

Energy band lineup at the porous-silicon/silicon heterointerface measured by electron spectroscopy

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The energy band gap of light-emitting porous silicon is determined by high-resolution electron energy loss spectroscopy, and the valence band edge of porous silicon with respect to its Fermi level is measured by ultraviolet photoelectron spectroscopy. By combining the results with that measured from clean Si, a picture of band lineup at the porous-silicon/*p*-Si heterointerface is proposed, in which 70% of the total band gap discontinuity occurs at the valence band edge.

Since the discovery of visible luminescence from highly porous Si (PS),¹ considerable attention has been paid to its luminescence properties and possible device applications. In measuring the electrical properties of PS or developing light emitting diodes and other electronic devices, the heterojunction between PS and the Si substrate is an essential part of the device or testing sample structures. However, very little is known concerning the electronic structures of PS/Si heterointerfaces. The most important parameter, the band offset, which determines crucially the properties of heterojunction device structures has not been established for PS/Si interfaces. The experimental methods which have been employed successfully for many semiconductor heterojunction systems face some technical difficulties in measurement of the band offsets of PS/Si systems. For example, photoemission is in principle valid to measure the valence band discontinuity between PS and Si, but it is necessary to know the band gap of PS simultaneously in the same experiment in order to derive the partition of band offsets between the valence band and conduction band. Since the band gap of PS varies from sample to sample, the valence band offset measured from one specific sample could not be considered as a universal reference generally applied to other PS samples.

In an earlier work by Lüth *et al.*,² it was found that the interband transition of carriers in InSb could induce a loss structure in the high resolution electron energy loss spectroscopy (HREELS). Later, this technique was successfully developed to measure the band gaps of binary and ternary III-V compound semiconductors and their heterointerfaces.³⁻⁵ The principle is as follows. For either direct gap or indirect gap materials, an incident low-energy electron with primary energy much larger than the band gap could excite the interband transitions in the solid by losing a part of its energy. In the energy loss spectrum, a loss structure at the energy below the elastic peak occurs and its threshold thus corresponds to the band gap of the material.

In this work, we find that the HREELS is also valid to measure the band gap of PS. Since this technique is compatible with the photoemission, it is thus possible to measure both the band gap and the valence edge for a PS sample in the same experimental setup. By combining the experimental results with that measured from a clean Si surface, the picture of band lineup at the PS/Si heterointerface is established.

The porous silicon sample was prepared on boron-doped

18–23 Ω cm *p*-type Si(100) substrate by anodizing it in a 47% HF:ethanol=1:1 solution at a current density of 10 mA/cm² for 3 min under natural light illumination. The temperature was 25 °C. The thickness of the PS layer was 1.4 μ m as determined by scanning electron microscopy on its cleaved edge. The small thickness is necessary to keep the surface of the PS film mirrorlike, which is very important in taking the HREELS measurements. Under the illumination of a UV lamp, the sample showed a visible emission which could be observed in the dark by naked eyes. A typical photoluminescence spectrum was peaked at 690 nm (1.8 eV). The corresponding porosity was about 70–80% as estimated from weight measurements. After removing from the anodic solution, the sample was immersed in ethanol for several minutes, and loaded immediately into the ultrahigh-vacuum chamber of the electron spectrometer, where the pressure was pumped down to 10⁻⁸ Pa. The total exposure time in the atmosphere and low vacuum was less than 10 min, so that the effect of surface contamination in air could be minimized.

The electron spectroscopic measurements were carried out in a VG ADES-400 spectrometer facilitated with the x-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS) and HREELS. First, the surface composition of the PS sample was measured by detecting the Si 2*p*, C 1*s*, O 1*s*, and F 1*s* signals. The Si 2*p* spectra measured from the PS sample and a virgin Si wafer are similar in terms of their line shapes and widths (FWHM) as shown in Fig. 1, where the peak positions have been moved to coin-

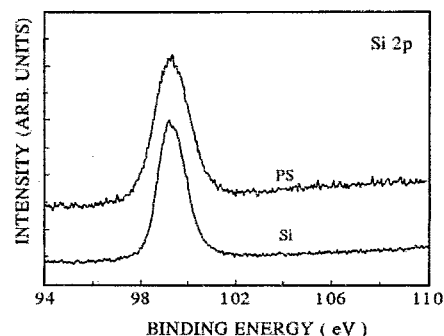


FIG. 1. Si 2*p* core level spectra of crystalline Si and porous Si.

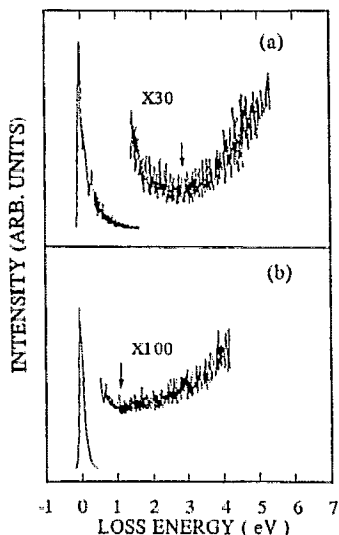


FIG. 2. HREELS results of (a) newly etched porous Si, (b) clean crystalline Si.

cide with each other. No chemical shift component of Si 2*p* from the oxide states could be observed. The surface compositions of O and C are approximately $\frac{1}{3}$ monolayer (ML) as estimated by the relative atomic sensitivity factors. Only trace amounts of residual F (<0.05 ML) could be detected. It is thus believed that the PS sample does not contain detectable SiO₂ except small amounts of surface contamination on the top of the film. The absence of oxides in our sample guarantees that the interference of surface oxidation on the HREELS and UPS measurements could be ruled out.

The HREELS was performed at the primary electron beam energy of 20 eV, with an incident angle of 45°. The scattered electrons were collected at the specular direction by a 127° sector analyzer and a channeltron multiplier. The overall energy resolution was about 50 meV. Figure 2 shows the HREELS of a typical PS sample (a) and that of a clean Si surface (b). Although the signal to noise ratios are rather poor, by using a curve smoothing treatment, the threshold energy corresponding to the interband transition could be identified with the accuracy of 0.1–0.2 eV depending on the steepness of the threshold. It could be seen that for Si the threshold (indicated by the arrow) at 1.1 eV corresponds closely with its indirect band gap, while for PS the threshold energy shifts to 2.9 eV, which is believed to be the interband transition energy of the quantum confined Si nanostructures.

The band gap obtained above seems to agree with previous work. Kanemitsu *et al.*⁶ observed a large Stokes shift of ~ 1 eV between the photoluminescence peak and the edge of the excitation spectrum of PS, the latter was found to be about 3.2 eV, which is suggested to be the band gap of PS. The photoluminescence excitation spectroscopic measurements by Wang *et al.*⁷ showed similar results. For example, the peak positions for the photoluminescence and the photoexcitation are 1.8 and 3.1 eV, respectively. The latter has also been attributed to the direct interband transitions.

The UPS spectra measured by using a HeI resonance lamp are shown in Fig. 3. The valence band maximum (VBM) with respect to the Fermi level (E_F) is derived from the onset

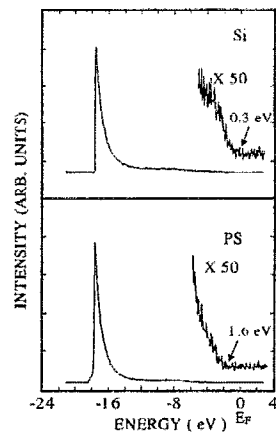


FIG. 3. Valence band spectra of crystalline Si and porous Si. The arrows indicate the valence band edges with respect to E_F .

of the valence band spectrum with the precision of 0.05–0.1 eV. For Si crystal, the VBM is located about 0.3 eV below the Fermi level, which is close to the predicted value of 0.24 eV for *p*-type Si with the resistivity of 18–23 Ω cm. For PS, the VBM is found to be 1.6 eV below the Fermi level. To avoid the interference of the charging effect during the measurement, the UV light was adjusted to produce rather weak flux. It could be seen that the secondary electron backgrounds of PS and Si cut off at the same energy, which implies that the charging effect is negligible. The UPS results are thus believable.

By combining the results obtained from HREELS and UPS, we can deduce a band lineup picture of our PS/*p*-Si heterostructure, as shown in Fig. 4, where E_c and E_v are the conduction band edge and valence band edge respectively. The Fermi level is located at the midgap of PS, which agrees with the high resistivity of PS ($\rho > 10^9 \Omega$ cm).⁸ In Fig. 4, the total energy band discontinuity ΔE_g is partitioned into valence band offset ΔE_v and conduction band offset ΔE_c with the ratio of 0.7 to 0.3.

Ren and Dow calculated the size dependence of the energy gap of hydrogenated Si clusters.⁹ The results showed an explicit quantum size effect. As the size of the Si cluster decreases, the highest occupied-state energy decreases and the lowest unoccupied-state energy increases. According to their calculation results, at a cluster size of about 14 Å, the

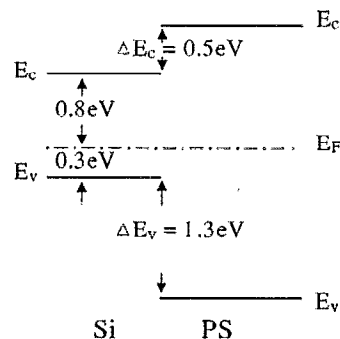


FIG. 4. Proposed band lineup at the PS/Si heterointerface.

energy gap reaches 2.9 eV, i.e., the widening of band gap ΔE_g is about 1.8 eV. The lowest conduction energy level moves upward 0.5 eV as compared with that of a large cluster (bulk Si), and the highest valence level moves downward 1.3 eV. The fairly good agreement between the calculation and our experimental results seems to provide an encouraging support to the band lineup picture shown in Fig. 4. A recent photoelectron spectroscopy measurements by van Buuren *et al.*¹⁰ found that the conduction and valence bands of PS are shifted relative to the bands for bulk silicon. The shift in the valence band they obtained was about a factor of 2 larger than the shift in the conduction band, i.e., $\Delta E_v \cong 2\Delta E_c$, which seems pretty close to the result of present work.

It is noteworthy to point out that the interface between PS and its Si substrate may not be uniform laterally, i.e., Si nanostructures with different dimensions contact the Si substrate to form different interfacial barriers. The experimental data are of course the weighted average in the probing area. Another point is that the band bending at the interface has not been considered. Since the PS layer is almost semi-insulating, the charge transfer at the heterointerface could be ignored.

In summary, the HREELS technique has been used to measure the band gap of light-emitting porous silicon. It is found that the interband transmission occurs at an energy of 2.9 eV, which is much larger than the photoluminescence

peak of 1.8 eV. The valence band edge of PS with respect to the Fermi level is measured by UPS. A band lineup picture of PS/*p*-Si heterointerface is proposed based on the above experiments. The band discontinuity is found to be partitioned into 70% and 30% at the valence band edge and the conduction band edge respectively.

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