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# Photoluminescence from impurity codoped and compensated Si nanocrystals

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Photoluminescence (PL) properties of B and P codoped and compensated Si nanocrystals were studied. The compensation of carriers in nanocrystals was confirmed by the annihilation of confined-carrier optical absorption in the infrared region. In the PL spectra obtained under the resonant excitation condition, the codoped samples did not exhibit structures related to momentum-conserving phonons, which were clearly observed for pure Si nanocrystals. The result strongly suggests that in impurity codoped Si nanocrystals, nonphonon quasidirect optical transition is the dominant recombination path for electron-hole pairs, and thus impurity codoping is a possible approach to further improving PL efficiency of Si nanocrystals. © 2005 American Institute of Physics. [DOI: 10.1063/1.2135214]

It has been recently demonstrated that photoluminescence (PL) properties of Si nanocrystals (Si-nc's) can be drastically modified by impurity doping.<sup>1-3</sup> The doping of either *n*- or *p*-type impurities results in the quenching of the PL because of the efficient Auger interaction between photo-excited electron-hole pairs and carriers supplied by the doping.<sup>3-7</sup> The PL quenching by impurity doping is effectively suppressed when *n*- and *p*-type impurities are doped simultaneously<sup>2,3</sup> due probably to the compensation of carriers in nanocrystals. The codoped Si-nc's exhibit room-temperature PL at the energy lower than that of the bulk Si band gap ( $\sim 0.9$  eV).<sup>2</sup> Therefore, by properly controlling impurities in Si-nc's together with the size, the tunable range of the PL energy of Si-nc's can be largely extended without losing much of the intensity.

Another advantage of impurity doping is that it localizes carriers further and increases the probability of nonphonon quasidirect recombination of electron-hole pairs, and thus the radiative recombination rate. Therefore, impurity doping is useful even in the energy range where pure Si-nc's can cover. In fact, in the previous work on Si-nc's doped into SiO<sub>2</sub> or borophosphosilicate glasses (BPSG), we observed the enhancement of PL intensity by P and B codoping compared to that of pure Si-nc's emitting at almost the same energy.<sup>3</sup>

If PL from the samples containing impurity codoped Si-nc's appears below the bulk Si band gap, it is clear that impurity states are involved in the luminescence process. On the other hand, if the PL appears above the bulk band gap, it cannot easily be distinguished whether the PL arises from impurity doped Si-nc's or those that remain undoped because of the statistical fluctuation of impurity concentration.

The purpose of this paper is to study PL properties of P and B codoped Si-nc's assemblies having the PL maximum above the band-gap energy of bulk Si crystals and demonstrate that the mechanism of the PL is different from that of pure Si-nc's. We will show that under resonant PL excitation condition, impurity codoped samples exhibit quite different PL spectra from those of pure Si-nc's. The result suggests

that quasidirect nonphonon optical transition is dominant in impurity-doped samples.

The samples studied were Si-nc's embedded in glass matrices prepared by a cosputtering method. Details of the preparation procedure are given in our previous paper.<sup>3</sup> PL spectra were measured using a single monochromator equipped with a liquid N<sub>2</sub> cooled InGaAs near-infrared diode array. The spectral response of the detection system was calibrated with the aid of a reference spectrum of a standard tungsten lamp. The wavelength of excitation light for conventional PL measurements was 532 nm [frequency-doubled cw Nd:yttrium vanadium oxygen (YVO) laser] and for resonant PL measurements it was changed from 700 to 1000 nm (cw Ti:Sapphire laser). The excitation light was loosely focused on the samples (spot size  $\sim 2$  mm) to avoid heating. For the resonant PL measurements, to suppress the laser light, the asynchronous mechanical chopping technique was applied.<sup>8</sup> The samples were mounted in a continuous-flow He cryostat and kept at 5 K.

First we will show the evidence that impurities are doped into substitutional sites of Si-nc's and are electrically active. Figure 1(a) shows the infrared absorption spectra of P and B doped Si-nc's. For the P-doped sample (without B doping), we can see the rising of the absorption coefficient to both the shorter and longer wavelengths. The absorption at the short wavelength side is due to the valence to conduction band transition of electrons, while that at the long wavelength side is due to the intra-conduction-band transitions of electrons supplied by P doping, i.e., free (or in this case "confined") carrier absorption.<sup>9</sup> By keeping the P concentration the same and increasing the B concentration, the absorption becomes weaker, indicating that carriers are compensated in nanocrystals by simultaneously doping P and B. By further increasing the B concentration, the absorption reaches minimum and again increases. This time the absorption is due to the intra-valence-band transitions of holes supplied by excess B. In Fig. 1(b), the absorption coefficient at 2.5  $\mu$ m and the PL intensity of the same samples are plotted as a function of B concentration. We can clearly see that the PL intensity is the largest when the confined carrier absorption is the weakest. The result demonstrates that the exact

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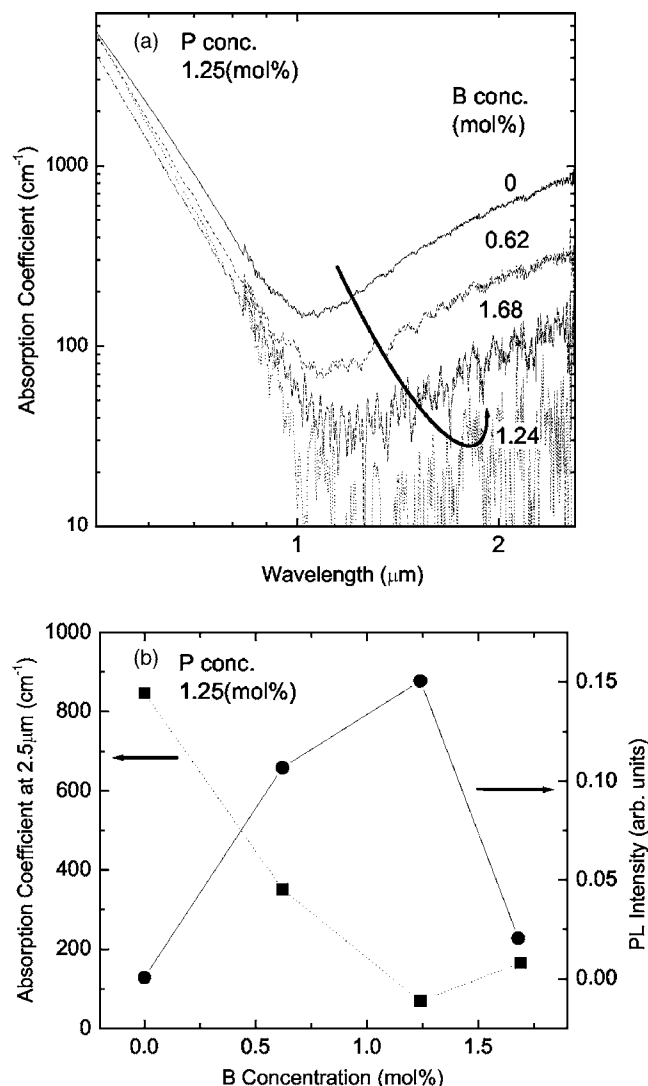


FIG. 1. (a) Infrared absorption spectra of P and B codoped samples. The P concentration is fixed to be 1.25 mol %, while the B concentration is changed from 0 to 1.68 mol %. (b) The absorption coefficient at 2.5  $\mu\text{m}$  (left axis) and the PL intensity (right axis) are plotted as a function of B concentration. P concentration is fixed to be 1.25 mol %.

compensation of carriers is crucial to achieve maximum PL intensity.<sup>3</sup>

Figure 2 shows the PL spectra at 5 K of pure [Fig. 2(a)], B-doped [Fig. 2(b)], P-doped [Fig. 2(c)], and B and P codoped [Fig. 2(d)] samples. The excitation power is changed from 0.7 mW to 1.43 W. The spectra are normalized at the maximum of the higher energy band to compare the shape. It is worth noting that PL intensities of either B- or P-doped samples are much smaller than those of pure and codoped samples because of the Auger effect. In the case of pure Si-nc's, with increasing the excitation power, the defect-related PL at around 0.9 eV grows significantly. The different excitation power dependence of the two bands arises from the difference in the lifetime; the lifetime of the exciton PL at low temperatures is very long ( $\sim 5$  ms) and it saturates easily at relatively low excitation power, while that of the defect-related PL is of the order of microseconds or less, and thus it grows in proportion to the excitation power. The lifetime of the exciton PL also depends on the size and is longer for larger Si-nc's, resulting in easier saturation of the intensity at the low-energy side of the exciton PL band. This size

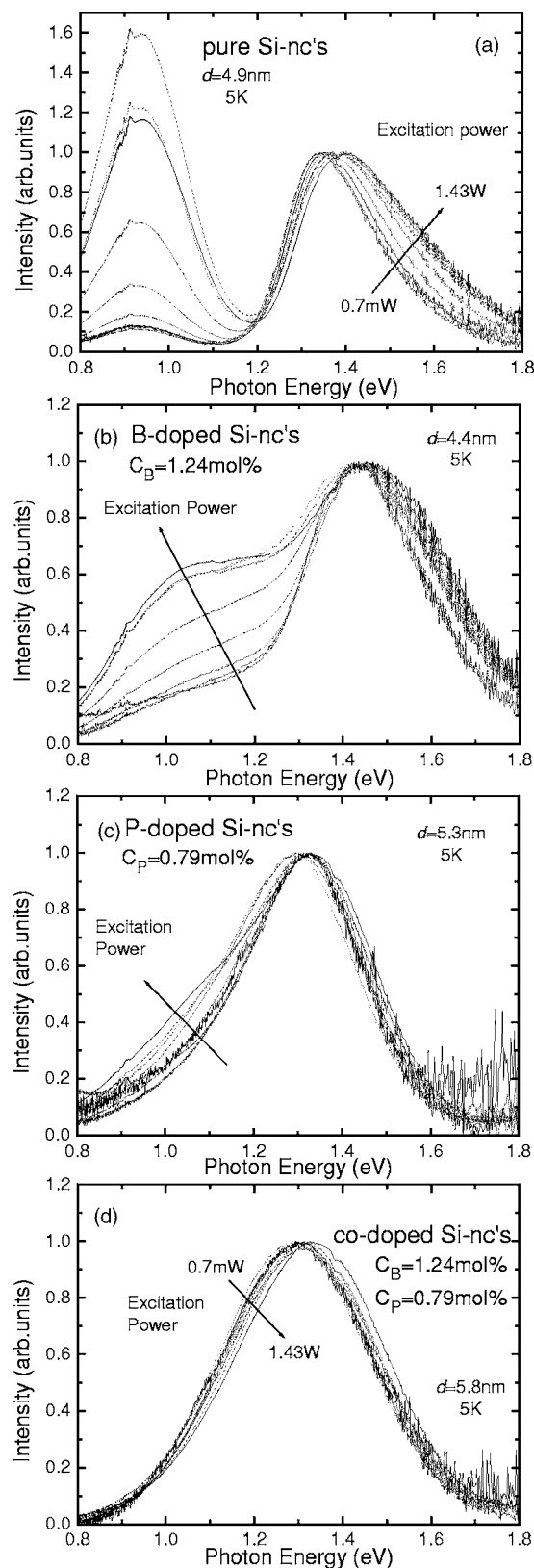


FIG. 2. Excitation power dependence of the PL spectra at 5 K for (a) pure, (b) B-doped, (c) P-doped, and (d) B and P codoped Si nanocrystals. The excitation power is changed from 0.7 mW to 1.43 W.

dependence of the lifetime results in the high-energy shift of the exciton PL with increasing the excitation power. In the present case, it shifts about 100 meV by changing the excitation power from 0.7 mW to 1.43 W.

Compared to pure Si-nc's, impurity-doped Si-nc's are less sensitive to the excitation power. In B-doped samples,

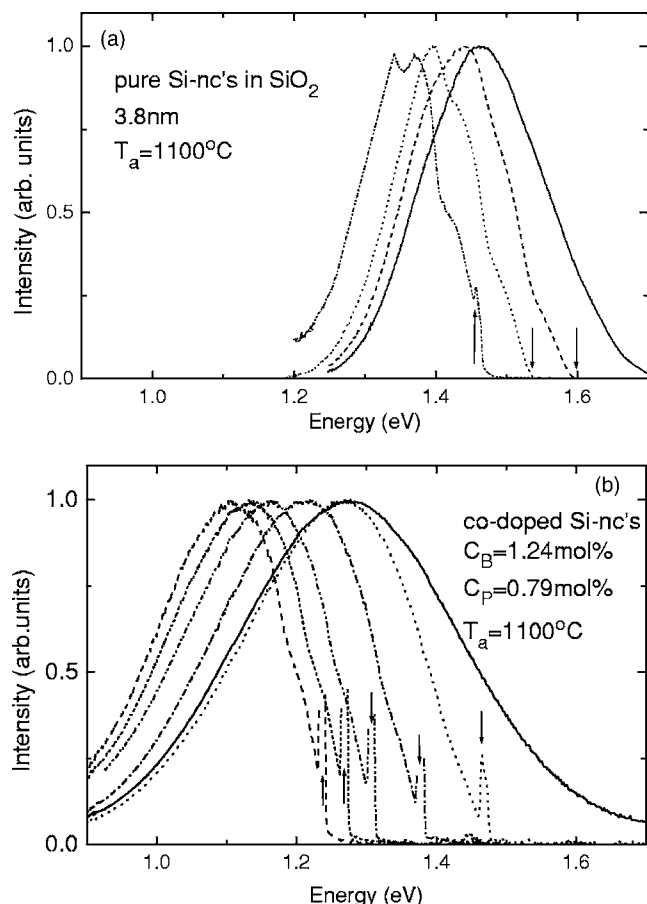


FIG. 3. Normalized resonant PL spectra of (a) pure and (b) B and P codoped Si-nc's at 5 K. Excitation energies are indicated by arrows.

the low-energy band is broader and weaker than that of pure Si-nc's, and also the excitation power dependence of the high energy band is smaller. In the P-doped sample, the low-energy band almost disappears.<sup>1</sup> The excitation power dependence of the spectral shape is the smallest for the codoped sample and is almost unaffected by the excitation power. Figure 2 strongly suggests that in impurity-codoped samples, the PL arises not from Si-nc's remaining undoped but from those really doped with B and P, and the mechanism of the PL is different from that of pure Si-nc's.

To demonstrate more clearly that the mechanism of PL is different between pure and codoped Si-nc's, we measured PL under resonant excitation condition. The essence of this technique is the size selectivity of the optical excitation.<sup>8</sup> In pure Si-nc's, the low-energy part of the PL band is governed by the emission coming from larger nanocrystals. When the energy of the exciting laser light is chosen to fall inside the low energy part of the PL band, only a very small subset of nanocrystals having band gaps below the laser energy is probed. Figure 3(a) shows the normalized resonant PL spectra of pure Si-nc's at different excitation energies. The energy positions of the exciting light are shown by arrows. When the excitation energy is moved down and into the band of the conventional PL spectrum, distinct features appear in the spectra. This PL feature becomes more pronounced when the excitation energy is at the low-energy tail of the PL band.

From the energy separation of these PL features they can be assigned to the optical transitions involving 1TA, 1TO, TO + TA, and 2TO momentum-conserving phonons in the absorption/emission cycle. The observation of these features is the direct evidence that pure Si-nc's strongly inherit the indirect band-gap nature of bulk Si crystals.<sup>8</sup>

Figure 3(b) shows the resonant PL spectra of B- and P-codoped Si-nc's. In contrast to pure Si-nc's, the spectra are featureless even when the excitation energy is below the maximum of the band of the conventional PL spectrum (solid curve), although the spectra become narrower with a decrease in the excitation energy. The absence of the phonon structures is the strong indication that in codoped Si-nc's electrons and holes recombine directly without the participation of momentum conserving phonons.

In Fig. 3, the maxima of the PL bands when excited nonresonantly (solid curves) are different between the pure and codoped samples. The PL maximum of the pure sample can be brought to lower energy by higher temperature annealing.<sup>10</sup> The higher temperature annealing usually results in more distinct phonon features under the resonant excitation condition. Therefore, to make the comparison fair, in Fig. 3 we fixed the annealing temperature to be 1100 °C. If we chose a set of samples having the PL maximum at almost an identical energy prepared by applying different annealing temperatures between pure and codoped samples, the difference in the spectral shape under resonant excitation will be more pronounced.

In conclusion, we demonstrated that by simultaneously doping *n*- and *p*-type impurities in Si-nc's, we can change the indirect band-gap nature of pure Si-nc's to direct ones without losing the intensity. This approach may further improve the luminescence efficiency of Si-nc's as well as extend the tunable range of the luminescence energy. However, to make the benefit of this effect maximum, carriers in all nanocrystals in a sample should be compensated. Technological development to realize this condition is strongly demanded.

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