Study of the Raman peak shift and the linewidth of light-emitting porous silicon

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The correlation between the Raman peak shift and the linewidth of porous silicon is studied. The experimental result does not fit with the relationship predicted by the phonon confinement model. By taking into account both the phonon confinement and the effect of strain, the calculated Raman line shape coincides fairly well with the measured spectrum. The built-in strain of porous silicon varies with the porosity of the sample and is on the order of 10^{-3}.

Since Canham discovered the efficient visible light emission from highly porous silicon (PS),[1] considerable attention has been paid to investigating its structural and electronic properties. Raman scattering spectroscopy is one of the powerful techniques for studying structure related information, especially information concerning nanostructures in crystalline materials. Tsu *et al.* reported the first correlated study of Raman spectroscopy and photoluminescence (PL) of PS and attributed the Raman peak shift of PS to the effect of phonon confinement.[2] Sui *et al.*[3] and Zhang *et al.*[4] also conducted Raman studies on PS, with emphasis on the linewidths and peak shifts of Raman spectra. However, the spectra they observed were very broad, with a tail extending to a wave number much lower than 480 cm^{-1}. It is very likely that some contribution from the amorphous phase may be involved in the light scattering. The possible inclusion of any amorphous band would make interpretation of the experimental line shape very difficult. In addition, the effect of the strain that may exist in PS was not considered in any of the previous studies.[2–4] In this communication, we present a Raman scattering study on a variety of light-emitting PS samples. All the Raman spectra show only a single peak, without the presence of an amorphous phase band, thus the precise correlation between the Raman shift and the peak width could be extracted. It was found that the experimental result could only be explained by taking into account of the strain induced expansion size in addition to the phonon confinement effect.

The samples used were all prepared on p-type Si (100) substrates with a resistivity of ~10 Ω cm. The electrochemical etching was carried out in a 48% HF:98% ethanol = 1:1 solution at a current density of ~10 mA/cm^2. The etching time varied from several minutes to several hours. All samples showed visible light emission under illumination by UV light. Near backscattering Raman measurements were performed at room temperature using the 457.9 nm line of an Ar^+ laser as an excitation source. The laser power was 50 mW and the spot size on the samples was about 200 μm. The thermal effect due to laser heating of the sample was negligible.

Figures 1(a) and 1(b) give two typical Raman spectra of light-emitting PS samples that were etched for 30 and 180 min, respectively. The spectrum from a crystalline Si wafer is also shown for comparison. The peak position and width of the sample in Fig. 1(a) only have small changes as compared to those of c-Si. But the peak intensity of the PS sample is several times stronger than that of c-Si, which is believed due to the remarkable change of its optical constants. In contrast to the scattering from c-Si, the scattering light from porous silicon is depolarized, indicating a breakdown of the scattering selection rules for the (100) surface. For sample 1(b), there exists a large peak shift from 520.0 to 515.6 cm^{-1} and a broadening of peak width full width at half maximum (FWHM) from 3.5 (symmetric) to 8.1 cm^{-1} (asymmetric). Neither spectra 1(a) nor 1(b) show any peak or shoulder around 480 cm^{-1}, indicating the absence of the amorphous phase in our PS samples.

In Fig. 2 the Raman red shift is plotted as a function of peak width for various PS samples. The experimental data are shown as dots, while the solid line is drawn to guide the eye. The Raman red shift and line broadening have been observed in polycrystalline and microcrystalline materials and were attributed to the confinement of optical phonons in a small crystalline particle.[5,6] When the size of the particle reduces to the order of nm, the wave function of optical phonons will no longer be a plane wave. The localization of wave function leads to a relaxation in the selection rule of wave vector conservation. Not only the phonons with zero wave vector $q=0$ but also those with $q>0$ take part in the Raman scattering process, resulting in the red shift of the peak position and the broadening of the peak width.

To quantitatively explain our experimental results in Fig. 2, the phonon confinement model just described is employed. The PS is modeled as an assembly of quantum dots, i.e., the confinement is three dimensional. The weight factor of the phonon wave function is chosen to be a Gaussian function as follows:

$$W(r,L) = \exp(-8\pi^2 r^2/L^2), \tag{1}$$

where L is the correlation length related with the size of dots. A square of Fourier transform,

$$|C(q)|^2 = \exp(-q^2 L^2/16\pi^2), \tag{2}$$

gives the scattering probability of phonons with the different wave vector q. The first-order Raman spectrum is thus given by
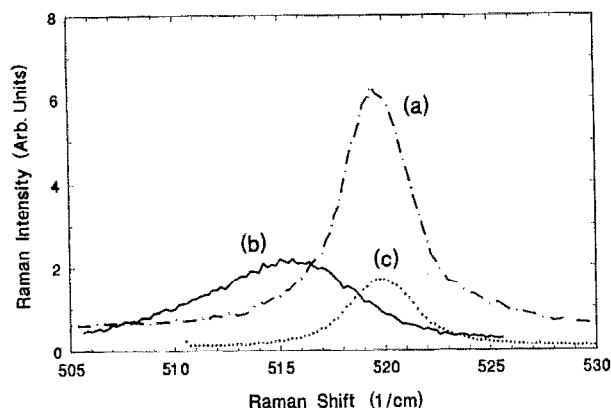
FIG. 1. Typical Raman spectra of light-emitting porous silicon samples with (a) 30 min etch time, (b) 180 min etch time, (c) and a c-Si sample.

FIG. 3. Measured (solid curve) and calculated Raman spectra without the strain effect (dotted curve) and with the strain effect (dot-dashed curve).

$$I(\omega) = \int_0^{2\pi/a_0} \frac{|C(q)|^2 4\pi q^2 \, dq}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2},$$ (3)

where a_0 is the lattice constant of the bulk Si crystal and Γ_0 is the Raman linewidth of the bulk Si (3.5 cm^{-1}, including instrumentation broadening). The phonon dispersion relation $\omega(q)$ is taken according to:[3]

$$\omega(q) = \omega_0 - 120(q/q_0)^2,$$ (4)

where $\omega_0 = 520 \text{ cm}^{-1}$ and $q_0 = 2\pi/a_0$. By using Eqs. (2)–(4), we can calculate the Raman spectrum and determine the relationship between the peak shift and the peak width. The result is shown as a dashed line in Fig. 2. It is clear that the phonon confinement model does not totally correlate to the experimental results.

The real structure of PS may be spongelike, i.e., it is composed of wires and/or dots of nonuniform dimensions. Although the dominant contribution to the light scattering is from those large parts that are more dotlike, some parts
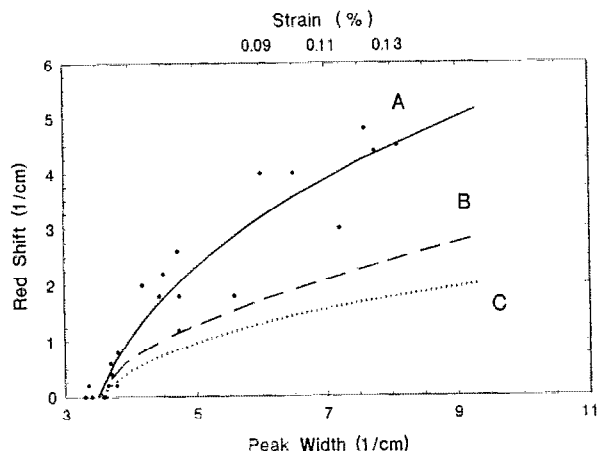

FIG. 2. The relationship between the linewidth and the peak shift with that of c-Si. The dots represent the experimental data, curve A is drawn to guide the eye, curves B and C are the calculated results using the three- and two-dimensional phonon confinement model, respectively.
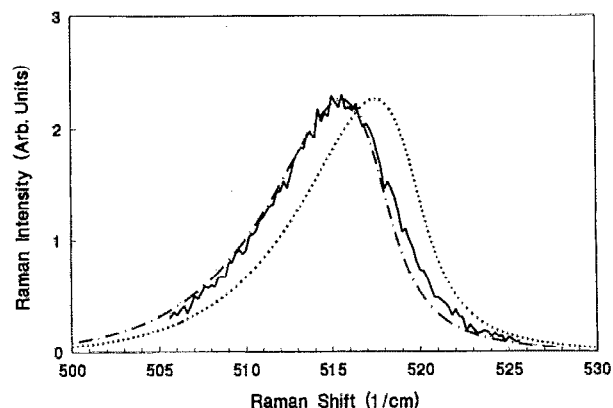
might be more wirelike and where the phonon confinement is two dimensional. If the quantum dot model is replaced by a quantum wire model, i.e., the phonon confinement is assumed to be two dimensional instead of three dimensional, the calculated result is then shown by the dotted line in Fig. 2. One can see there is even less agreement between the calculated and the measured results.

It has been shown by x-ray double crystal diffraction that the PS layer is strained, with the lattice constant increasing as the porosity increases.[7] The lattice expansion will cause an additional red shift of the Raman peak. We suggest that the difference between the solid curve A and the dashed curve B is attributable to the effect of strain. The following relationship gives an estimation of the strain by measuring the difference of peak shifts at a specific linewidth:

$$\frac{\delta\omega_s}{\omega_0} = -3\gamma \frac{a_{PS} - a_0}{a_0},$$ (5)

where $\delta\omega_s$ is the vertical interval between curve A and curve B, a_{PS} is the lattice constant of PS nanostructures, and $\gamma \approx 1.0$ is the Grüneisen constant. The derived values of strain $(a_{PS} - a_0)/a_0$ are indicated on the upper abscissa in Fig. 2. The value of strain increases as the linewidth or red shift increases, with the latter being related to the size of the Si nanostructures.

Taking into account both the phonon confinement and the effect of strain, reconstruction of the Raman spectrum by computer simulation is shown in Fig. 3, where the solid curve is the measured spectrum, the dash-dotted curve is the result of computer simulation, and the dotted curved is the calculated spectrum without consideration of the strain effect. Although the strain is only on the order of 10^{-3}, it affects the shift of the Raman spectrum significantly. In addition, it illustrates that Raman scattering is quite sensitive to the small built-in strain in the PS layer that has not yet been considered in other studies such as photoluminescence.

In conclusion, we have established the relationship between the Raman peak shift and the peak width of PS that

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constitutes crystalline nanostructures. For a specific linewidth, the experimental peak shift is larger than that predicted by the phonon confinement model. The additional part of the peak shift is attributed to the effect of lattice expansion in PS nanostructures. Using computer simulation, the calculated Raman line shape agrees well with the experimental spectrum and the lattice strain in the PS layer, which is porosity-dependent and is estimated to be on the order of 10^{-3}.

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