 nm thick  $\text{SiO}_2$  layer is negligible at take-off angles of  $5^\circ$  and  $10^\circ$ . The  $\text{Si}^{0}2p_{3/2}$  signal for the dots is broad because of the size distribution and shifted to higher binding energy by about 0.5

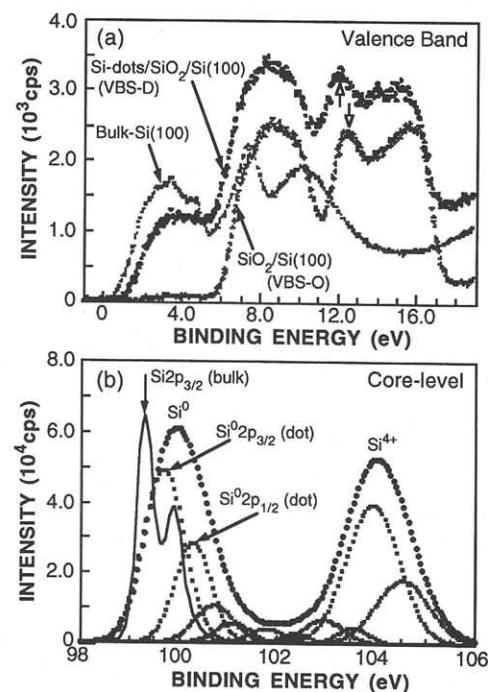


Fig. 1 The valence band spectra for bulk-Si, Si-dots/5.5 nm  $\text{SiO}_2/\text{Si}$  and 5.5 nm  $\text{SiO}_2/\text{Si}$  structures for a take-off angle of  $10^\circ$  (a), and the  $\text{Si}2p$  core level spectra for bulk-Si (solid line) and the Si-dots/ $\text{SiO}_2/\text{Si}$  structure (large dot curve) where the suboxide signals are also indicated (b). The spectra were not corrected for charging effect. The Si dots were deposited at  $580^\circ\text{C}$ .

eV in Fig. 1(b) with respect to the  $\text{Si}2\text{p}_{3/2}$  bulk signal mainly due to the charging effect of silicon dots induced by photoelectron emission. In order to reveal the quantum size effect in nanometer Si dots, we focus attention to the valence band edge and the  $\text{Si}2\text{p}$  core-level peak for the Si-dots.

Both the charging effect and the quantum confinement in the Si dots result in an energy shift of the valence band spectrum for the dots. We have obtained the same energy difference between the valence band maximum(VBM) and  $\text{Si}2\text{p}$  peak energy for the bulk-Si(100) and a 3.2 nm  $\text{SiO}_2/\text{Si}(100)$  structure, indicating that the energy shift is hardly influenced by the escape depth difference between the valence band photoelectron and  $\text{Si}2\text{p}$  core level. Therefore, it is reasonable to conclude that the charging effect causes almost the same amount of energy shift for both the valence band top and  $\text{Si}2\text{p}$  core level of the dots. Consequently, the dot charging effect for the Si-dots/ $\text{SiO}_2/\text{Si}$  structure can be eliminated by employing the  $\text{Si}2\text{p}$  core-level for the dots as a reference energy. Unlike the valence band edge energy, the core level energy is not influenced by the quantum size effect in Si dots because the wave functions are strongly localized. To keep the dot charging effect identical during the XPS measurements of the  $\text{Si}2\text{p}$  core level and valence band spectra, each set of the two spectra was obtained without any change in measurement conditions. Since the  $\text{Si}2\text{p}$  core level photoelectron peak energy from the Si dots was used as a reference, the average coulombic charging effect of the dots could be canceled out as a difference between the  $\text{Si}2\text{p}$  reference energy and the valence band edge. Thus the measured energy shift of VBM with respect to that in bulk-Si can be attributed to the quantum size effect.

Taking the binding energy of  $\text{Si}2\text{p}_{3/2}$  for bulk Si as the energy reference for all the other  $\text{Si}2\text{p}$  signals from Si-dot/ $\text{SiO}_2$  structures, the energy scale of the valence band spectra has been corrected by shifting each spectrum by a value given by the difference between the respective  $\text{Si}2\text{p}_{3/2}$  peak position for the dots and that for bulk Si to eliminate the charging effects in Si dots. Thus the valence band spectra for Si-dots/ $\text{SiO}_2$  structures with different dot sizes can be directly compared with the bulk Si signal by eliminating the charging effect. As shown in Fig. 2, the valence band spectrum shifts towards the higher binding energy with decreasing average dot height from 4.3 nm to 1.2 nm. By linearly extrapolating the leading edge of the valence band to zero intensity, the VBM positions were determined for bulk Si and Si dots with different average

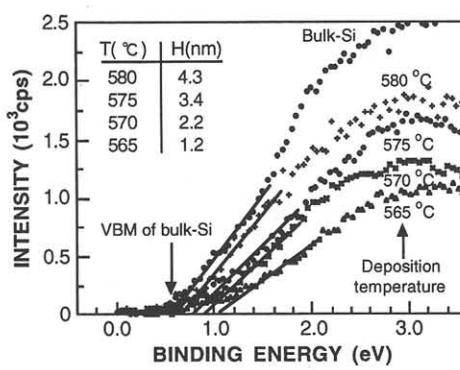


Fig. 2 The valence band edge spectra for bulk Si and Si quantum dots measured at a take-off angle of 5°. The valence band spectra are aligned by taking  $\text{Si}2\text{p}_{3/2}$  peaks for bulk Si and Si dots as energy references. The deposition temperature (T) and the corresponding dot height (H) are tabulated in the inset.

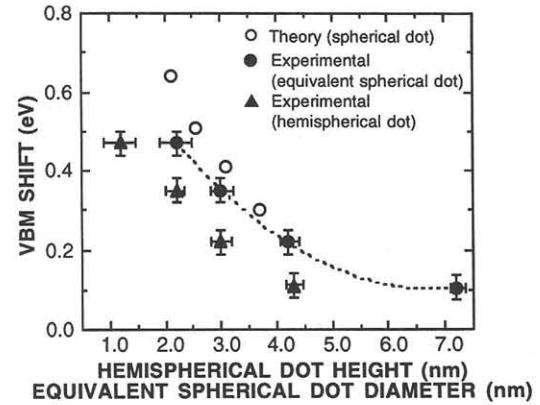


Fig. 3 Comparison between measured energy shift of the valence band maximum in Si quantum dots and theoretical result in Ref. 7. The equivalent diameter of the hemispherical dot is defined as the diameter of sphere with the same volume as the dot. The dashed line should be compared with the theory (open circles).

heights. The extrapolated VBM energy for Si quantum dots is plotted as a function of the dot height as shown in Fig. 3. The height of hemispherical dot is an important dimension to assess the quantum size effect, while theoretical calculations were made mostly for spherical dots. We therefore introduce an equivalent sphere diameter for the hemispherical dot, which is defined as the diameter of a sphere with the same volume as the dot to preserve the total number of electronic states. Thus, the VBM energy for the corresponding equivalent dot diameter is also represented in Fig. 3. There exists significant difference between the dependence of calculated VBM energy shift on spherical dot diameter and that of experimental VBM shift on hemispherical dot height, while the difference becomes small if replacing the hemispherical dot height by the diameter of equivalent sphere as shown by the dashed curve in Fig. 3. Therefore, the experimental VBM shifts are consistent with the theoretical values if considering the difference between real dot shape and the theoretical model.

#### 4. Conclusions

The quantum confinement effect in nanometer Si dots is confirmed by using high resolution photoelectron spectroscopy. The measured VBM energy shift is considered to be consistent with theoretical calculation.

#### Acknowledgments

This work has been supported by the Core Research for Evolutional Science and Technology (CREST) of the Japan Science and Technology Corporation (JST).

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