Control of photoluminescence properties of Si nanocrystals by simultaneously doping *n*- and *p*-type impurities

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The effects of B and P codoping on photoluminescence (PL) properties of Si nanocrystals (nc-Si) are studied systematically. It is shown that the PL intensity of codoped nc-Si is always higher than that of either P- or B-doped nc-Si. The intensity is sometimes even higher than that of pure nc-Si at relatively low P and B concentrations and low annealing temperatures. By doping P and B simultaneously to very high concentrations, the PL peak shifts below the band gap of bulk Si. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1779955]

Si nanocrystals (nc-Si) show strong luminescence in the visible range.[1–7] The luminescence is considered to arise from the recombination of excitons across the widened band gap of nc-Si. The luminescence energy is controlled from the bulk band gap to visible range by size.[5,7] The range can be extended below the bulk band gap by properly controlling impurities in nc-Si;[8] by doping P and B simultaneously, photoluminescence (PL) appears at around 0.9 eV at room temperature. The low-energy luminescence is probably due to donor to acceptor transitions. The near-infrared (NIR) luminescence at room temperature may open up applications of nc-Si-based materials in the optical telecommunication field, because silica-based fiber telecommunications utilize light in the wavelength range of to 1.3 to 1.6 μm.

The largest problem of shallow impurity doping in nc-Si is that it is accompanied by the radiationless Auger recombination, in which the energy released by the recombination of an exciton is consumed by giving kinetic energy to an electron (hole) supplied by doping.[9–14] The Auger recombination could be avoided if isoelectronic impurities are doped or carriers in nc-Si are perfectly compensated by simultaneously doping *n*- and *p*-type impurities.

In nc-Si, an exciton is confined in a space comparable to or smaller than the Bohr radius, and the wave function of the exciton as well as shallow impurities are extended in a whole nanocrystal. If for example one P atom and one B atom are doped simultaneously in a nanocrystal a few nanometer in diameter, it could be treated as a perfectly compensated single system with no excess carriers, and thus the exciton could enjoy the enhancement of oscillator strength due to further localization by impurity doping without being afraid of the Auger recombination. Therefore, impurity control of nc-Si may add optical properties on nc-Si which cannot be realized by pure nc-Si, and thus is worth studying in detail.

The above model is qualitatively supported by our previous observation that the simultaneous doping of *n*- and *p*-type impurities in nc-Si recovers the very low PL intensity of either *n*- or *p*-type impurity-doped nc-Si.[8] However, systematic studies on the relation between PL properties and the concentration and valance of *n*- and *p*-type impurities have not been made so far. In this work, we have prepared B- and/or P-doped nc-Si embedded in glass matrices by controlling the B and P concentrations in a wide range, and studied the PL properties.

The samples studied were nc-Si embedded in glass matrices prepared by a cosputtering method. A multitarget sputtering system was used. Four 2 in. sputtering guns with Si (No. 1), SiO_2 (No. 2), a mixture of P_2O_5 and SiO_2 (5:95 by wt. %) (phosphosilicate glass) (No. 3), and a mixture of B_2O_3 and SiO_2 (5:95 by wt. %) (borosilicate glass) (No. 4) targets were operated simultaneously. The sputtering rate of each gun was controlled by a rf power. To keep excess Si concentration, which is a major factor to determine the size of nc-Si, nearly the same for all the samples, the rf power of the Si sputtering gun was fixed to 20 W, while the sum of the powers of other three guns was set to 240 W. For example, for the sample with the maximum P and B concentration, the powers of the gun Nos. 3 and 4 were set to 120 W and No. 2 to 0 W, while for the sample with maximum P concentration without B doping, those of gun Nos. 2 and 3 to 120 W and No. 4 to 0 W. The thickness of the film was fixed to be about 1 μm for all samples. After depositing the mixture films, a cap layer of pure SiO_2 (100 nm) was deposited. The samples were then annealed in a N_2 gas (99.999%) atmosphere for 30 min at temperatures ranging from 1100 °C to 1250 °C to grow nc-Si.

The evidence that impurities are doped into substitutional sites of nc-Si and are electrically active was obtained by the observation of the free-carrier absorption, i.e., intraconduction (valence)-band transitions of electrons (holes), in infrared absorption spectra[13] and by electron spin resonance (ESR) spectroscopy.[14] Unfortunately, the number of active dopants or excess carriers in each nanocrystal cannot simply be estimated from the average P or B concentrations in a whole film. However, it is clear that the number is very small and is changed digitally even when the impurity concentration is very high, e.g., an impurity concentration of 1×10^{20} cm^{-3} corresponds to in average 1.4 impurities per a nanocrystal 3 nm in diameter.

In Figs. 1(a)–1(d), PL spectra of pure, B-doped, P-doped, and P and B codoped nc-Si are compared. The average impurity concentration in a whole film is written in each figure. The annealing temperature is changed from 1100 °C to 1250 °C. All spectra are taken with the same condition. The intensity can thus be compared to each other. The vertical axis is a logarithmic scale. Figure 1(a) shows PL spectra of pure nc-Si. We can see that higher-temperature annealing results in a lower-energy shift of the peak because of the increase of nc-Si size.[7] The peak stays always above the band gap of bulk Si crystals, although a weak tail, probably originating from disorder at the surface of nc-Si, pen-

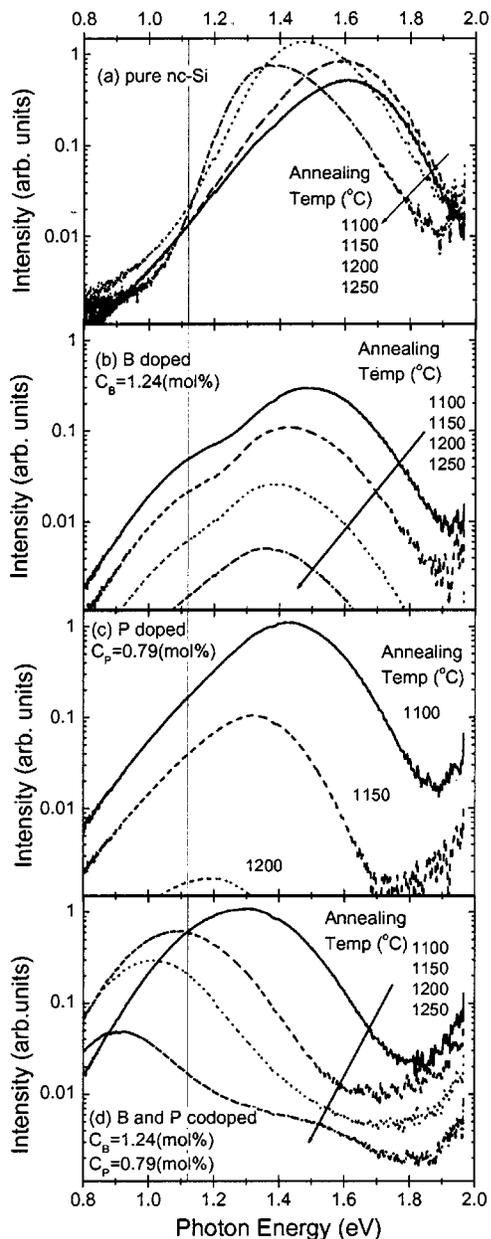a)Electronic mail: fujii@eedept.kobe-u.ac.jp

FIG. 1. Annealing temperature dependence of (a) pure nc-Si, (b) B-doped nc-Si, (c) P-doped nc-Si, and (d) B- and P-codoped nc-Si. All spectra are taken at the same condition. A vertical line is drawn at the band-gap energy of bulk Si crystals (1.12 eV).

etrates below the bulk band gap. In the present annealing temperature range, PL intensity does not strongly depend on the temperature.

The situation is changed if either P or B is heavily doped. The spectra become broader and the low-energy tail grows. In both cases, the intensity drops, especially at higher annealing temperature. The intensity of the P-doped samples is more sensitive to the annealing temperature; by 1250 °C annealing, the P-doped sample does not show any luminescence. The strong suppression of PL intensity is considered to be due to the Auger recombination of excitons with the interaction of electrons or holes supplied by doping. The suppression becomes more significant at a higher annealing temperature, because of a larger size of nc-Si and resultant higher probability of containing electrically active impurities in nc-Si. The different degree of PL quenching between B- and P-doped samples may come from different solid solubil-

ity in Si.[15] The spectral shape is also slightly different between the two kinds of dopants. The spectra of the B-doped samples consist of two broad bands, while those of the P-doped samples are composed of a single band. It should be stressed here that although higher annealing temperature brings the PL peaks to a lower energy, the PL maximum is always above the bulk band gap.

The PL properties of B- and P-codoped nc-Si is qualitatively different from those of either B- or P-doped nc-Si. PL peak energy shifts significantly to lower energy and crosses the bulk band gap. Furthermore, suppression of PL intensity by high-temperature annealing is smaller in spite of the fact that the total number of dopants is nearly twice as that of B- or P-doped samples in Figs. 1(b) and 1(c).The result demonstrates that the PL property of nc-Si can be modified without losing the intensity so much by carefully controlling the amount of simultaneously doped n- and p-type impurities.

Figure 2 shows contour plots of the PL peak energy [Figs. 2(a)–2(d)] and intensity [Figs. 2(e)–2(h)] as a function of B and P concentration. The B concentration was changed from 0 to 1.24 mol % and P from 0 to 0.79 mol %. In total, the data of 16 samples with different P and B concentrations are plotted in each figure after a smoothing procedure. Annealing temperatures are changed from 1100 °C to 1250 °C. We can see that the PL peak tends to shift to lower energy by higher-temperature annealing regardless of impurity concentration. Within the same annealing temperature, higher impurity concentration results in a lower peak energy. It is noted that codoped samples exhibit PL peaks at energies lower than either B- or P-doped ones even if the total amount of impurities is the same, indicating that the energy is determined by the valance of n- and p-type impurities as well as the total amount.

The PL intensity also depends strongly on the valance of impurities. In Figs. 2(e)–2(h), we can see a ridge of the intensity along the white line, where the average concentration of B and P in a whole film is the same; if we fix the total amount of impurities the same the intensity is the highest when the amounts of n- and p-type impurities are nearly the same. This behavior can clearly be seen if we look along the black lines in Figs. 2(e)–2(h), where the sum of C_B and C_P is fixed to 0.8 mol %. The observation of the ridge is the direct evidence that impurity compensation works in nc-Si, and is a very important factor to determine the PL intensity. For the samples containing nearly the same amount of B and P, the number of perfectly compensated nc-Sis is larger than others, resulting in the ridge in Figs. 2(e)–2(h).

In Figs. 2(h) and 2(g), if we look along the white line, the intensity first increases, reaches maximum at the B and P concentrations of 0.2–0.4 mol %, and then decreases. This means that the PL intensity of properly impurity controlled nc-Si samples can be larger than that of pure nc-Si samples. Two different routes have to be considered as the origin of the intensity enhancement. The first one is the improvement of PL quantum efficiency of an individual nanocrystal because of the shorter radiative lifetime of an exciton trapped at a donor–acceptor pair than a free exciton.[8] The other one is that number of optically active, i.e., defect free, nanocrystals increases by doping.

After crossing the maximum intensity point, the PL intensity decreases along the ridge. This declining of the PL intensity may be explained by the increase in the number of doped impurities per nanocrystal. When impurity concentra-
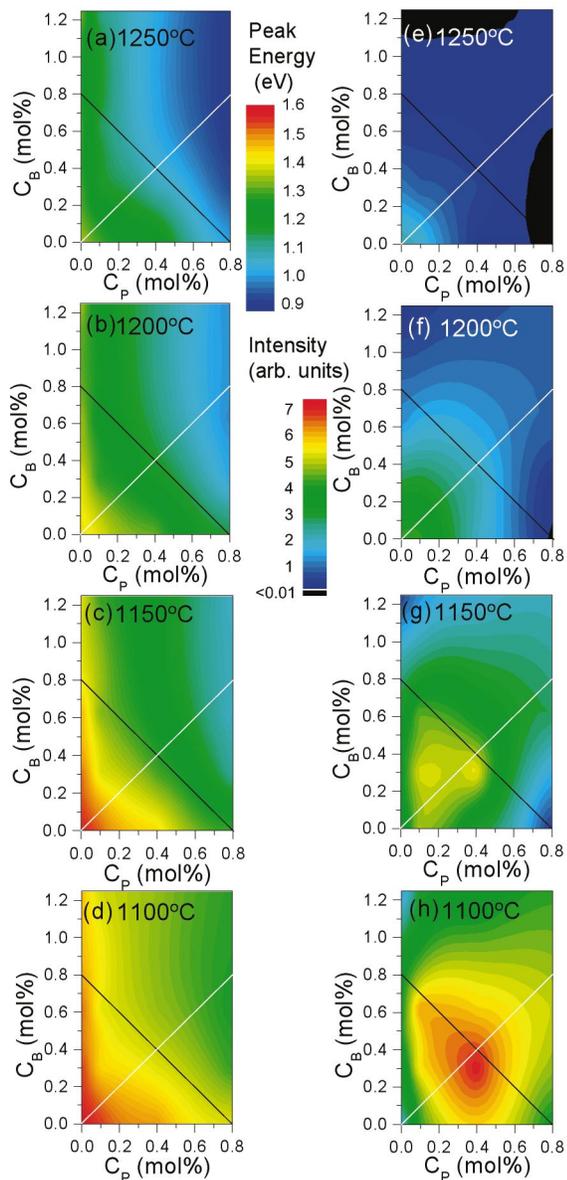
FIG. 2. (Color) Contour plots of PL peak energy [(a)–(d)] and intensity [(e)–(f)] as a function of B and P concentrations. Annealing temperatures are 1100 °C [(a) and (e)], 1150 °C [(b) and (f)], 1200 °C [(c) and (g)], 1250 °C [(d) and (h)]. P concentration was set to 0, 0.10, 0.40, and 0.79, and B concentration to 0, 0.30, 0.62, and 1.24 mol %. The data of 16 samples are plotted in each graph after a smoothing procedure. On the white lines, C_B and C_P are the same, while on the black lines, the sum of C_B and C_P is fixed to be 0.8 mol %.

tion is larger than a certain value, typically the total concentration of larger than about 1 mol %, even if the annealing temperatures is the same, the size of nc-Si becomes larger because of the softening of glass matrices and resultant longer diffusion length of Si during annealing.[8] The number of solvable impurities in a nanocrystal will thus increase. As a result, the number of impurities in each nanocrystal can fluctuate and the probability to have a perfectly compensated nc-Si will be small, even if total number of P and B in a whole sample is the same. Since *n*- or *p*-type nc-Si fall victim to Auger recombination, the total PL intensity will drop. The effect is more prominent for higher-temperature annealed samples because of the larger size. However, it should be stressed here that even for relatively large nc-Si, the prob-

ability to have a perfectly compensated nc-Si is not zero. The intensity of codoped samples is thus always much higher than those containing the same amount of either P or B.

As discussed above, one of the reasons for the enhancement of PL intensity by impurity doping is the increase of the number of optically active nc-Si. Doping of B or P results in the softening of a silica matrix. This can reduce stresses exerted on nc-Si by annealing, and prevent the formation of dangling bonds at nc-Si/matrix interfaces. The other mechanism is the inactivation of surface dangling bonds by P doping. An electron supplied by P doping is transferred from a P atom to a surface dangling bond, creating a lone pair which does not trap the optically excited electron. This mechanism has been studied in detail for P-doped nc-Si by ESR and infrared PL spectroscopies at low temperatures.[13,14,16]

Although it is very plausible that these mechanisms work in codoped samples, they cannot explain the observed ridge of the intensity along nearly the same B and P concentration line [Figs. 2(e)–2(h)] or the maximum intensity at nearly the same concentration points [Figs. 2(g) and 2(h)]. Therefore, the enhancement of oscillator strength of perfectly compensated nc-Si due to the donor to acceptor transitions contributes to the observed high PL intensity of the codoped samples.

In conclusion, we have demonstrated that impurity compensation really works in nanometer size Si crystals. By properly controlling impurities, the PL intensity can exceed that of pure nc-Si and the tunable range of the PL peak energy can be extended out of that covered by pure nc-Si.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] P. D. J. Calcott, K. J. Nash, L. T. Canham, M. J. Kane, and D. Brumhead, J. Phys.: Condens. Matter **5**, L91 (1993).

[3] *Light Emission in Silicon: From Physics to Devices*, edited by D. J. Lockwood (Academic, San Diego, 1998).

[4] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82**, 909 (1997).

[5] D. Kovalev, H. Heckler, G. Polisski, and F. Koch, Phys. Status Solidi B **215**, 871 (1999).

[6] M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1999).

[7] S. Takeoka, M. Fujii, and S. Hayashi, Phys. Rev. B **62**, 16820 (2000).

[8] M. Fujii, K. Toshikiyo, Y. Takase, Y. Yamaguchi, and S. Hayashi, J. Appl. Phys. **94**, 1990 (2003).

[9] C. Delerue, M. Lannoo, G. Allan, E. Martin, I. Mihalcescu, J. C. Vial, R. Romestain, F. Muller, and A. Bsiesy, Phys. Rev. Lett. **75**, 2228 (1995).

[10] C. Delerue, M. Lannoo, G. Allan, and E. Martin, Thin Solid Films **255**, 27 (1995).

[11] G. Allan, C. Delerue, M. Lannoo, and E. Martin, Phys. Rev. B **52**, 11982 (1995).

[12] A. Mimura, M. Fujii, S. Hayashi, and K. Yamamoto, Solid State Commun. **109**, 561 (1999)

[13] A. Mimura, M. Fujii, S. Hayashi, D. Kovalev, and F. Koch, Phys. Rev. B **62**, 12625 (2000).

[14] M. Fujii, A. Mimura, S. Hayashi, Y. Yamamoto, and K. Murakami, Phys. Rev. Lett. **89**, 206805 (2002).

[15] S. M. Sze, *Physics of Semiconductor Devices* (Wiley-Interscience, New York, 1981).

[16] Z. Zhou, R. A. Friesner, and L. Brus, J. Am. Chem. Soc. **125**, 15599 (2003).