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SURFACE STATES AND PHOTOLUMINESCENCE FROM POROUS SILICON

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Photoluminescence (PL) spectra of freshly electrochemically etched porous silicon layers anodized under various condition have been measured and analyzed according to quantum confinement (QC) model and surface state models. The results support the combination of QC and surface state models for visible PL from fresh PS layers.

Keywords: POROUS SILICON, PHOTOLUMINESCENCE, QUANTUM CONFINEMENT, SURFACE STATES, RAMAN SCATTERING.

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1. INTRODUCTION

The discovery of visible photoluminescence (PL) at room temperature from electrochemically etched porous silicon (PS) has generated enormous interest in nanocrystalline silicon (nc-Si) for their possible applications in optoelectronic integration [1]. Several techniques have been invented to produce nc-Si films. However, PS has attracted special attention due to its easy processing.

In order to understand the origin of room temperature PL from PS nanostructures, various models have been proposed. It is generally accepted that the quantum confinement effect (QCE) [1-3] in the nanocrystallites opens up the band gap as well as relaxes the selection rules for radiative transitions giving rise to above band gap PL in the visible region for crystallite sizes below ~5 nm [3]. However, QCE alone cannot explain the role of various surface treatments and surrounding media [4, 5]. The participation of the localized surface states [6,7] or defects in the oxide [8] has been suggested to influence PL peak energy and line shape. Theoretical calculations [9] have shown that the surface states indeed exist in the form of self-trapped excitons which are stabilized in smaller crystallites due to band gap widening. The surface distortion and disorder induced surface states are intrinsic to nanocrystallites. Since surface to volume ratio increases as the crystallite size decreases, the influence of surface states on the PL from smaller crystallites will be highly enhanced. Thus, the room temperature PL signal may be generated through more than one recombination mechanism and surface states may play a crucial role.

In this paper, we present analysis room temperature PL spectra from PS nanostructures in the light of recently developed phonological model of PL combining the QCE and effects of surface states.

2. EXPERIMENTAL DETAILS

The thick PS layers fabricated by electrochemical anodization of *p*-Si (100) wafers of 6-10 $\Omega\cdot\text{cm}$ resistivity in a Teflon cell using HF (40 %-48 %) and $\text{C}_2\text{H}_5\text{OH}$ (99.9 %) (1:1 by volume) as electrolyte and a platinum disc as the counter electrode. For a uniform current distribution over the exposed area, an Ohmic back contact of Al film was provided. The wafers were anodized at a current density of about $10 \text{ mA}\cdot\text{cm}^{-2}$ for a wide range of anodization times under ambient light as well as external white light illumination. After PS layer formation, samples were rinsed in deionized water and then in methanol and soaked in propanol for few minutes to minimize the structural damage during drying. In order to remove the moisture and electrolyte residues, PS layers were vacuum dried at an elevated temperature.

Unpolarized Raman and PL spectra were recorded in back scattering configuration at room temperature in a Spex Micro-Raman setup fitted with triplet monochromator. Both Raman and PL were on the same sample spot excited with a 514.5 nm line from Ar⁺ laser source. The Raman intensity was measured with liquid nitrogen cooled charge-coupled-device detector. The PL intensity was measured using a photo multiplier tube which was kept at low temperature (-30°C) for the best response. Care was taken to avoid sample heating due to incident laser beam.

3. RESULTS AND DISCUSSION

Figs. 1 and 2 depict the representative PL spectra from thick and fresh PS samples fabricated under two different conditions. Thick and fresh specimens were chosen to minimize the effects of substrate-induced strains and contaminated native oxide induced surface states. The thicknesses of these two samples labeled NI02 and NI25 were $25 \mu\text{m}$ and $20 \mu\text{m}$ respectively.

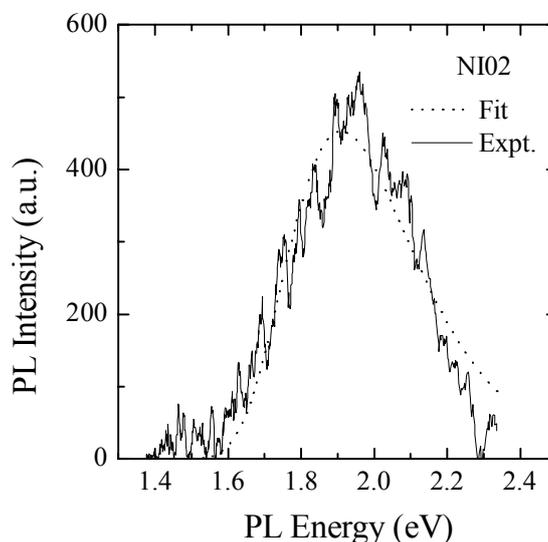


Fig. 1 – PL spectra of fresh PS layer NI02 anodized for 120 min without external light illumination

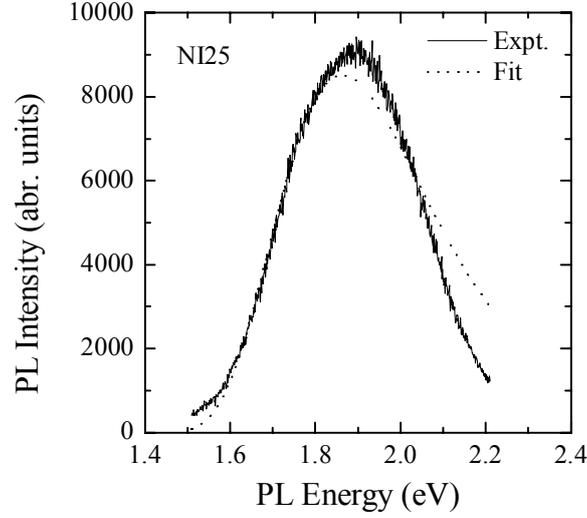


Fig. 2 – PL spectra of fresh PS layer NI25 anodized for 30 min with external light illumination

In order to formulate and describe the PL spectra from nc-Si structures, we consider nc-Si (or PS) as an ensemble of nanometer sized spherical particles having a well defined size distribution. The optical band gap widening in crystallites is due to QCE in nanoparticles. On excitation with high energy photons, photocarriers are generated inside the crystallites and then a fraction of these relax nonradiatively to the surface states. Subsequently, the relaxed carriers recombine to ground states radiatively giving PL. The emitted energy from a nanocrystallite of size L will be lower than the band gap energy of the bulk crystallite by an amount determined by the localized surface state energy E_s and exciton binding energy E_b . The emitted photon energy from a crystallite will then be given as

$$E_{pl}(L) = E_g + \Delta E(L) - E_s(L) - E_b(L), \quad (1a)$$

where ΔE is the amount of band gap upshift due to QCE in the nanocrystallites and E_g is the band gap corresponding to the bulk crystalline material. Rearranging Eq. (1a) Rewriting, band gap upshift is expressed as

$$\Delta E(L) = E_{pl}(L) - \{E_g - E_b(L) - E_s(L)\}. \quad (1b)$$

According to QCE in the nanocrystallite of diameter L , band gap upshift can be modeled as $\Delta E = C / L^n$, where C and n are constants due to QCE.

For a normal distribution of particle sizes in PS, the PL expression is written as

$$I(\Delta E) \propto \frac{(C/\Delta E)^{(6-\alpha+n)/n}}{nC\sigma} \exp \left[-\frac{\left\{ (C/\Delta E)^{1/n} - L_0 \right\}^2}{2\sigma^2} \right], \quad (2)$$

where α is related to the oscillator strength f ($\propto 1/L\alpha$), L_0 is the mean crystallite size, and σ is the standard deviation.

The values of n and C depend on the models employed for the band gap calculations. According to the calculations of Proot et al. [3], these are taken to be $n = 1.39$ and $C = 4.122$ eV (when L_0 is in the units of nm). Following our approach in [10], we take constant values $E_b = 0.07$ eV, $E_s = 0.05$ eV, $E_g = 1.12$ eV, and $\alpha = 3.0$. By putting the values of all constants, Eq.(2) is readily reduced to

$$I(\Delta E) \propto \frac{(4.122/\Delta E)^{3.16}}{\sigma} \exp \left[-\frac{\left\{ (4.122/\Delta E)^{0.72} - L_0 \right\}^2}{2\sigma^2} \right]. \quad (3)$$

Assuming that the PL from our PS samples are due to QC effects in nanocrystallites, the PL spectra were simulated using Eq.(3) with the values of L_0 and σ obtained from micro Raman data using an improved technique[11] based on the phonon confinement model [12]. Raman spectra (not shown here) were recorded from the same spot as the PL spectra under identical conditions. The simulated PL spectra are shown in Fig. 1 and Fig. 2 (dotted lines) along with experimental ones (solid lines). In these simulated PL spectra, the proportionality constant is the only free parameter in Eq.(3). These results exhibit an excellent agreement between the theoretical and the experimental PL spectra obtained from different PS samples prepared under different conditions.

4. CONCLUSION

The quantitative agreement of simulated PL the experimental PL data supports the role of QC models of visible PL from freshly prepared PS layers, and suggests the importance of surface states of crystallites. The band gap widening takes place due to the confinement of electrons within Si skeletons and the radiative recombination of photo-excited carriers occurs via surface states.

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