COMMUNICATIONS

Raman and high-pressure photoluminescence studies on porous silicon

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We show that there is no correlation between the blue shift of the visible photoluminescence band and red shift of the Raman phonon line in porous silicon, in contrast to the recently reported results. We also report a drastic red shift of the photoluminescence peak position with pressure up to 6 GPa and show that this is much larger than that of the crystalline silicon. These observations cast doubt on the suggested mechanism of quantum size effects in porous silicon.

Highly porous silicon prepared by electrochemical anodic etching has recently been a subject of intense interest due to its strong visible photoluminescence (PL) at room temperature.[1] The origin of this luminescence, as well as the blue shift of the fundamental absorption edge of porous silicon layer[2] (PSL), is not understood and is a matter of controversy. In one interpretation, quantum wires of diameter ~ 30 Å are formed in crystalline silicon due to a decrease in the dimensions of the silicon pore walls and hence a quantum size effect is responsible for the blue shift of the band gap of the silicon. Experimental evidence for this interpretation are transmission electron microscopy (TEM) studies,[3] dependence of the luminescence peak position on the porosity,[1,3] and correlation between Raman and PL spectra.[4] It has been shown[4] that the luminescence peak shifts to higher energy as the Raman line shifts to lower energy. In contrast, an alternative interpretation has been put forward in which the effect is not intrinsic to crystalline silicon. It has been suggested that siloxene derivatives[5] like $Si_6O_3H_6$ or SiH_x (Ref. 6) present in the PSL are responsible for the visible luminescence. The former suggestion[5] is supported by the fact that the luminescence (time decay, dependence of peak position on excitation energy, and luminescence fatigue) and vibrational properties (Raman and infrared) of PSL are essentially the same as that of pure siloxene $Si_6O_3H_6$ (Kautsky compound) or Wöhler compound $Si_6O_{3+m}H_{6-m}$. The suggestion of SiH_x being responsible for visible luminescence[6] is supported by the observation that hydrogen comes out from the PSL upon heating it to 390 °C, accompanied by a red shift and general disappearance of the PL. Also, for 1 Ω cm p-type silicon, open circuit etching that increases the porosity does not blue shift the luminescence peak.[6]

In this communication, we investigate the correlation between the PL and Raman of the PSL and also study the pressure dependence of the PL, which can be further used to arrive at the correct mechanism of the visible luminescence. We show that there is no correlation between the

Raman and the PL, in contrast to the recent report.[4] There is a drastic pressure-induced redshift of the PL band, much more than that of the indirect band gap of the crystalline bulk silicon (c-Si). Our results do not support the suggestion of quantum size effects being responsible for the visible luminescence from the PSL.

A large number of PSLs were prepared by anodic etching of boron-doped p-type Si wafers of ⟨100⟩ orientation and resistivity of 1 Ω cm with different current densities, HF concentrations, and etching times. The samples exhibited strong visible PL in the spectral range of 1.6–1.9 eV with a typical width of ~ 300 meV. PL and Raman spectra were recorded in the backscattering geometry using the 5145 Å line of an argon ion laser as excitation source and a Spex Ramalog model 14018 equipped with a cooled photomultiplier tube RCA 31034A and photon counting system. For high-pressure experiments, PSLs were carefully peeled off from the silicon substrate. High-pressure PL experiments were done on the platelets of free standing PSL using a Mao–Bell-type diamond anvil cell and paraffin oil as pressure transmitting medium. We did not use the more conventional methanol-ethanol mixture as a pressure transmitting medium, because it was found to react with the PSL. The pressure calibration was done using the pressure dependence of the Raman line of c-Si (which in turn was measured using the ruby-fluorescence technique[7]). This calibration procedure was adopted because the PL from the PSL and the ruby fluorescence occur in the same spectral range.

Both Raman and PL spectra were recorded in a single run at the same spot on the sample. As reported before,[4] the PL spectra is slightly different at different parts of the sample. Figure 1 shows the PL spectra of four different PSL samples produced as follows; A:15 mA/cm² for 30 min in 20% aqueous HF; B:15 mA/cm² for 40 min in 48% aqueous HF; C:3.5 mA/cm² for 20 min followed by 7 mA/cm² for 20 min in 10% aqueous HF; and D:15 mA/cm² for 30 min in 10% aqueous HF. The corresponding Raman Spectra are shown in Fig. 2, wherein the Raman line of the unetched bulk c-Si is also shown (dotted line). It can be seen that the reported correlation[4] between a large blue shift of the PL and the red shift of the Raman line of the

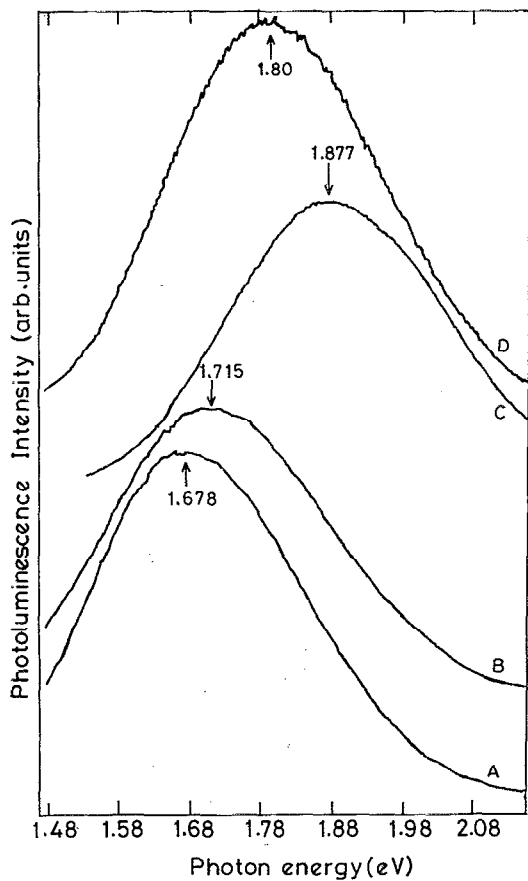[a] Also at Jawaharlal Nehru Center for Advanced Scientific Research, IISc. Campus, Bangalore-560 012, India.

FIG. 1. Photoluminescence spectra recorded at 300 K for four different samples A, B, C, and D. Sample A:15 mA/cm² for 30 min in 20% aqueous HF; B:15 mA/cm² for 40 min in 48% aqueous HF; C:3.5 mA/cm² for 20 min followed by 7 mA/cm² for 20 min in 10% aqueous HF; and D:15 mA/cm² for 30 min in 10% aqueous HF.
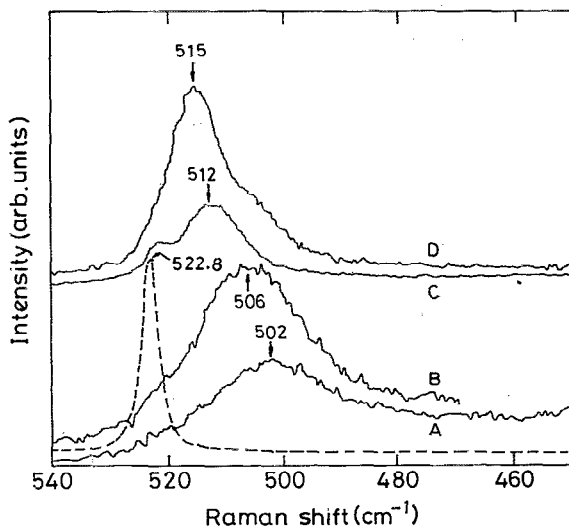

FIG. 2. Raman spectra recorded on the same spot as the corresponding photoluminescence spectra for different samples. The dotted line is the Raman spectrum of c-Si. The spectral resolution is 1.23 cm.⁻¹
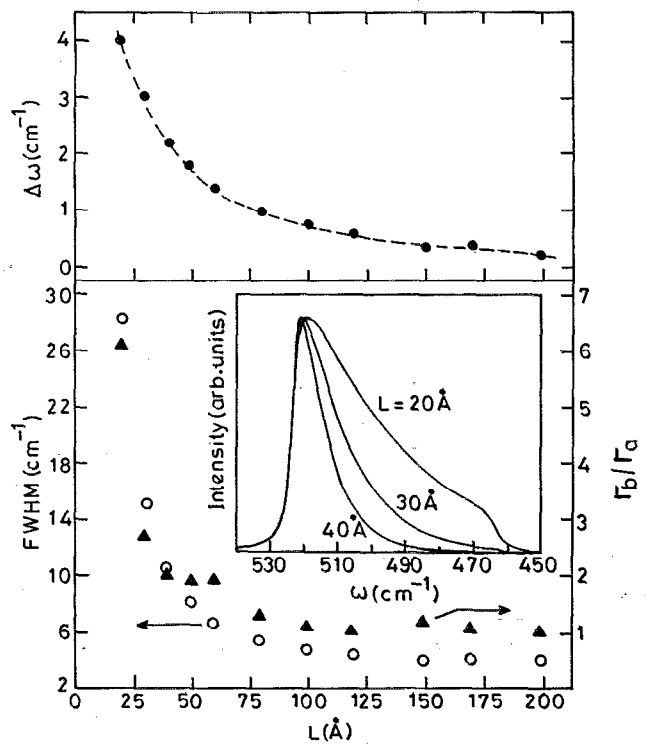

FIG. 3. The calculated peak position (top panel) FWHM (open circles in bottom panel) and Γ_a/Γ_b (triangles in the bottom panel) as function of cylinder diameter L. The inset shows the calculated Raman line shape for L=20, 30, and 40 Å [using Eq. (1) and Ref. 8].

PSL with respect to that of c-Si (both implying smaller diameter quantum wires) is not seen in our experiments. The sample A that has the least blue shift of the luminescence has the largest redshift of the Raman line. Our Raman results do not show any peak at 480 cm⁻¹, which rules out the formation of amorphous silicon, in agreement with the earlier reports.[5]

In order to see the quantum size effect on the first-order Raman line, we have calculated the Raman line shape for a cylindrical shaped crystal using[8]

$$I(\omega) = A \int d^2q \, |c(0,q)|^2 / \{[\omega - \omega(q)]^2 + \Gamma_0^2\}, \qquad (1)$$

where $\omega(q)$ is the phonon dispersion curve for the bulk silicon, Γ_0 is the half width at half maximum (HWHM) of the c-Si, and A is a constant. Here $c(0,q)$ are the Fourier coefficients of the phonon confinement function.[8] Taking the phonon confinement function to be Gaussian,[8] which is found to be suitable for microcrystalline silicon spheres, $|c(0,q)|^2 = \exp(-q^2L^2/16\pi^2)$, where L is the diameter of the cylinder whose length has been assumed to be infinite. The calculated Raman line shapes are asymmetrical, as shown in the inset of Fig. 3, and can be characterized, by the peak position, full width at half maximum (FWHM) and Γ_a/Γ_b (the ratio of the HWHM on the low-energy side to the HWHM on the higher energy side). Figure 3 shows these quantities as a function of L. Here the phonon dispersion is taken to be $\omega(q) = \omega_0(1 - 0.18q^2)$, which fits the experimental dispersion curve[9] in the direction $\Gamma - X$ with

$\omega_0 = 522.8$ cm^{-1} and wave vector q expressed in units of $2\pi/a_0$ (a_0=lattice constant of silicon=5.4 Å). It can be seen that for L=20 Å, the shift $\Delta\omega$ is only 4 cm^{-1}, whereas the FWHM is 28 cm^{-1}. The observed large red shift of the Raman line of the porous silicon in Fig. 2 ranges from 7.5 cm^{-1} (sample D) to 20.8 cm^{-1} (sample A) and hence would imply a wire of diameter <15 Å in the above model. This in turn should result in very large FWHM and Γ_a/Γ_b, which are not seen in the observed Raman spectra of the porous silicon. The other forms of the phonon confinement functions do not alter the above argument. Hence, the observed Raman spectra of the PSL are not consistent with the model of confinement of phonons in the quantum size wires.

Brandt *et al.*[2] have shown that the Raman line of siloxene compounds occurs at 514 cm^{-1} and has a shoulder at 480 cm^{-1}. It may be possible that the derivatives of the siloxene compound or silicon hydrides formed under different etching conditions may exhibit different red shifts. This should be examined further.

The pressure dependence of the optical gaps in semiconductors is an important fingerprint of the nature of the gap. For example, the indirect gap in c-Si or in GaAs associated with the conduction-band minimum at X-point decreases with pressure, whereas the direct gap in GaAs associated with conduction-band minimum at Γ point increases with pressure.

The magnitude of the red shift is found to vary somewhat from sample to sample, which can be partly due to different levels of porosities and microstructures. Figure 4 shows the red shift of the PL band, ΔE_g, for three different samples. In comparison, the red shift of the optical energy gap of crystalline bulk silicon that relates to the minimum of the conduction band near X point and amorphous a-Si:H films prepared by reactive sputtering is -15 meV/GPa up to the transition pressure of 15 GPa. In a-Si:H films prepared by glow discharge, the optical gap decreases more slowly till 5 GPa, but decreases more rapidly above this pressure. It can be seen from Fig. 4 that the decrease of the PL position for all the samples is much higher than that in bulk c-Si and a-Si:H. This suggests that the visible luminescence from porous silicon is perhaps not intrinsic to c-Si. It would, of course, be more appropriate to compare the observed pressure-induced red shift with that of the crystalline silicon quantum wires or quantum dots. The latter is not known as yet. At present, the pressure dependence of the luminescence from siloxene derivatives or silicon hydrides is also not known. The pressure experiments give other important data to help in understanding the origin of the visible luminescence from the porous silicon.

In conclusion, we have shown that there is no correlation between the blue shift of the PL peak and the red shift of the Raman line in porous silicon. The characteris-
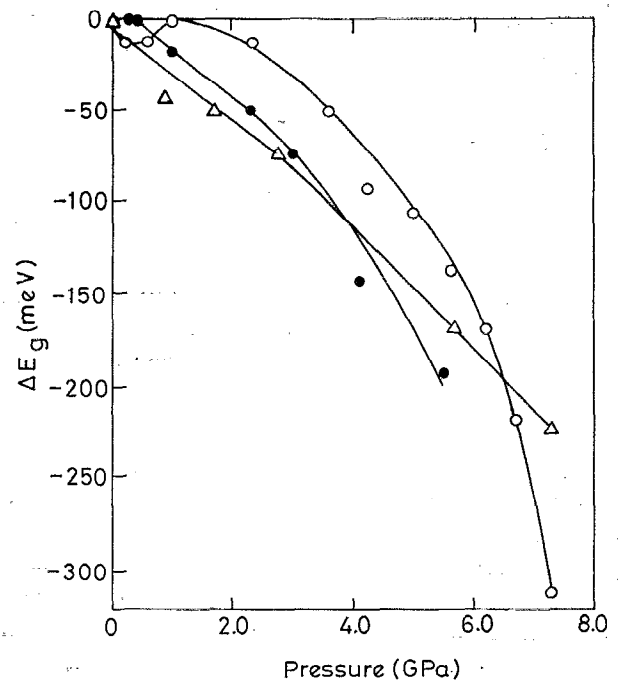

FIG. 4. The red shift of the photoluminescence peak position with respect to its value at ambient pressures for three different porous silicon samples. The solid lines are drawn as a guide to the eye.

tics of the Ramam lines observed in the PSL are not consistent with the model of phonon confinement in cylindrical geometries. The pressure dependence of the PL from the PSL is very different from that of c-Si. All these observations cast doubt on the picture of quantum size effects being responsible for the observed visible PL from the PSLs.

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