Photoluminescence from B-doped Si nanocrystals

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Boron-doped Si nanocrystals as small as 3.5 nm were prepared and their photoluminescence (PL) properties were studied. The PL properties were found to be very sensitive to the B concentration. For the sample without B doping the temperature-dependent shift of the PL peak was almost the same as that of the bulk band gap. As the B concentration increased, the temperature dependence deviated from that of the bulk band gap, and the peak exhibited a low-energy shift as the temperature decreased. The anomalous temperature dependence is considered to be due to the contribution of the PL from excitons bound to the neutral B states. © 1998 American Institute of Physics.

I. INTRODUCTION

During the past decade, optical properties of Si nanostructures have been the subject of intensive investigations because the quantum confinement effects of electrons and holes lead to optical properties much different from those of bulk Si crystals. 1-7 Photoluminescence (PL) properties in particular have widely been studied and the relationship between the size of nanostructures and the PL peak energy has been revealed experimentally for at least red and infrared PL. 4,7 However, there remain large differences between the PL peak energies observed and the calculated band gap, 4,7 and thus the mechanism of the PL is not yet fully understood. Furthermore, the role of impurity atoms on photoluminescence properties has not been clarified and little is known about the electronic states associated with impurity atoms. To fully understand the optical and electrical properties of Si nanostructures and to achieve various device applications, systematic studies of impurity-doped Si nanostructures are indispensable.

In our previous work, 5,6 we succeeded in preparing B-doped Si nanocrystals (nc-Si) by a cosputtering method. We have confirmed the doping of B atoms into Si nanocrystals by Raman spectroscopy. The transverse optical (TO) peak of B-doped nc-Si observed under excitation of a 676.5 nm line of a Kr-ion laser was asymmetric with a tail at the high-energy side of the peak due to the discrete-continuum Fano-type interference between the phonon scattering and the scattering of free carriers generated by the B doping. In this work, we have studied PL properties of B-doped nc-Si as small as 3.5 nm in diameter prepared by the same method. We will demonstrate that the PL properties of Si nanocrystals, in particular the temperature dependence, are very sensitive to the B concentration.

II. EXPERIMENT

The B-doped nc-Si were prepared by the cosputtering method. 5,6 Small pieces of Si chips (5 × 15 mm²) and B₂O₃ pellets (10 mm in diameter) were placed on a SiO₂ sputtering target (10 cm in diameter) and they were cosputtered in Ar gas of 2.7 Pa. Films about 2 μm in thickness were deposited on fused quartz plates and Si wafers. The films were then annealed under N₂ gas flow at 1100 °C for 30 min to grow nc-Si in the SiO₂ matrices. During the growth of nc-Si, B atoms are thought to be incorporated into nc-Si.

In this method, the size of the nc-Si can be controlled by changing the number of Si chips during the cosputtering and by changing the annealing temperature. The B concentration can also be controlled by changing the number of B₂O₃ pellets during the cosputtering. In the annealed samples, B-doped nc-Si are embedded in the matrices that consist of B₂O₃ and SiO₂ (borosilicate glass). Although the B concentration in each nanocrystal is impossible to determine, the concentration of B₂O₃ in the matrix region [C₆ (mol %)] can be determined from the intensity ratio of the B-O (∼1400 cm⁻¹) and Si-O (∼1080 cm⁻¹) vibration peaks in the infrared (IR) absorption spectra. 8 Since C₆ is considered to be roughly proportional to the B concentration in a film as a whole, in the following we will use C₆ to distinguish the samples. The maximum C₆ studied was about 1.3 mol %. The size of nc-Si was determined by cross-sectional high-resolution transmission electron microscopic (HRTEM) observations [using JEM-2010 (JEOL)]. The samples for the HRTEM observations were prepared by the standard procedures including mechanical and ion thinning methods. Photoluminescence spectra were measured using a HR-320 (Jobin-Yvon) monochromator and an EO-817L (North Coast) Ge detector. The spectral responses of the detection systems were corrected by reference spectra of a standard tungsten lamp. The excitation source was the 457.9 nm line of an Ar-ion laser with a power density of less than 1 W/cm². The measurements were made in the temperature range between 5 and 300 K in a CF1204 continuous-flow He cryostat (Oxford Instruments).

III. RESULTS

Figure 1 shows a typical HRTEM image of a sample. We can clearly see lattice fringes corresponding to the {111}
planes of nc-Si with the diamond structure. The Si nanocrystals are well dispersed in a SiO\textsubscript{2} matrix. The average size obtained from the HRTEM images was about 3.5 nm. It should be noted that the size of nc-Si was almost independent of the B concentration.

In our previous work, we have studied B-doped nc-Si as small as 8 nm in diameter by Raman spectroscopy\textsuperscript{5,6}. We demonstrated that, under blue excitation, the nanocrystals show a broad Raman peak with a tail towards the low-energy side of the peak due to phonon confinement effects. As the excitation wavelength was increased, the spectral shape changed gradually and under the excitation of 676.5 nm light, we observed an asymmetric peak with a tail towards the high-energy side of the peak. The asymmetric spectral shape and its excitation wavelength dependence can be explained well by the discrete-continuum Fano-type interference between the phonon scattering and the scattering of free carriers generated by the B doping. The observation of the Fano-type spectral shape indicates that the Fermi level of the nanocrystals is located in the valence band due to the very high doping (\(\approx 10^{19} / \text{cm}^3\)).

Similar in the present nc-Si, B atoms are also considered to be heavily doped, because the B concentration of the present samples is nearly the same as that of the previous ones (\(C_B \approx 1 \text{ mol } \%\)). In the case of a nc-Si 3.5 nm in diameter, one B atom corresponds to the very high concentration of about \(8 \times 10^{19} / \text{cm}^3\), provided that the crystal structure and the lattice constant of the nanocrystals are the same as those of the bulk Si crystal. Since the solid solubility of B atoms in bulk Si crystal at room temperature is smaller than \(4 \times 10^{20} / \text{cm}^3\) (solid solubility at 1000 °C),\textsuperscript{5} the maximum number of B atoms doped into each nanocrystal is expected to be very small. Therefore, it should be noted here that, if the B concentration in a film is low, both doped and undoped nanocrystals are thought to coexist and, as the B concentration increases, the ratio of the doped nanocrystals increases.

Figure 2 shows the room temperature PL spectra of B-doped nc-Si with three different \(C_B\) and that of an undoped nc-Si. All the spectra are normalized at their maximum intensities. The scaling factors are shown (a larger factor corresponds to a larger PL intensity). For the sample without B doping, we can see a peak at about 1.4 eV. In our previous work,\textsuperscript{7} we demonstrated that the PL peak energy is very sensitive to the size of the nc-Si and the peak exhibits a high-energy shift as the size decreases. From the observed size dependence, we attribute the peak to the recombination of electrons and holes confined in the nc-Si. As the B concentration increases (i.e., as the number of doped nanocrystals increases), the peak becomes weak and is broadened, while the peak energy is almost independent of the B concentration. The decrease in the PL efficiency may be ascribed to the increase in the nonradiative Auger recombination process in a nanocrystal, because in B-doped nanocrystals the recombination energy of an exciton can be transferred to a hole in a neutral acceptor by exciting the hole deep into the valence band. As the B concentration increases, the number of doped nanocrystals increases. This results in an increase in the number of “dark” nanocrystals and thus the PL is quenched.

Figure 3 shows the temperature dependence of the PL spectra for the samples without doping [Fig. 3(a)] and with \(C_B \approx 1.3 \text{ mol } \%\) [Fig. 3(b)]. In both the samples, as the temperature decreases, another peak appears at about 0.9 eV. This peak becomes intense with decreasing temperature. Similar PL spectra have often been observed for porous Si and the origin of the low-energy peak is considered to be due
to the recombination of carriers trapped at $P_b$ centers at the surface of Si nanostructures.\textsuperscript{10,11} We have studied in detail the size and temperature dependence of the low-energy peak. The results will be published elsewhere. In this article we will restrict our attention to only the high-energy peak.

In Fig. 3(a), as the temperature decreases, the high-energy peak at about 1.4 eV shifts monotonously to higher energies. On the other hand, in Fig. 3(b), the peak shifts to lower energies. Figure 4 shows the peak energies of the high-energy peak as a function of temperature. The ordinate in Fig. 4 represents the peak energy shift relative to the peak energy at 290 K. The band-gap shift of bulk Si crystal is also shown as a solid curve. Figure 4 demonstrates that the temperature dependence of the peak energy is very sensitive to the B concentration. For the sample without doping, the temperature dependence is almost the same as that of the bulk band gap. As $C_B$ increases, the temperature dependence deviates from that of the bulk band gap. For the sample with $C_B \geq 0.8$ mol \%, the peak shifts in the direction opposite to that of the bulk band gap.

IV. DISCUSSION

In the B-doped nc-Si at low temperatures, excitons are considered to be bound to the neutral B states and the bound excitons may recombine radiatively. The PL spectra will thus consist of the main band originating from the recombination of unbound electron-hole pairs and the additional band related to the bound excitons (bound-exciton band). The bound-exciton band will appear at the low-energy side of the main band. The energy difference between the two bands corresponds to the binding energy of the bound exciton. If the widths of the bands are much larger than the binding energy, the two bands will not appear as two isolated peaks; instead they will overlap resulting in a broad peak. By assuming that the PL peak observed for the B-doped nc-Si (Figs. 2 and 3) consists of the two bands, we can explain the observed anomalous temperature dependence of the PL spectra as follows.

The relative intensity of the main band and the bound-exciton band will depend on the temperature. At room temperature, excitons are considered to be thermally released from the neutral B states. The PL peak energy at room temperature is thus not affected by the B doping. At low temperatures, a part of the excitons is bound to the neutral B states and emits light at the low-energy side of the main band. This causes the low-energy shift of the observed peak.
from that of the undoped nc-Si. As the temperature decreases further, the relative intensity of the bound-exciton band increases and the deviation of the peak energy from that of the undoped nc-Si becomes large. If the binding energy of bound excitons is larger than the widening of the band gap caused by the temperature variation from 300 to 5 K (about 45 meV), the widening is canceled out and the PL peak of the doped nc-Si will shift to lower energies as the temperature decreases.

In actual B-doped samples, both the doped and undoped nc-Si coexist. The PL spectra will thus be a mixture of doped and undoped nanocrystals, and the observed PL peak energy versus temperature curve is expected to be located between the curves of the undoped and doped nanocrystals. In Fig. 4, the temperature dependence of the undoped sample is almost the same as that of the bulk band gap. As \( C_B \) increases, the temperature dependence deviates from that of the undoped sample. The deviation becomes large as \( C_B \) increases. This may result from the increase in the ratio of the doped nc-Si in the samples. If we assume that all the nanocrystals in the sample with \( C_B \approx 1.3 \text{ mol}\% \) are doped with B atoms and that only the bound-exciton band appears at 5 K, a rough estimate of the binding energy of the bound excitons can be obtained from Fig. 4 by the deviation of the peak energy from that of the undoped sample at 5 K. The estimated value is about 80 meV.

The energy levels of hydrogenic impurities in nc-Si have been studied on the basis of the tight binding theory by Delerue et al.\(^2\) In their calculations, the binding energy of a hole on a bare acceptor located at the center of a nanocrystal as small as 3.5 nm in diameter is about 550 meV. In the bulk Si crystal, the binding energy of a bound exciton on a neutral donor (acceptor) is about 0.1 of the binding energy of an electron (hole) on a bare donor (acceptor).\(^3\) If we assume that this empirical rule can be applied to the nc-Si, the binding energy of bound excitons in the present samples becomes about 55 meV. Although this value is derived under the assumptions stated and in spite of the fact that size distributions exist in actual samples, the agreement between the estimated binding energy and the experimentally obtained one (80 meV) is rather good.

In the above discussion, we assumed that the widths of the main and bound-exciton bands are much larger than the binding energy of excitons. The width of the main band is thought to be nearly the same as the PL peak width of the undoped sample (full width at half maximum is about 300 meV). This value is much larger than the experimentally obtained binding energy. The large width is considered to be mainly due to the inhomogeneous broadening caused by the size distribution (standard deviation is about 1 nm). The size distribution also causes the broadening of the bound-exciton band, and thus the width of the band is also considered to be much larger than the binding energy.

The above discussion is based on the assumption that the observed PL peak consists of the bound and unbound exciton bands. Although the model could well explain the experimental results, the assumption is not fully justified. Study of the PL decay dynamics may provide useful information for a more definite determination of the origin of the bands.

In previous PL studies of porous Si, both positive and negative temperature dependences of the PL peak have been observed.\(^4\)–\(^9\) However, no uniform explanation of the observed temperature dependence has been given so far. Porous Si is prepared by the electrochemical anodization of p-type Si wafers. The resistivities of the Si wafers used in the previous studies were distributed over a wide range (0.001–50 \( \Omega \) cm).\(^10\)–\(^19\) This suggests that the impurity concentration of the nanostructures in the porous Si prepared from these wafers was also distributed over a wide range. The results of the present work strongly suggest that the variety in the temperature dependences previously reported for porous Si was caused by the variety of impurity concentrations in the nanostructures resulting from the variety of resistivities of the Si wafers used to prepare porous Si.

V. CONCLUSION

We have studied photoluminescence properties of B-doped nc-Si as small as 3.5 nm. We demonstrated that the temperature dependence of the PL peak energy strongly depends on the B concentration. For the sample without B doping, the temperature dependent shift of the PL peak was almost the same as that of the bulk band gap. As the B concentration increased, the temperature dependence deviated from that of the undoped sample, and the peak exhibited a low-energy shift as the temperature decreased. The anomalous temperature dependence is considered to be due to the contribution of the PL from excitons bound to the neutral B state.

In previous PL studies of porous Si, both the positive and negative temperature dependences of the PL peak energy were reported. The present results strongly suggest that the different impurity concentrations in the nanostructures in porous Si result in different temperature dependences reported.

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