Photoelectron spectroscopy measurements of the band gap in porous silicon

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(Received 28 June 1993; accepted for publication 21 September 1993)

Photoemission and x-ray absorption spectroscopy show that both the conduction and valence bands of porous silicon are shifted relative to the bands for bulk silicon, as expected in the quantum confinement model for the optical properties of porous silicon. The shift in the valence band is larger than the shift in the conduction band and proportional to it, with a proportionality constant that is consistent with effective mass theory. No oxygen is detected in the as-prepared porous silicon.

Various explanations have been proposed for the strong visible luminescence from porous silicon (p-Si), the most popular being quantum confinement in nanometer size silicon crystallites. An alternative explanation for the visible photoluminescence is emission from a surface siloxene layer. This is difficult to reconcile with experiments which show that freshly prepared p-Si does not contain oxygen. However, the microstructure and optical properties of p-Si have not been determined with enough resolution to confirm the quantum confinement model directly. A prediction of the quantum confinement model is that the energies of the valence and conduction band edges should be correlated and depend on the size of the Si microstructures. In this letter we use x-ray absorption and photoemission to measure the energies of the conduction and valence band edges of p-Si relative to bulk Si and compare the results with the quantum confinement model.

Porous Si samples were prepared by chemically or electrochemically etching n- or p-type silicon as described elsewhere. After fabrication, all p-Si samples are kept in high purity concentrated HF for 10 min, blown dry with nitrogen, then loaded immediately into the UHV analysis chamber, with less than 5 min of exposure to air. X-ray absorption spectra were measured by total electron yield with synchrotron radiation at the CSR F in Stoughton, WI. The samples were held in tantalum baskets that could be heated resistively. The measurements were made in a UHV chamber (1 x 10^-9 Torr) equipped with an electron energy analyzer so that we were able to measure both electron yield and photoemission without moving the sample. The resolution is 0.06 eV for the absorption spectra and 0.2 eV in the photoemission at a photon energy of 100 eV.

The Si L-edge absorption is shown in Fig. 1 for HF-rinsed bulk Si, electrochemically prepared p-Si and the same electrochemical p-Si after a 3-h soak in HF. The Si L edge in the p-Si is shifted to higher energy relative to bulk Si (Ref. 2) and none of the samples show evidence of the peaks at 104.5 and 106 eV corresponding to SiO and SiO2, respectively. Photoemission is more sensitive to surface oxygen than the absorption measurements. A photoemission spectrum for the valence band of p-Si taken at a photon energy of 150 eV is shown in Fig. 2(a) together with the valence band of HF-rinsed (111) Si. The spectrum for HF-rinsed Si is similar to earlier measurements.5 The p-Si valence band in Fig. 2(a) is shifted by 1.5 eV to higher binding energy compared with bulk Si, partly due to charging. Because the p-Si is highly resistive, the photoemission current creates a positive charge in the sample which shifts the photoemission spectrum to higher binding energy. We chose not to use an electron flood gun to reduce charging in order to ensure that there was no possibility of a local negative charge being induced by the flood gun. The charging effect was intensity dependent and present in all p-Si samples to varying degree. Differences in the Fermi level or changes in the electronic structure of the porous material due to its microstructure could also cause energy level shifts. However one can eliminate the effects of charging and changes in the surface Fermi level, at least for the top of the valence band, by using the low binding energy side of the Si 2p core level as a reference. The Si 2p core level will have the same charging and Fermi-level induced shifts as the valence band, but unlike the valence band it will not depend on the microstructure of the p-Si.

In order to keep the charging effect the same during the photoemission measurements of the valence band and the Si 2p core level, the two spectra were measured one after the other without moving the sample or changing the photon flux. The resulting Si 2p core level spectrum is shown in Fig. 2(b) for the same p-Si sample as in Fig. 2(a). Compared with the spectrum for bulk Si, the 2p photoemission peak for p-Si is broadened and shifted to larger binding energy. The shape of the 2p core level spectrum varied from sample-to-sample and the width increased with x-ray intensity. We attribute these effects to differential charging associated with the inhomogeneous structure of the p-Si. Since charging shifts the spectrum to higher binding energy, the low binding energy side of the 2p photoemission spectrum will be due to that part of the material that charges the least. The charging effect on the low binding energy edge of the photoemission spectrum was sample dependent and we estimate from the flux de-
To confirm that the broadening of the Si 2\( p \) core level is not due to an oxygen chemical shift we heated the p-Si in situ without moving the sample, and remeasured the photoemission spectrum. After annealing the p-Si at 600 °C for a few minutes, the 2\( p \) photoemission spectrum shifts and narrows to the point where it matches the binding energy and width of the bulk Si 2\( p \) level as shown in Fig. 2(b) with no indication of a chemically shifted component associated with oxygen. By 600 °C we expect the hydrogen to evaporate and the mobility of the surface atoms to be high enough for the pore structure to begin to collapse. If the as-prepared p-Si did contain oxygen, after annealing one would have expected to see a 3.5 eV chemically shifted component in the Si 2\( p \) level, due to SiO\(_2\).

Further evidence for the absence of oxygen in the p-Si can be obtained from the valence band photoemission. If the surface of the p-Si was oxidized one would expect to see peaks at 10 and 30 eV binding energy in the photoemission spectrum corresponding to the oxygen 2\( p \) and 2\( s \) orbitals, respectively.\(^5\)\(^,\)\(^9\) The valence band of HF passivated Si has a peak near 10 eV unrelated to oxygen,\(^8\) which complicates the identification of the oxygen 2\( p \) orbital; however no peak is observed in Fig. 2(a) at 30 eV corresponding to the oxygen 2\( s \) orbital. On the other hand, if the p-Si sample is exposed to air for a few hours strong oxygen 2\( s \) and 2\( p \) peaks are clearly visible in the photoemission. Cross-section calculations show that the oxygen 2\( s \) and 2\( p \) orbitals have significantly larger cross sections at 150 eV than the Si 3\( s \) and 3\( p \) orbitals that make up the valence band.\(^{10}\)

This means that the valence band photoemission spectrum is particularly sensitive to oxygen. In addition, at 150 eV photon energy the valence band photoelectrons have an escape depth of a few atomic layers. Accordingly even a fraction of a monolayer of oxygen should be easily detectable in photoemission.

In order to detect changes in the electronic structure of the valence band in p-Si, we measured the binding energy of the top of the valence band relative to the top of the Si 2\( p \) orbital (low binding energy side). This was done by first locating the top of the valence band by a linear extrapolation of the low binding energy edge of the photoemission spectrum; a similar extrapolation gives the top of the Si 2\( p \) core level. Subtracting these two quantities produces a valence band binding energy relative to the core level which is independent of charging and the Fermi-level position. The corrected valence band spectra for p-Si can then be compared with that of bulk Si as shown in Fig. 3. If the valence band recedes due to quantum confinement, then one would expect the separation between the top of the valence band and the Si 2\( p \) level to be smaller than in bulk Si. A reduction in this separation is observed, as shown in Fig. 4 where we plot the conduction band edge shift determined from the L-edge data, as a function of the valence band shift determined from photoemission, for a series of different samples. The error bars indicate measurement accuracy and do not include systematic errors that might arise from incomplete correction for charging. Figure 4 shows that there is a range of energy shifts for the conduction and valence band edges in p-Si and that these shifts are correlated. This result is consistent with quantum confinement in a granular material whose microstructure depends on the preparation conditions. The p-Si with the largest quantum shift in Fig. 4 also shows the largest blue shift in the photoluminescence.

FIG. 1. Total electron yield measurements of Si L-edge absorption for HF passivated p-type (111) Si (broken line), and p-Si (solid lines). The "new" p-Si was prepared by an electrochemical etch of p-type (111) Si in 30% HF in ethanol under illumination at 10 mA/cm\(^2\) for 20 min. The other p-Si spectrum is for the same sample after soaking in concentrated HF for 3 h.

FIG. 2. Photoemission spectra with \( h\nu = 150 \) eV for (a) the valence band and (b) the Si 2\( p \) core level for HF rinsed bulk Si (broken line) and p-Si (solid lines). The spectra are not corrected for charging. The p-Si data in (a) are for as-prepared material the p-Si in (b) are as-prepared ("new") and annealed at 600 °C.

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The relationship between the quantum shifts in the valence and conduction band edges can be predicted from effective mass theory, in the limit that the confinement energy is small compared to the band gap. The quantum shifts depend on the dimensionality of the confinement and its orientation relative to the principle axes of the crystal. Since we know very little about the microstructure of the Si, for simplicity we compare the experimental data with the quantum shifts one would expect for (100) oriented quantum wires with square cross sections. In this calculation we neglect both the spin-orbit splitting and the off-diagonal elements in the effective mass Hamiltonian in the valence band. A perturbation calculation shows that the off-diagonal part of the effective mass Hamiltonian (band warping) has no effect on the lowest energy eigenstate for a (100) oriented quantum wire. The calculated relationship between the energies of the lowest quantum states in the conduction and valence bands is shown by the solid line in Fig. 4. The lateral dimension of the wire is a parameter which has a minimum value of 3 nm at the right-hand side of the line. The corresponding lines for a (100) oriented quantum box and a (111) oriented quantum well have the same slope as the wire to within a few percent. The slope of the line in Fig. 4, is in good agreement with the data even though the measured quantum shifts are not small compared to the band gap. A more elaborate electronic structure calculation is needed to make a meaningful comparison with the data over the entire range in Fig. 4.

It is interesting to note the largest quantum shift that we were able to obtain corresponds to a band gap of 3.1 ±0.1 eV, which is close to the 2.75-eV band gap calculated for a single hexagonal sheet of silicon terminated on both sides with hydrogen. Thus we conclude that if the confinement structures are two dimensional then they must be on the order of a single atomic layer thick in the samples with the largest "quantum" shift.

We thank K. Tan, S. Patitsas, and J. Tse for helpful discussions and the Natural Sciences and Engineering Research Council of Canada for financial support.

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**FIG. 3.** Photoemission spectra of the top of the valence band corrected for charging, for HF rinsed bulk Si (broken line), and for electrochemical and stain-etch p-Si (solid lines). For the electrochemical p-Si the current density was held at 1 mA/cm² for 40 min followed by 40 mA/cm² for 1 min by increasing the illumination intensity on the n-type starting material.

**FIG. 4.** Energy of the conduction band edge vs the energy of the valence band edge for a series of electrochemical (solid) and stain-etch (open) p-Si samples, relative to bulk Si indicated by the open triangle. The electrochemical samples showed quantum shifts with increasing current density during preparation and time spent soaking in HF after preparation. The solid line is a theoretical calculation as discussed in the text.

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