

Effects of hydrostatic pressure on the photoluminescence of porous silicon

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We have measured the room-temperature photoluminescence (PL) of free-standing porous silicon films under hydrostatic pressures up to 60 kbar. The pressure dependence of the PL for two films collected from the same porous silicon wafer is very different, depending on whether the pressure medium used is either helium or the standard 4:1 methanol:ethanol mixture. This result is not compatible with the standard quantum confinement model of the PL in porous silicon, which claims that the PL occurs between the confined electron and hole states in the core silicon region.

The room-temperature red photoluminescence (PL) from porous silicon¹ has drawn much interest in recent years due to the possible application of the material in integrated photonic devices. The origin of this PL, however, is still controversial. Some researchers have explained it as originating from radiative recombination of electrons and holes confined in wirelike silicon core surrounded by a surface passivated by hydrogen and/or oxygen atoms (the quantum confinement model²), while others have argued that the PL originates either from excitons trapped in the surface states of the silicon core³ or from Si-O-H compounds such as siloxene derivatives formed on the surface.⁴ A high-pressure experiment can be used to test the quantum confinement model: if the model is correct, the change in the PL energy with pressure should be consistent with the change in the energies of confined electron and hole states due to the band-structure change of the host material (silicon) and the size reduction of the silicon core. Several high-pressure measurements have been reported, but their results so far have been inconsistent.⁵⁻¹¹ In a number of measurements where the standard 4:1 methanol:ethanol mixture^{5,10,11} or ethanol⁸ was used as the pressure medium, the PL peak shifted to higher energy with increasing pressure (blueshift) at low pressures and to lower energy (redshift) at higher pressures. Some authors^{8,10} explain this behavior in terms of the quantum confinement model, although a calculation by Yeh, Zhang, and Zunger¹² of the pressure dependence of the fundamental energy gap between quantum confined electron and hole states in silicon quantum wires predicts only a small redshift. When other pressure media were used ("organic essence,"⁶ paraffin oil,⁷ or fluorocarbon⁹), only a redshift was observed. Due to this lack of consistency among the results, it has been impossible to use the pressure experiments as critical tests of the quantum confinement model. In this paper, we report the measurements of the pressure dependence of the PL for two free-standing porous silicon films from the same wafer up to 60 kbar at room temperature, using helium and the alcohol mixture as the pressure media, respectively. Since helium is the best hydrostatic pressure medium available and can be assumed to be inert (or nearly so), the measurement with helium can serve as the reference, while that with alcohol can test the previous results.

The porous silicon was made by anodically etching a boron-doped silicon wafer with a resistivity of 3–7 Ω cm in

a solution of HF:H₂O:CH₃OH (1:1:2). The wafer was etched for 25 min at a current density of 15 mA/cm². Porous silicon flakes were detached from the crystalline silicon substrate by scraping with a clean stainless-steel razor blade. In separate experiments, two flakes (samples *A* and *B*) of approximately 150×50 μ m² dimension were collected from the surface of this wafer and loaded into a gasketed diamond anvil cell¹³ along with ruby chips approximately 20 μ m in size for pressure calibration. Sample *A* was loaded with liquid helium as the pressure medium, and sample *B* with the 4:1 mixture of methanol:ethanol. These pressure media have been shown to be hydrostatic at room temperature for the pressure range used.^{14,15} The PL spectra of these samples were measured at pressures up to 60 kbar through two cycles of pressure each, using the UV lines (351 and 364 nm) of an Ar⁺ laser with an intensity of \sim 3 W/cm², focused to a diameter of \sim 200 μ m, as the excitation source. A magnified image of the pressure compartment was projected onto a screen *in situ* to ensure proper focusing of the laser beam on the sample or on the ruby chips. The luminescence was dispersed by a Spex double monochromator and detected with a cooled GaAs photomultiplier tube. The data were acquired using conventional photon-counting electronics and recorded by a computer. The spectral resolution of the system was \sim 0.1 meV. The pressure was calibrated with an accuracy of \sim \pm 1 kbar using the pressure shift of the ruby R1 luminescence line.

Figure 1 shows the PL spectra of sample *A* in helium at several pressures for a single cycle. The tail of a diamond defect luminescence band at the higher energy side has been subtracted from the spectra. As a function of the time of laser exposure (from the bottom spectrum to the top one), a monotonic decrease in the PL intensity, comparable to a similar effect observed at atmospheric pressure, is observed. Also observed is a slight nonreversible increase in the width of the peak with application of pressure. Figure 2 shows the pressure dependence of the PL peak energy of sample *A* for two consecutive pressure cycles. In the low-pressure range (0–20 kbar) the PL peak shifts little with pressure, while in the higher-pressure range the peak shifts to lower energy with a pressure coefficient of -1.3 ± 0.2 meV/kbar. No significant hysteresis is seen. Figure 3 shows the PL spectra of sample *B* in the alcohol mixture at several pressures in a cycle. The energy and the width of the PL peak at the lowest pressure

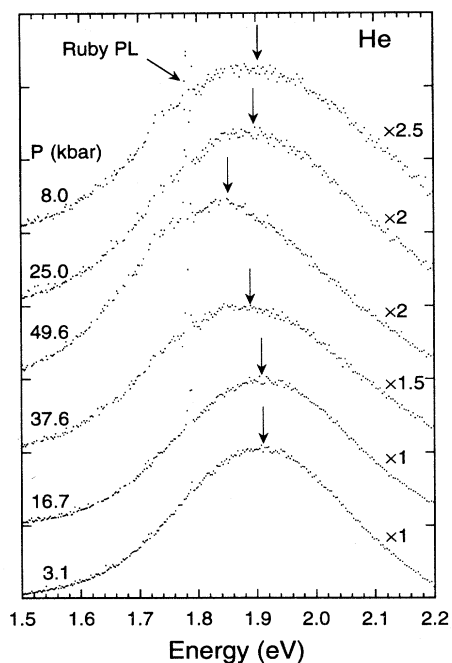


FIG. 1. The PL spectra of sample A in helium at several pressures during a pressure cycle, with the arrows indicating the peak energies. The sharp peak at ~ 1.78 eV is due to the ruby R1, R2 luminescence lines. The tail of a diamond defect luminescence band at the higher-energy side has been subtracted from the spectra.

are almost identical to those for sample A (Fig. 1). The intensity decreases with time as in the case of sample A, although here the intensity seems to go through a minimum in the middle-pressure range. Figure 4 shows the pressure dependence of the PL peak energy of sample B for two pressure cycles. Unlike the case of sample A, the peak displays a

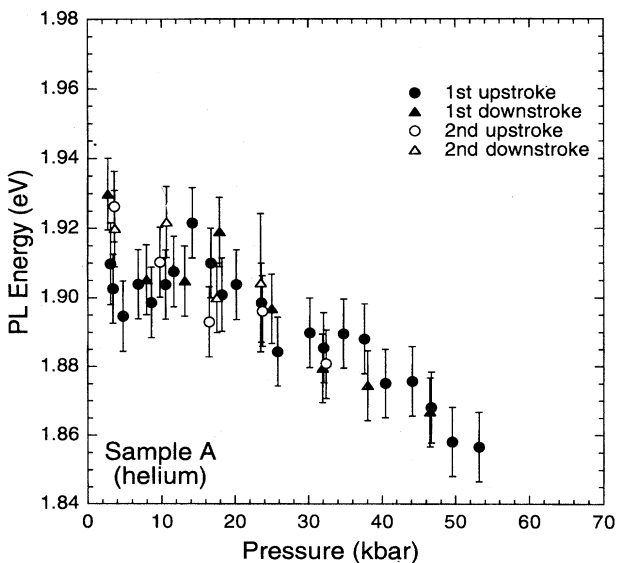


FIG. 2. The pressure dependence of the PL peak energy for sample A in helium. The filled symbols indicate data for the first pressure cycle and the open symbols for the second cycle.

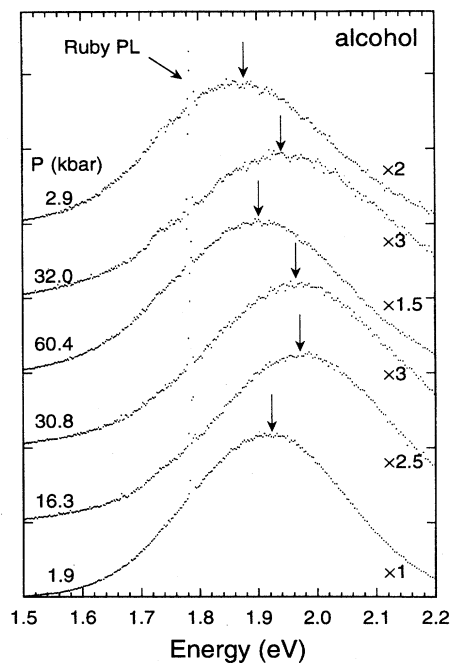


FIG. 3. The PL spectra of sample B in the 4:1 mixture of methanol:ethanol at several pressures during a pressure cycle, with the arrows indicating the peak energies.

blueshift with increasing pressure in the low-pressure range (≤ 20 kbar) with a pressure coefficient of $+2.5 \pm 0.3$ meV/kbar, while showing a redshift in the higher-pressure range (≥ 30 kbar) with a pressure coefficient of -2.0 ± 0.2 meV/kbar. There is a significant hysteresis in the first pressure cycle, but not in the second cycle.

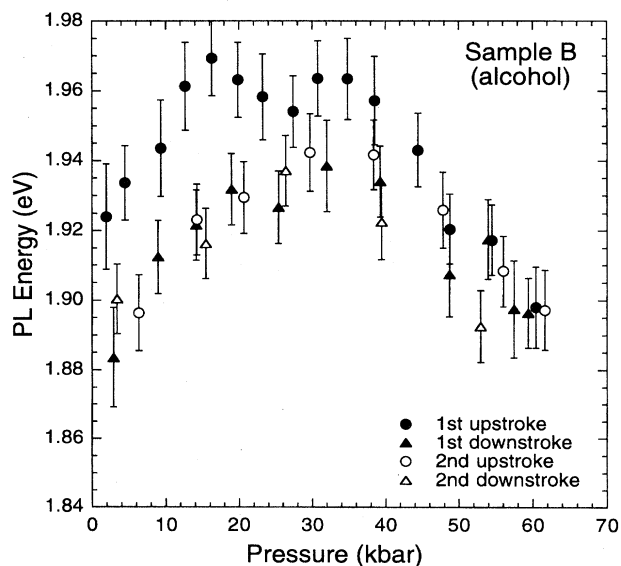


FIG. 4. The pressure dependence of the PL peak energy for sample B in the 4:1 mixture of methanol:ethanol. The filled symbols indicate data for the first pressure cycle and the open symbols for the second cycle.

The absence of the blueshift at low pressures for sample *A* in helium is unambiguous evidence that the blueshift observed for sample *B* is not an intrinsic property of porous silicon but a phenomenon associated with the use of alcohol as the pressure medium. This blueshift is not a result of a "pressure-induced size-reducing chemical reaction"¹² either, because such a chemical reaction would not be reversible as the data for the second pressure cycle indicate.

The fact that the pressure dependence of the PL depends on the pressure medium used is a strong indication that the origin of the PL cannot be explained in terms of the standard quantum confinement model. The pressure dependence of the energy levels of the confined electronic states in the core silicon should be the same regardless of the hydrostatic pressure medium used, since the confined states should not be affected by the presence of a pressure medium beyond the passivated surface layer. Even if they were perturbed, for example, by dipole moments of the molecules in the medium, the pressure dependence of the states would be close to that of unperturbed states unless the dipole moments change dramatically with pressure. Since the difference in the PL energies at the lowest pressures for samples *A* and *B* is very small compared to the blueshift observed in sample *B*, this scenario is unlikely; the pressure-induced change in the perturbation due to the dipole moments is unlikely to be much larger than the initial magnitude of the perturbation.

The fact that the pressure dependence of the PL is sensitive to the choice of pressure media suggests that the surface plays a dominant role in determining the PL energy. Although comparison of the pressure coefficients of the PL of siloxene [-2.4 ± 0.3 meV/kbar (Ref. 16)], measured with xenon as the pressure medium, and sample *A* (-1.3 ± 0.2 meV/kbar) indicates that a molecular-like transition in siloxene is

not likely to be the origin of the PL, it is still possible that another form of Si-O-H complex on the surface of the porous silicon is responsible for it. If this is the case, the PL energy and its pressure dependence would be determined by both the electronic structure of porous silicon and that of the surrounding material, i.e., the pressure medium; the pressure dependence of the PL from states formed by the association of porous silicon and alcohol can be completely different from that of porous silicon in contact with an inert medium such as helium. It should be pointed out here that the pressure coefficient for sample *A* in helium (-1.3 ± 0.2 meV/kbar) is very close to that of the indirect gap of crystalline silicon [-1.5 ± 0.1 meV/kbar (Ref. 17)], which indicates that the indirect band gap may still play a major role in determining the PL energy for porous silicon in an inert environment.

In conclusion, we have measured the pressure dependence of the PL of porous silicon using both helium and the standard alcohol mixture as the pressure media. The pressure dependence of the PL in the two cases is very different; there is only a redshift when helium is the pressure medium, and a blueshift at low pressures and a redshift at higher pressures when the alcohol mixture is the pressure medium. This result shows that the blueshift previously reported by other authors is not an intrinsic property of porous silicon. It also indicates that the PL is not a result of simple quantum confinement of electrons and holes in the silicon core. Our result is a strong indication that the PL energy is determined by states at or near the surface of porous silicon.

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