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Photoluminescence spectroscopy in nanocrystallinesillcon-silicon dioxide super lattices

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ABSTRACT

In the present paper, a strong interest in the optical properties of Si nanocrystals has been stimulated, at high-efficiency, room-temperature photoluminescence (PL) in porous Si, and by the PL origin. The main aim of this research paper is to compare PL properties in nc-Si/a-SiO_2 super lattices with similar data obtained in other materials containing Si nanocrystals (porous Si, Si nanocrystals prepared by CVD, ion implantation, etc.), and a correlation has been established between Si nanocrystal structure (i.e., size, shape and crystallographic orientation) and light-emitting properties.

Key words: Nanocrystal, Photoluminescence and Si/a-SiO_2.

INTRODUCTION

Since the beginning of these studies, it was obvious that, the relatively large size (> 20nm) of Si nanocrystals of well defined, brick-like shape and <111> crystallographic orientation, and should continue toward much smaller, but less controlled in shape, Si nanograins. This research strategy provides a unique opportunity to observe the transformation of phonon-assisted carrier recombination controlled by well-understood selection rules to a much less ordered process where phonons are still involved in carrier recombination but all selection rules are significantly relaxed. [1-6].

The Theoretical Ideology

A set of narrow PL lines in a bulk Si sample with the dominant TO-phonon line practically does not move, but broadens and slightly changes the ratio between TO-, TA-, and second TO- phonon lines in Si nanocrystals with sizes down to 8.6 nm in vertical dimension. Continuing to decrease the Si nanocrystal size down to ~ 6 nm, we observe a blue (toward higher photon energy) shift in the PL peak (which is at ~ 1.32 eV) and significant broadening up to ~ 100 meV in the PL full width at half maximum (FWHM). The phonon involvement can be recognized by the much less pronounced but still observable structure, with the main PL peak separated by ~ 60 meV (TO-phonon) from a shoulder at lower photon energy (Fig. 1). Further decrease in Si nanocrystal size down to 4.2 nm results in a shift of the PL peak to 1.4 eV and an almost 200 meV FWHM. This PL looks quite different compared to PL from bulk Si and at the same time, is similar to PL spectra observed in porous Si and Si nanocrystals prepared by ion-implantation]. The dependence of the PL peak position and FWHM as a function of Si nanocrystal size is summarized in [Figure 2], showing a clear correlation between the PL broadening and PL peak

blue shift. Note that the PL peak in smaller Si nanocrystals shifts to higher photon energy in a just slightly super linear fashion, but the PH FWHM increases exponentially as the Si nanocrystal size decrease. To our surprise, we have found that the observed selection rule relaxation in PL from small Si nanocrystals is very similar to the conclusions that we were able to draw out of Raman studies.

Methodology

The origin of the broad PL bank, we concentrate on two major possibilities. During more than a decade of searching for a convincing experiment on the origin of a broad and featureless PL in Si nanocrystals, the technique of resonant PL excitation has been widely recognized as the most useful one.

The PL has been linked to carrier recombination is Si nanocrystals due to a clear indication of the phonon- assisted PL mechanism and the observation of structure in PL spectra where almost all characteristic Si phonons and their combinations are found. In addition, resonant PL excitation may require phonon absorption due to the indirect nature of optional transitions in Si nanocrystals. These measurements have been described Si nano crystals. In the case of nc-Si/a-SiO_2 super lattices, an additional contribution to the in homogeneous broadening is, most likely, coming from the previously mentioned uncertainties in the shape and crystallographic orientation of small-size Si nanocrystals. This is particularly important for Si due to its indirect ban structure and strong dispersion in the effective mass along different crystallographic directions.

Technically, the experiment requires a source of tunable excitation, which is usually a tunable laser (e.g., Ti : Al_2O_3, etc.) because the desired condition is to bring the excitation wavelength as close as possible to the PL line. This is demonstrated in Fig. 18a, where a decrease of the excitation photon energy from 1.66 to 1.42 eV depicts a step-like structure more clearly. [Figure 3] shows a higher resolution PL spectrum under resonant excitation and contributions for specific Si phonons and their combination are indicated.

However, the fact that the PL lifetime has strong temperature dependence (Fig. 4) indicates that at least two competing recombination mechanism (most likely radiative and non-radiatie) may contribute to the overall PL signal. Interestingly, the PL kinetics look single exponential compared to the more complex, usually stretched.

Exponential behavior reported in Si nanocrystals prepared by other techniques [7]. Another indication that the PL may have a more complex rather than single origin comes from the data in Gig. 5, where we compare PL spectra in a nc-Si super lattice with an average Si nanocrystal size of ~ 4.2 nm. At low excitation power (0.05 W/cm^2), the PL peak is at ~ 1.4 eV but with the increase of the excitation up to 10 W/cm^2, the PL spectrum broadens and the PL peak shifts to > 1.7 eV. The observed broadening and the PL spectra has triggered a search for another technique that is able to separate different possible contributions to luminescence in nc-Si super lattices.

RESULTS

The most interesting results with a very clear interpretation have been found in studies of the PL spectral response as a function of external magnetic and electric fields. Since the initial report that an external magnetic field increases the gap between singlet and triplet states in Si nanocrystals, the fact that the PL lifetime increases and intensity decreases in Si nanocrystals. However, our studies show that in nc-Si super lattices this PL quenching

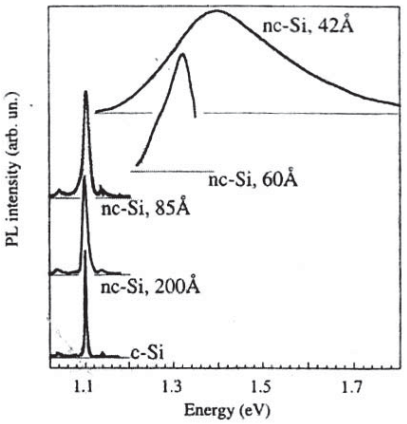

Fig. 1: PL spectra from samples of nc-Si/a-SiO_2 superlattices with different (indicated) sizes of Si nanocrystals

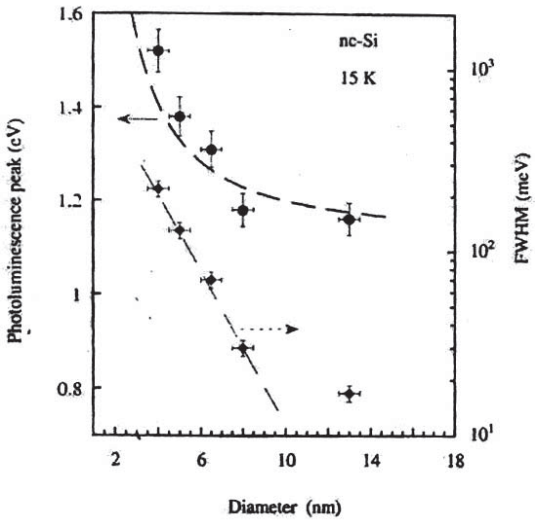

Fig. 2: The PL peak and full width of half maximum as a function of Si nanocrystal size

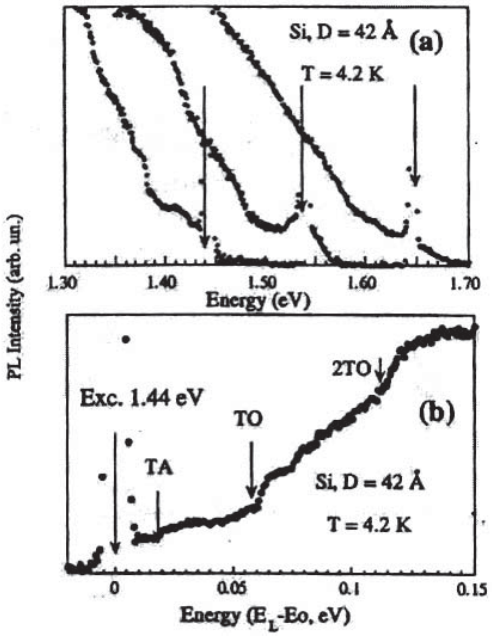

Fig. 3: (a) An example of resonantly exited PL specstra in nc-Si/a-SiO_2 superlattice with 42A diameter of Si nanocrystal showing better resolved PL structure as the excitation photon enerty decreases. (b) A high resolution resonantly excited PL spectrum with indicated energies of characteristi Si phonon

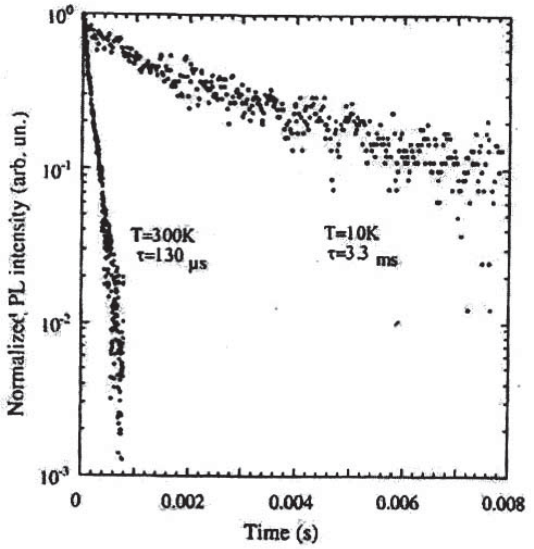

Fig. 4: PL decay in fully crystallized nc-Si/a-SiO_2 superlattice with 42A diameter Si nanocrystals showing a single exponential decay and strong PL lifetime temperature dependence

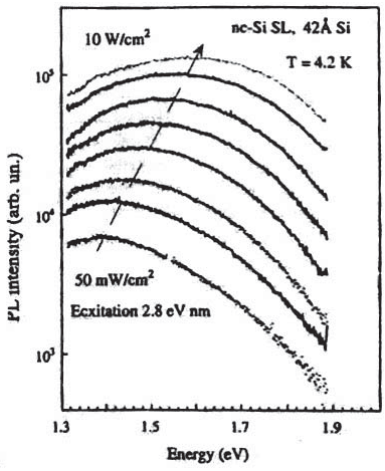

Fig. 5: PL spectra in nc-Si/a-SiO_2 superlattice with 42A diameter Si nanocrystals under different intensity of excitation

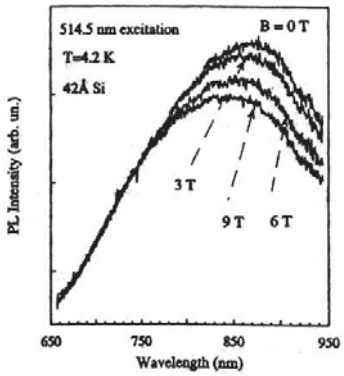

Fig. 6: PL spectra in nc-Si/a-SiO_2 superlattice with 42A diameter Si nanocrystals under magnetic field of different intensities. A selective quench of PL intensity is clearly shown

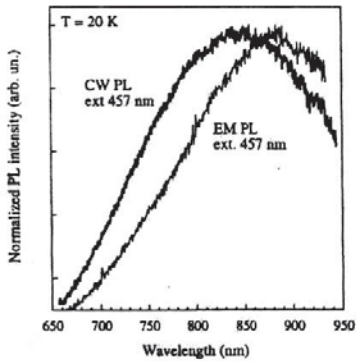

Fig. 7: Strong red shift of the electric field modulated (EM) PL spectrum in 20 period nc-Si/a-SiO_2 superlattice with 42A diameter Si nanocrystals measured using a lock-in amplifier and ac voltage of 15v

is selective and affects only PL at wavelengths longer than ~ 750 nm. The PL intensity at shorter wavelength does not show any quenching under an applied magnetic field as high as 9 T, as shown in (Fig. 6). The observed that the PL origin is more complex than just a single mechanism based on the quantum confinement effect in Si nanocrystals.

CONCLUSION

The present study describes PL dependence as a function of the applied electric field in nc-Si/a-SiO_2 super lattices. Our technique is based on the application of an AC electric field and detection of a modulated PL component using a lock-in amplifier. The technique is more sensitive compare to the standard technique where CW PL is influenced by an applied DC electric field. We have found that an electric field dependent PL spectral component is strongly correlated with magneto PL measurements: the modulated PL component is red-shifted compared to CW PL at zero electric field, and the electric field modulates only the PL at wavelengths longer than 750 nm. [Fig.7]. This data is in complete agreement with the magneto-PL measurements. Therefore, we can conclude that a portion of the PL in nc-Si super lattices at shorter wavelengths does not depend on electric or magnetic field and most likely has a different origin than PL associated with confined exact in Si nanocrystals.

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