

## Analysis of the Structure of Light-emitting Porous Silicon by Raman Scattering

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### ABSTRACT

Raman spectra from a thick porous silicon film ( $\sim 100 \mu\text{m}$ ) that strongly emits in the visible ( $\sim 6350 \text{ \AA}$ ) at room temperature are obtained. An asymmetric peak with a Raman shift of  $\sim 508 - 510 \text{ cm}^{-1}$  and a width of  $\sim 40 \text{ cm}^{-1}$  is seen in every spectrum. This Raman feature resembles that of  $\mu\text{c-Si}$ , suggesting that the local structure of the porous silicon is a network of interconnected crystalline silicon islands with the island size in the nanometer range, and that the shape of the islands is more sphere-like than rod-like. The characteristic dimension of the islands in these porous silicon films is estimated to be  $\sim 2.5 - 3.0 \text{ nm}$  on the basis of an empirical model calculation of phonon confinement.

### INTRODUCTION

There have been several recent reports of strong visible luminescence at room temperature from porous silicon with high porosity.[1-3] Porous silicon, which consists of a network of randomly spaced pores, is formed by anodization of a crystalline silicon wafer in a hydrofluoric solution. The pore size and porosity can vary over a wide range depending on the electrochemical parameters and the doping conditions of the initial Si wafer.[4-8] The mechanism of light emission is still uncertain. However, several possible mechanisms have been suggested, including: 1) quantum confinement in silicon [1,2,9]; 2) the effect of incorporated hydrogen,[3] as in light-emitting hydrogenated amorphous Si; 3) surface effects; and 4) emission as in some Si-based organic compounds. The result of this Raman study can impact these suggested mechanisms, especially the first one.

Raman scattering is a non-destructive tool for the characterization of semiconductors,[10] which has been used to determine grain sizes in microcrystalline materials.[10-14] The first-order Raman peak in c-Si is shifted by  $520.5 \text{ cm}^{-1}$ ; it is symmetric and has a width of  $3.0 \text{ cm}^{-1}$  (FWHM). As the grain size in microcrystalline silicon ( $\mu\text{c-Si}$ ) decreases below  $\sim 200 \text{ \AA}$ , the Raman shift decreases, the width increases, and the peak becomes increasingly asymmetric, with an extended tail at low frequencies.[12] The Raman spectrum of amorphous silicon (a-Si) peaks near  $480 \text{ cm}^{-1}$  and is usually weaker in intensity and very broad.[12] The first-order Raman spectra of both degenerate and non-degenerate porous silicon films have been reported by Goodes et al.[15]

## EXPERIMENTAL PROCEDURE AND RESULTS

Thick porous silicon films ( $\sim 100 \mu\text{m}$ ) were made out of float-zone p-type Si (001) (resistivity of  $150 \Omega\text{-cm}$ ) using techniques described by Canham.[1] These films are thick enough so that the underlying silicon substrate is not probed by Raman scattering. Before etching, the wafers had a minority carrier lifetime of  $\sim 4$  msec. In the etched areas very bright photoluminescence is seen at room temperature, which peaks at  $6350 \text{ \AA}$  and has a full-width at half maximum of  $\sim 850 \text{ \AA}$  when excited by  $4880 \text{ \AA}$  from an argon-ion laser. The estimated photoluminescence efficiency is  $\sim 1\%$ . Polarized Raman spectra of the samples were taken at room temperature after several months of storage in air. A backscattering configuration was used with the  $4880 \text{ \AA}$  line, with a triple monochromator for dispersion and an intensified photodiode array for detection. The resolution of the spectra is typically less than  $1 \text{ cm}^{-1}$ . The laser power used in Raman analysis was  $\sim 1 \text{ mW}$  and the spot size on the sample was  $\sim 10 \mu\text{m}$ . Because of the low thermal conductivity of porous silicon and the temperature dependence of the Raman spectra, care was taken to avoid laser heating of the sample.

Raman spectra of the light-emitting porous silicon were collected in six polarization configurations to help identify the structure. With the laser impinging normal to the surface,  $z(x, y)\bar{z}$  and  $z(x, x)\bar{z}$  spectra were taken. Backscattered spectra of the porous silicon film were also taken with the laser impinging normal to the edge of the porous silicon film on the c-Si wafer (in the middle of the film), with the laser polarization either parallel or perpendicular to the plane of the substrate.

The Raman spectrum of the light-emitting porous silicon film is shown in Figure 1. The background was verified to be from the high energy side tail of the photoluminescence spectrum. As indicated in Figure 2, the Raman shifts vary from  $508.0$  to  $510.1 \text{ cm}^{-1}$  and the widths from  $32$  to  $42 \text{ cm}^{-1}$  (FWHM) for the different polarizations and probing positions. Also, the peaks are very asymmetric. These spectral parameters lie between those of  $\mu\text{c-Si}$  and a-Si. Essentially the same Raman lineshape is seen for each of the six polarization configurations, with the relative peak intensities varying by a factor of  $\sim 2$ . Since spectra taken on the top and in the middle of the edge of the film are almost the same, the structure of the film is fairly homogeneous. No

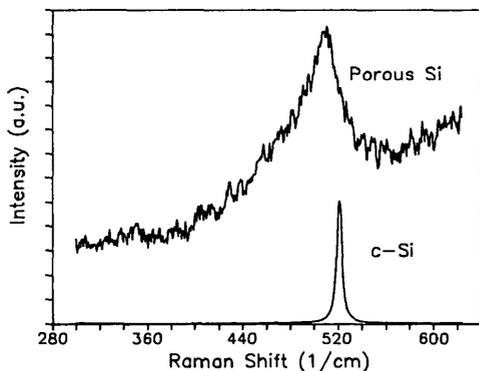


Figure 1. The unpolarized Raman spectrum of a thick light-emitting porous silicon film, with the Raman spectrum of the c-Si substrate shown for comparison. The background in the porous silicon spectrum is due to the tail of the photoluminescence spectrum.

noticeable differences were seen in Raman spectra taken in air and in vacuum. Also, since Raman spectra taken with 2 mW were the same as those presented here at 1 mW, laser heating is not important.

## ANALYSIS AND DISCUSSION

The phonons involved in first-order Raman scattering have  $\mathbf{q} = 0$  and hence are at the center of the Brillouin zone ( $\Gamma$  point). However, disorder or finite-size effects may partially or completely relax "momentum" conservation, leading to a downshift and broadening of the Raman peak. Based on these effects, a model was developed and then used to estimate successfully the average size  $L$  of microcrystals in microcrystalline Group IV and Group III-V semiconductor films from their Raman spectra.[10-13] In this model, the first-order Raman spectrum  $I(\omega)$  is

$$I(\omega) \propto \int \exp(-q^2 L^2/4) \frac{d^3 q}{[\omega - \omega(q)]^2 + (\Gamma/2)^2} \quad (1)$$

where  $q$  is expressed in units of  $2\pi/a$  and  $L$  is in units of  $a$ , with  $a = 0.54$  nm being the lattice constant.  $\Gamma$  is the natural linewidth ( $= 4.0$   $\text{cm}^{-1}$  for c-Si at room temperature including instrumental contributions) and  $\omega(q)$  is the dispersion relation of optical phonons in c-Si. The analytic form  $\omega(q) = A - Bq^2$  with  $A = 520.5$   $\text{cm}^{-1}$  and  $B = 120$   $\text{cm}^{-1}$  reproduces the dispersion relation quite well for LO phonons and the nearly degenerate TO phonons near zone center along (001) in Si. Equation 1 assumes spherical crystal grains. However, the long cylindrically shaped structures, whose length  $\gg$  diameter, are also considered by making the integral in Equation 1 two dimensional.[12,13]

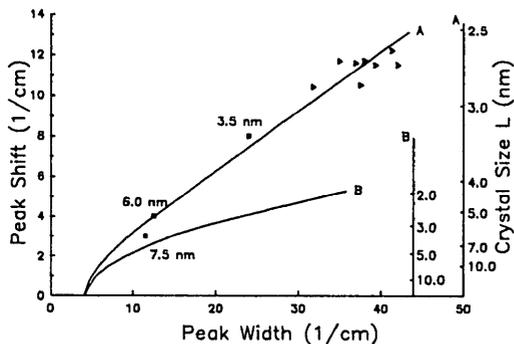


Figure 2. The calculated relationship between the width and shift with respect to those for c-Si, and the nanocrystal size  $L$  for spherically-shaped nanocrystals (curve A,  $L$  is the sphere diameter) and cylindrically-shaped nanocrystals (curve B,  $L$  is the rod diameter). Triangles are the experimental data taken with different polarizations on different places on the sample. Squares are Raman data for  $\mu\text{-c-Si}$  from Ref. 12, with the crystallite dimensions from X-ray diffraction.

Figure 2 gives the calculated relationship between the Raman width and shift with respect to those for c-Si, and the crystal size for both spherical and cylindrical microcrystals. The cumulative data for light-emitting porous Si taken at different points and for different

polarizations are plotted. These Raman data lie along the spherical grain model, and suggest that the local structure is more like a sphere, with a diameter between 2.5 to 3.0 nm, than like a rod. The measured Raman spectra are very well fit by the asymmetric spectra predicted by this model, suggesting that the distribution of the crystalline sizes has a single peak, which is relatively narrow. If the porous structure consisted of an array of columns,[1] the incident laser would be transmitted into the material along the crystal axes and the polarized spectra would vanish in some configurations (such as  $z(x, x)\bar{z}$ ). However, if the porous structure were highly irregular, then the light that is transmitted into the structure would be greatly refracted, and the different experimental polarization configurations would give roughly the same signal intensities. The latter possibility is suggested by these experiments.

In summary, the Raman spectrum from a thick film of light-emitting porous silicon resembles that of  $\mu\text{-Si}$  with an average grain size of 2.5 to 3.0 nm. The shape and the polarization properties of these Raman spectra suggest that the porous film is not an ordered array of silicon columns.

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