Observation of Phonon Structures in Porous Si Luminescence

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(Received 23 November 1992)

Steplike phonon structures are observed in the luminescence spectrum of porous Si under excitation within the luminescence band at liquid He temperature. The shape of the phonon structures are successfully interpreted in terms of a model based on phonon assisted indirect transitions. From the spacing of the structures, it is concluded that the luminescence occurs in an entity which has a phonon spectrum very similar to crystalline Si. The broad spectrum of luminescence is attributed to an inhomogeneous distribution of the indirect band gap energy of Si particles.

PACS numbers: 78.55.−m

Since the discovery of efficient luminescence of porous Si in the visible region [1], a number of reports appeared on its luminescent properties both in static and dynamic measurements. Although there are many different models for the structures and origin of the luminescence in this material, they are mainly classified into three categories. The first one is based on a moleculelike picture; Brandt *et al.* [2] proposed to ascribe the luminescence to molecules like siloxene which may be produced chemically during anodizing process. The second one assumes a strong electron phonon interaction within the solid in analogy to color centers or self-trapped excitons (STE) in ionic crystals [3]. In this case the broad bandwidth of the luminescence spectrum is ascribed to a Frank-Condon factor, which will give a Gaussian shape. The third one is based on the recombination luminescence of quantum confined carriers in semiconductor particles [4].

In studying the systems with a high degree of disorder or highly inhomogeneous materials, site-selective spectroscopy is a powerful method to extract individual information from an inhomogeneously broadened spectrum. In the case of a CuCl microcrystallite embedded in alkali halides, which is a system similar to the porous Si in the sense that both includes size distributed microscopic semiconductor particles, Ito and Furumiya [5] successfully applied the selective excitation spectroscopy. In their case, the particles with similar sizes were selectively excited by a laser light which is in resonance with the excitons in the CuCl particles. Thus they could study the luminescence spectrum corresponding to particles with certain size. In the following, we describe a different type of spectroscopy with which we could remove the effect of inhomogeneous broadening and observe fine structures in the luminescence spectrum of porous Si.

The porous Si samples we used were made from (100) oriented, 9–11 Ω cm resistivity, *p*-type silicon substrates. Thin Al films were deposited on the back surface to ensure a uniform anodic current distribution. The porous Si layers were formed by anodization in a HF solution at a constant current density of 30 mA/cm^2 for 20 min. The anodizing solution used was a 1:1 dilution of commercially available 49 wt.% aqueous HF solution in ethyl alcohol. After the anodized wafers were rinsed in deionized water for 40 min, subsequent chemical etching in a 1.5 wt.% aqueous HF solution was carried out for 30 min [6].

The luminescence was measured in a flow type He cryostat in a He atmosphere. For exciting the luminescence we used an Ar laser or a cw dye laser with DCM or Rh6G. The luminescence was analyzed by a 85 cm double grating monochromator (SPEX 1402) and recorded with a photomultiplier (Hamamatsu R928 multialkali) and a picoammeter. The spectral response of the measurement system was calibrated by using a tungsten standard lamp, and all the spectra were corrected for the response. In time resolved measurements the laser light was chopped by an acoustic-optic modulator and the signal was averaged and recorded by a digital oscilloscope.
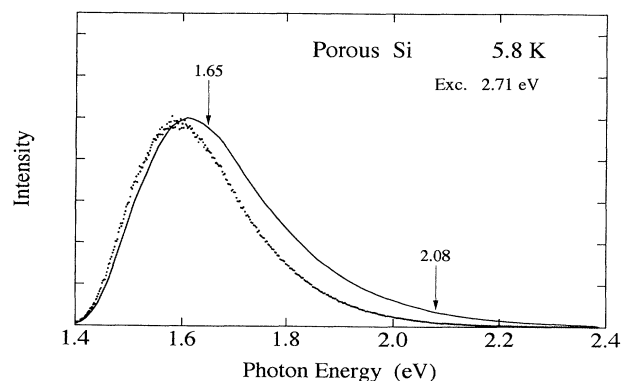
The dotted curve in Fig. 1 shows the luminescence

FIG. 1. Dotted curve is the luminescence spectrum excited by a 4579 Å (2.71 eV) line of an Ar laser, and the smooth curve is the distribution function $P(E)$ of the indirect gap energy. The arrows indicate the energies of excitation and observation in lifetime measurement. The ordinate scale is proportional to the photon number per unit energy interval.

spectrum excited by a 4579 Å Ar laser line at 5.8 K. The peak appears around 1.6 eV and the spectral shape reasonably agrees with that in other reports. The luminescence spectra were investigated under excitation at photon energies within the luminescence band by using a DCM dye laser. Figure 2 shows the spectra taken with 1.81, 1.88, and 1.94 eV excitations. The high energy side of the luminescence spectrum is limited by the excitation photon energy and the intensity at the anti-Stokes side is practically zero at 5.8 K. On the other hand, the low energy side (both in Figs. 1 and 2) seems to be limited always at the same energy, regardless of excitation photon energy between 1.81 and 2.71 eV. Thus the half-width and the intensity decrease, as the excitation photon energy decreases. This behavior is reminiscent of an inhomogeneously broadened band with energy relaxation or transfer to lower energy.

In contrast to the spectrum taken with an excitation in the blue region, the spectra in Fig. 2 show some clear structures just below the excitation laser line, especially for 1.81 eV excitation. As we will see later in a quantitative analysis, the interval of the steplike structures is close to the phonon energy at a maximum of density of state in crystalline Si. This fact suggests that the fine structure is related to Si-like phonons.

In order to estimate the contribution from the resonant luminescence, which might originate from selectively excited species, we examined the tail of the Rayleigh component carefully. However, no line-narrowed resonant luminescence was observed (less than 0.1% of total luminescence power) at any temperature from 300 K to 5.8 K. The lack of resonant luminescence can be understood in the following ways: (1) The homogeneous width of the luminescent level is too small to be discriminated against the Rayleigh line, or is too large to be recognized as a resonant component. (2) The resonant luminescence

is very weak because the excited state produced by light absorption is subjected to energy relaxation or energy transfer to a lower state sufficiently faster than the luminescence lifetime.

Usually the homogeneous width has a strong temperature dependence (T^2 to T^7 dependence in localized centers in crystals, and T^1 to T^2 dependence in glassy materials). For example, in CuCl microcrystals in NaCl, intense resonant fluorescence (around 90% of the luminescence power) was observed and the FWHM width varies from 1 meV at liquid He temperature to 20 meV at 160 K [5]. If there was such a component, it should have been observed at a certain temperature in our case (the spectrum was examined down to 5 meV from excitation energy). Therefore, we are forced to consider that the excited species relax to lower energy before emitting a photon and that the resonant component is really weak [case (2)].

We measured also the luminescence lifetime at 1.65 eV under excitation by 2.08 eV light. Since the decay curve has a nonexponential shape, we estimated the characteristic lifetime τ from the center of gravity of the decay curve. The value of τ was 50 μsec at room temperature, but it increases significantly at lower temperatures and was about $\tau = 3$ msec at 5.8 K.

The experimental results are summarized as follows. (1) The clear fine structures observed in the luminescence spectra suggest that the relevant electronic state couples with Si-like phonons. (2) The long lifetime observed at low temperature suggests that the luminescent entity conserves the indirect gap nature of bulk Si. (3) The lack of resonant luminescence suggests a fast relaxation to lower energy. (4) The low energy cutoff is independent of excitation photon energy, suggesting the shape of the luminescence spectrum reflects an inhomogeneous distribution of luminescent energy levels.

In order to interpret these results, we propose a model based on recombination luminescence associated with phonons. In principle, fine structures in the luminescence spectrum can be explained in two alternative ways. One possibility is to assume fine structures in the *luminescence spectrum* for each particle. If the particles with the same size are selectively excited, these fine structures will appear in the luminescence spectrum. The other assumes fine structures in the luminescence *excitation spectrum* for each particle. If we assume a very sharp luminescence spectrum for each particle, an inverted excitation spectrum will appear in the luminescence spectrum under monochromatic excitation. In the former case, however, the phonon structure will appear as discrete lines with an interval of phonon energy, which does not explain the steplike structure observed. Therefore, in the following, we assume the latter case.

The shape of the absorption edge in indirect gap materials was discussed by Elliott [7]. Near the first exciton absorption edge of phonon assisted transitions, the absorption coefficient is proportional to $\Delta E^{1/2}$, where ΔE
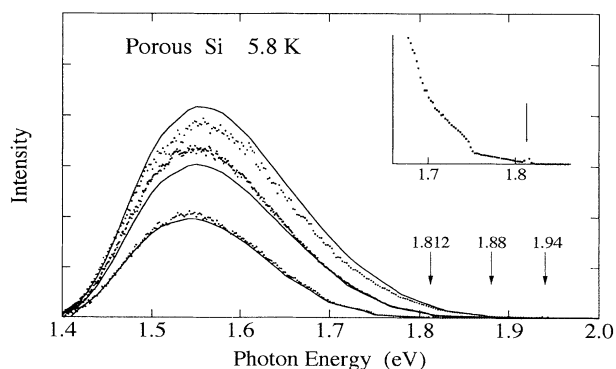

FIG. 2. Dotted curves are the luminescence spectra excited at 1.81, 1.88, and 1.94 eV. Solid curves are the best fits calculated by using Eq. (4). The ordinate scale is proportional to the photon number per unit energy interval. The inset shows the details of the spectrum near the laser line for 1.81 eV excitation.

$=E-E_{\text{gap}}+E_B\pm\hbar\Omega$, E_{gap} is the indirect gap energy, E_B ($=14$ meV) is the exciton binding energy, and Ω is the phonon frequency. At energies sufficiently higher than the band edge, the absorption coefficient is proportional to ΔE^2. Although the behavior is complicated in the intermediate range, we express the absorption spectrum shape for individual phonon structure as

$$\alpha(E)=A(\Delta E^{1/2}+r\Delta E^2).\tag{1}$$

The absorption-edge spectrum in Si was analyzed in a similar way by Macfarlane et al. [8]. Although they used an empirical basic spectrum function instead of a simple ΔE^2 dependence, we confirmed that the above expression is sufficiently good for our purpose. We assume further that the indirect gap energy E_{gap} depends on the size and/or shape of the particles due to the quantum confinement effect, while the shape of the absorption edge is the same. The total absorption coefficient at E for a particle which has a band gap energy of E_{gap} is given as

$$\alpha_{\text{tot}}(E-E_{\text{gap}}+E_B)=\sum_{n=-3}^{3}A_n(\Delta E_n^{1/2}+r\Delta E_n^2)$$
$$\times(N+\tfrac{1}{2}\pm\tfrac{1}{2})^{|n|},$$
$$\Delta E_n=E-E_{\text{gap}}+E_B\mp\hbar\Omega_n,\quad A_{-n}=A_n,\tag{2}$$

and N is the Bose factor

$$N=[\exp(\hbar\Omega/k_BT)-1]^{-1},\tag{3}$$

where Ω is the mean energy of the contributed phonons. In these expressions, the upper sign is for phonon emission ($n>0$) and the lower for absorption ($n<0$). We included a no-phonon transition with $n=0$ and a multiphonon process up to three phonons. In the multiphonon process, Ω_n will be a sum of several phonon frequencies. We did not consider phonon difference processes. We assume that the excited electron relaxes to the bottom of the conduction band in X valley and form an exciton with a hole at the top of the valence band at the Γ point. Then a sharp luminescence spectrum will appear at $E_{\text{gap}}-E_B$ due to radiative decay of the exciton for one particle. For a fixed excitation wavelength, the excited volume defined by the penetration depth (or by the thickness of the porous Si layer) is constant, so that we do not need an absorption correction in discussing the spectrum under monochromatic excitation. Then the luminescence intensity of a particle with a certain size will be proportional to the absorption coefficient of this particle at the excitation photon energy, if we neglect an energy dependence of quantum yield. The luminescence spectrum of the ensemble of various size particles excited at an energy of E_{exc} with an intensity of $I(E_{\text{exc}})$ is then given as

$$S(E)=P(E)\gamma\alpha_{\text{tot}}(E_{\text{exc}}-E)I(E_{\text{exc}}),\tag{4}$$

where γ is a constant including the quantum yield and $P(E)$ is a distribution function of E_{gap}. In calculating the spectrum at temperatures higher than 78 K, we assumed

a Boltzmann distribution for the Γ-X exciton. Then the spectrum is obtained by replacing $\alpha_{\text{tot}}(E_{\text{exc}}-E)$ in Eq. (4) by

$$\int_0^E\alpha_{\text{tot}}(E_{\text{exc}}-E')(k_BT)^{-1}\exp[-(E-E')/k_BT]dE',\tag{5}$$

where we approximated $P(E')$ by $P(E)$ and took it out of the integral, because $P(E)$ is a slowly varying function.

The distribution function $P(E_{\text{gap}})$ is estimated from the luminescence spectrum at 5.8 K taken with 4579 Å excitation by using Eq. (4). In this case, $E_{\text{exc}}-E_{\text{gap}}\gg E_B$ and α_{tot} is practically a simple parabola as a function of $E_{\text{exc}}-E_{\text{gap}}$. The obtained $P(E)$ is plotted in Fig. 1 by a solid curve. In a TEM dark-field photograph, we can find many small crystallites with a typical size of 30 Å in diameter with a very large distribution up to 200 Å [9]. A theoretical calculation [10] shows that the excitation energy in a Si quantum dot is very sensitive to the particle size and values of 2.3 eV for 30 Å or 1.5 eV for 60 Å are reported. Although we have no quantitative information about the distribution width, the peak (1.6 eV) of $P(E)$ seems in a reasonable range.

The spectrum taken with 1.81 eV excitation at $T=0$ K is calculated by using Eq. (4). In this case the parameters Ω_n and A_n are chosen to reproduce the experimental curve. The best parameters are $\Omega_1=61$ meV, $\Omega_2-\Omega_1=56$ meV, $\Omega_3-\Omega_2=48$ meV, $A_1/A_0=3.06$, $A_2/A_0=4.12$, $A_3/A_0=2.94$, and $r=11$ eV$^{-9/2}$.

The details of the spectrum around $E=E_{\text{exc}}$ is shown in Fig. 3(a). In this case, the experimental luminescence spectrum taken with an excitation at 1.81 eV was divided by $P(E)$ and this curve can be directly compared with an "absorption" spectrum. The curve calculated by Eq. (2) is in surprisingly good agreement with the experiment. We can clearly see the existence of no-phonon absorption, which indicates a breakdown of momentum conservation. From the position of the one-phonon edge, we obtain 61 meV (492 cm^{-1}) for the involved phonon. This value is in excellent agreement with the phonon frequency (61 meV) at the maximum of the density of state in bulk Si [11]. Since the maximum phonon frequency in Si is 65 meV [11], the edges at Ω_2 and Ω_3 should not correspond to any one-phonon process, but to two- and three-phonon processes, respectively, as we have already assumed in the calculation. The decrease of the phonon energies in higher order multiphonon structures may be due to the increased combination possibility of involved phonons in k space.

Once we determine these parameters we can calculate a spectra for arbitrary excitation photon energy and temperature. Calculated curves for 1.88 and 1.94 eV excitation are also shown in Fig. 2. The peak positions, peak intensity, and the shape near the excitation energy are well reproduced. Finally, the temperature dependence of the spectrum near the edge is shown in Figs. 3(b) and 3(c). The experimental "absorption" curves are plotted
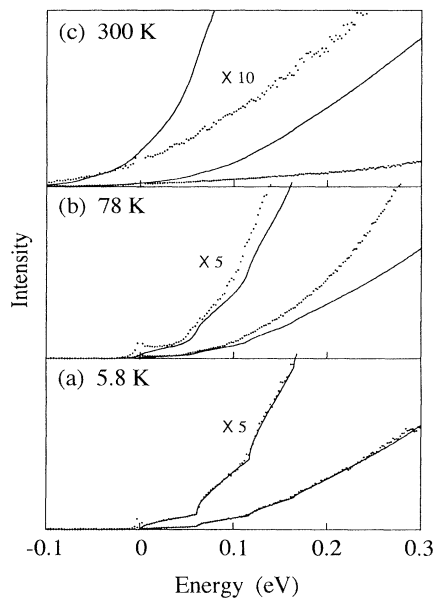
FIG. 3. Details and the temperature dependence of the absorption edge structures at (a) 5.8 K, (b) 78 K, and (c) 300 K. The dotted curves are measured luminescence spectra divided by $P(E)$ (see text) and the solid curves are calculated by using Eq. (5). The abscissa is the energy difference from the band edge.

the same way as in (a) and the calculation was done by using Eq. (5). The smearing of clear structures and the intensity growth near the laser line at higher temperatures are well reproduced. Especially, a rather long tail of the anti-Stokes luminescence can be explained in this way. The main contribution on the anti-Stokes side comes from the one-phonon absorption band and the tail of the no-phonon band. The apparent "temperature" obtained from the fitting with an exponential function on the anti-Stokes side is 470 K in calculation and 680 K in experiment. The agreement is not satisfactory, but the deviation of the slope from the ambient temperature (300 K) can be understood. The large deviation of the fitting at higher energies at room temperature may be ascribed to nonradiative recombination which is larger at energies remote from the band edge. Actually Vial *et al.* observed a significant luminescence quenching due to a tunneling escape of the carriers at temperatures above 300 K, which became larger as the temperature or the photon energy increased [4].

Up to this point, we have neglected possible phonon assisted transitions in the light emission process. If we have a light emission process with one-phonon emission, for example, a replica of the steplike spectra discussed above will be superposed which is shifted to lower energy by just one-phonon energy. Thus the basic shape of the luminescence spectrum will not be altered greatly. However, the weight of each phonon step amplitude may be changed. Rather large values of A_2/A_0 and A_3/A_0 might be ascribed to this effect.

In conclusion, phonon structures are observed in porous Si luminescence and are successfully interpreted in terms of recombination luminescence from the quantum confined indirect band edge. From the coupled phonon energy, it is shown that the luminescent entity has a phonon spectrum very similar to bulk Si. Breakdown of the momentum conservation law is directly shown from the existence of a no-phonon transition. Temperature dependence and the anti-Stokes luminescence at room temperature were qualitatively understood in terms of our model. A more precise model should include contribution of acoustic phonons in the absorption process, anisotropic mass of the electron in the X valley, and the effect of the complicated geometry of the "particles."

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