

Short Communication

Study of Photoluminescence Behaviour of Porous Silicon Samples Prepared at 20 mA Current Density

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The paper presents a study on a series of porous silicon films of various thicknesses, prepared at 20 mA current density using a photoluminescence fitting model to determine the average crystallite size of spherical shaped interconnected silicon quantum dots. Discrepancy in photoluminescence behavior of the samples is well explained with this model.

Keywords: Photoluminescence, Quantum dots, Nanoparticles.

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1. INTRODUCTION

Porous silicon (PS) is considered to be composed either of spherical shaped interconnected silicon quantum dots or combination of quantum dots and columns. During the last decades, there has been a rapid research to introduce porous silicon [1] in optoelectronics and medical field [2]. Every field of applications, require an optimized PS structures under experimental conditions. As PS-based solar cells require thin and highly porous structures [3] and the drug loaded in PS depends on the properties of both the micro particles and the loaded substances [2] therefore, it is the need to study the distribution of crystallites size in a PS system through existing theoretical models. Therefore, the main objectives of present work are to determine the average diameter of the crystallites from extend of the photoluminescence (PL) spectra broadening and to verify the results and prediction of Islam-Kumar model, explaining the shape of the PL spectra.

As PL signal of PS at room temperature is a recombination process of different radiative channels, two of them are dominant and size dependent; the excitonic transitions for the crystallite size range of 4-2.5 nm [4] and phonon assisted transition [5]. The phonon assisted transition dominates radiative recombination of excitons for crystallite greater than about 2 nm. The cause of such channels has been recognized in the form of surface states which arise due to natural oxidation or by surface passivation.

2. EXPERIMENTAL

Present series of PS samples in table 1 were fabricated from (100) oriented single side polished boron-doped silicon wafers (thickness 600-650 μm), with a resistivity ranging from 0.8 to 1.2 ohm-cm. An aluminium back contact was deposited with a vacuum coating machine. Nano-PS layers of different thicknesses were prepared by a computer (interface) controlled electro-

chemical etching (anodization time was varied) of the front side of the silicon wafer at fixed 20 mA current density in a solution consisting of a mixture of hydrofluoric acid (HF 48%) and pure ethanol (volume proportion HF:CH₃COOH; with a volumetric ratio of 1:1). As-prepared samples were cintered at 550°C in nitrogen environment; in order to avoid evolution of the PS structure in the presence of oxygen. Thickness of the samples were determined by scanning electron microscope (SEM). The PL spectra were monitored using a FLSP920 Phosphorescence lifetime spectrometer setup. A 300 nm line of a continuous Ar⁺ laser of power 4 Wcm⁻² was used as an excitation source. The PL spectra were measured after stabilization of the PL intensity, where no evolution of the PL peak energy with time was observed.

Table 1 – Optimized fitting parameters

Sample	PL Peak (eV)	Mean crystallite (nm)	Variation (nm)	Confinement energy (eV)	FWHM (eV)	Oscillator Strength (α)
PS1	1.83	3.16	0.25	0.83	0.59	3
PS2	1.91	2.96	0.23	0.91	0.55	3
PS3	1.88	3.03	0.24	0.88	0.56	3
PS4	1.88	3.04	0.27	0.88	0.63	4
PS5	1.89	3.02	0.27	0.89	0.63	3

Variation = Variance, Confinement = confinement, Oscillator Strength = Oscillator Strength

3. RESULTS AND DISCUSSION

An analytical expression [6], explicitly included the surface states for low crystallite sizes with the quantum confinement effect, which assumed an ensemble of nanometer sized spherical particles having a well-defined size distribution. A quantitative agreement of this application model with the experimental PL data

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is depended on the exactness of average size and its dispersion, exciton binding energy (E_b), on the models or band gap and oscillator strength calculations. This model proposed the equation for PL energy with the explicitly inclusion of an amount of localization of energy (E_s) of surface states. Therefore, the PL energy is given by

$$\hbar\omega = E_g + \Delta E_0 - (E_b + E_s), \quad (1)$$

where the confinement (energy up shift) associated with a wire of width d is given by

$$\Delta E_0 = \frac{c}{d^2}$$

Thus, the emitted photon energy from a nanocrystallite is lower than the band gap energy of the crystallite by an amount of localization energy E_s of the surface states and the exciton binding energy E_b . Both, in general, are functions of crystallite size.

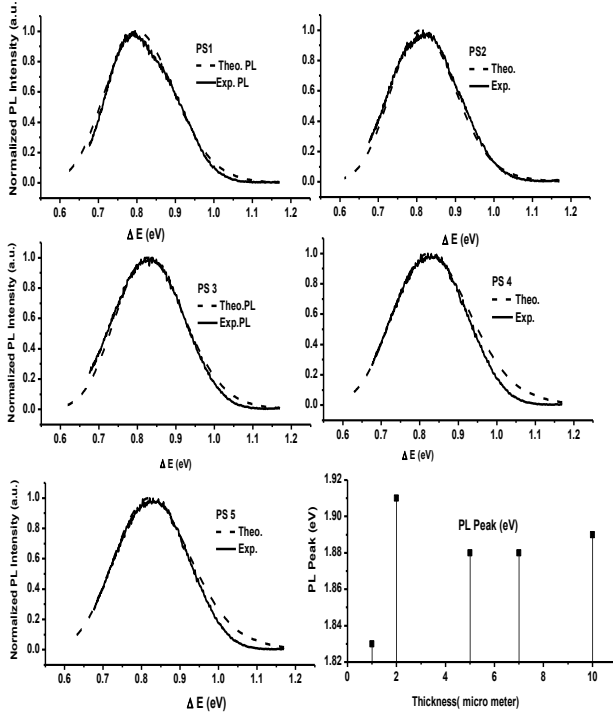


Fig. 1 – Comparison of the experimental (—) and the theoretical (- -) PL spectra for the samples PS1, PS2, PS3, PS4 and PS5 respectively as well as the PL peak variation with thickness of each sample

Therefore, emitted photon energy from a crystallite is given as

$$E_{pl} = E_g + \Delta E - E_s - E_b \quad (2)$$

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. With a log-normal distribution the expression for PL intensity transforms to

$$I(\Delta E) \propto \frac{(c/\Delta E)^{5-\alpha+n/n}}{\sigma n c} \exp \left[\frac{\left\{ \ln(c/\Delta E)^{1/n} - \ln(L_0) \right\}^2}{2\sigma^2} \right] \quad (3)$$

The value of band gap i.e. $E_g = 1.12$ eV for c-Si was taken at room temperature. The constant value of $E_b = 0.07$ eV was taken over the mean crystallite size ranging from 2.5-4.0 nm and surface localization energy E_s was the order of optical phonon energy of 0.05 eV. In Eq. (2.3) the value of n was taken 1.39 and c has the value 4.122 eV (when d_0 is in units of nm) calculated [7] (to retain the constraints imposed by model used). The comparison of the experimental and theoretical PL spectra for the samples PS1, PS2, PS3, PS4 and PS5 respectively is shown in figure 1. The fitting parameter obtained from PL model used (table 1) explains the same discrepancy. As the sample PS2 has maximum confinement energy (0.91) and lowest mean crystallite size (2.96 nm) with oscillator strength of 3, the reason for its shift at highest energy place is due to its lowest full width half maximum (FWHM) = 0.55 eV and lowest variance (0.23) among samples. Generally, the decrease in crystallite size results in increase of the FWHM of PL curve but if the decrease in mean crystallite is followed by a decrease in the disorder (lowest variance) as well, it results in decrease of width of experimental PL. It supports the relevant explanation for shift of sample PS2. Further, the position of peaks of sample PS3 and PS4 at same energy (1.88 eV) is understood in terms of oscillator strength of samples. However, PL fitting data in table 1 shows that sample PS4 has greater value of mean crystallite (3.04 nm) and variance (0.27 eV) as compared to sample PS3, it is supposed to show red shift but it lies at same peak position as that of sample PS3. The reason for it lies in higher value of oscillator strength of 4 because as the oscillator strength increases, it causes blue shift [6]. The anomalous behavior of PL of PS sample could be explained on the basis of observations obtained from the model.

4. CONCLUSION

Statistical study made on systematic series of samples establish the significance of theoretical models to study PL behaviour which is helpful for optimization of parameters to achieve desired PS for template and device purpose as well as to develop better model explaining the behaviour of samples prepared at particular conditions.

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