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Photoluminescence and free-electron absorption in heavily phosphorus-doped Si nanocrystals

Atsushi Mimura
Division of Mathematical and Material Science, The Graduate School of Science and Technology, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

Minoru Fujii* and Shinji Hayashi
Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

Dmitri Kovalev and Frederick Koch
Technische Universität München, Physik-Department E16, D-85747 Garching, Germany

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Heavily phosphorus-doped Si nanocrystals several nanometers in diameter are studied by photoluminescence (PL) and optical absorption spectroscopy. It is demonstrated that P doping results in the quenching of the PL. The quenching is accompanied by the appearance of the optical absorption in the infrared range. The absorption was assigned to the intravalley transitions of free electrons generated by P doping (free-electron absorption). The generation of free electrons and the resultant three-body Auger recombination of excitons is considered to be responsible for the observed PL quenching.

I. INTRODUCTION

Optical properties of Si nanocrystal assemblies (nc-Si) have been studied intensively, because they are promising materials for Si-based optoelectronic devices.[1–6] Application of nc-Si to commercial devices requires deeper knowledge of its energy band structure. In particular, the information related to the electronic properties of impurity atoms is essential, since for nanometer-sized crystallites a high impurity concentration can be realized by doping a single nanocrystal with only one impurity atom. Thus the electrical and optical properties of *nc*-Si are expected to be very sensitive to doping level. However, it has not been fully understood how a dopant atom works in such a confined and dielectric discontinuous medium. In fact, it is not established whether generation of free carriers is possible by group III or V impurity doping of *nc*-Si.

In porous Si layers, if the carrier concentration in an initial Si wafer is preserved after anodization, those prepared from n^+ and p^+ wafers should have free carriers. However, no evidence indicating the existence of free carriers has been detected by electron spin resonance (ESR) technique[7] and optical absorption spectroscopy.[8] A possible explanation is that dopant atoms can ''shift'' to the surface of the porous Si and no longer contribute as donor or acceptor.[3] This shift occurs due to the chemical etching process, which takes place only at Si–Si, Si–O, and Si–H bonds and does not attack the Si–dopant bonds. Another explanation is that the free carriers are captured on deep defects, e.g., surface dangling bonds.[7–9]

In the case of oxidized nc-Si, i.e., nc-Si in SiO_2 matrices, the effects of P and B doping have been studied by photoluminescence (PL) and ESR.[10–14] Quenching of the exciton PL by B doping and the improvement in the PL efficiency by P doping have been reported. The quenching has been explained by the Auger recombination process among a free hole and a photoexcited exciton,[13,14] while the improvement has been shown to be due to the modification of the surface termination.[10–12] Although these previous studies demonstrated that doping of P and B atoms strongly affects PL properties of nc-Si, no clear evidence for the generation of free carriers has been given. In this work, generation of free electrons in nc-Si due to P doping is demonstrated by optical absorption spectroscopy in the infrared region, and the effects of free electrons on the PL properties are discussed.

II. EXPERIMENT

P-doped Si nanocrystals were prepared by the same method as used in our previous work.[10–12] Small pieces of Si chips were placed on a phosphosilicate glass (PSG) sputtering target and they were co-sputtered in Ar gas. As the substrates fused quartz plates and Si wafers were used. The thickness of the films was about 50 μm. After the co-sputtering, the films were annealed in a N_2 gas atmosphere for 30 min at 1100 °C to grow nc-Si in PSG matrices. The P concentration can be controlled by changing the P_2O_5 concentration in the PSG sputtering target. The average P concentration in a whole film [C_P (mol %)] was determined by an electron probe microanalysis. C_P was varied from 0 (without P doping) to 1.2 mol %. The size of nc-Si was estimated by cross-sectional high-resolution transmission electron microscopic (HRTEM) observations and was about 4.7 nm in diameter. The size was not affected by P doping. The HRTEM observations revealed that each nc-Si crystal is isolated from the others by PSG barriers several nanometers in thickness, i.e., carrier transport between adjacent nc-Si is prevented by thick PSG barriers.

PL spectra were measured using a single monochromator equipped with a Ge detector. The excitation source was the 457.9 nm line of an Ar-ion laser. The excitation power was 250 mW/cm^2. For all the spectra, spectral response of the detection system was corrected by the reference spectrum of a standard tungsten lamp. For optical absorption spectros-

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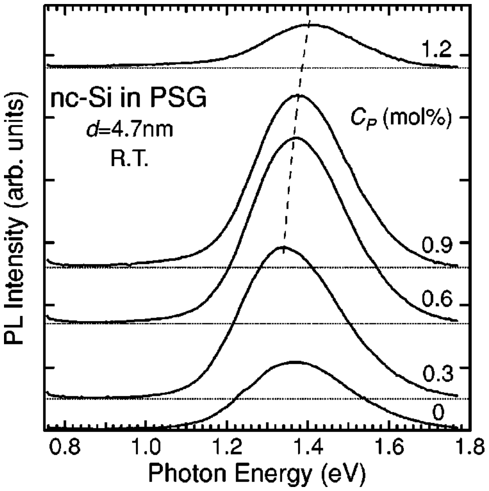

FIG. 1. Room-temperature PL spectra of nc-Si dispersed in PSG matrices. The P concentration (C_P) is varied from 0 (without P doping) to 1.2 mol %.

copy, samples deposited on fused quartz plates were used in a spectral range between 0.19 and 3.2 μm, and those on Si wafers between 3.2 and 4.8 μm. The long-wavelength range is limited due to the strong absorption of the SiO_2 matrices in the midinfrared region.

III. RESULTS AND DISCUSSION

Figure 1 shows room-temperature PL spectra for the samples with four different C_P and without doping. A broad peak is observed at around 1.4 eV for all the samples. The peak can be assigned to the recombination of excitons confined in nc-Si.[4] The PL intensity depends strongly on C_P. In Fig. 2, the integrated PL intensities are plotted as a function of C_P. The PL intensity first increases with increasing C_P, reaches the maximum at around 0.6 mol % and decreases with further doping. The improvement in the PL intensity at small P concentration has been observed in our previous work and is found to be caused by the decrease in the number of electronically active defects at the interfaces between nc-Si and their matrices (P_b centers).[10–12] In Fig. 1, we can also find that the PL peak energy depends on C_P. The PL peak position shifts from 1.34 to 1.40 eV with increasing C_P.

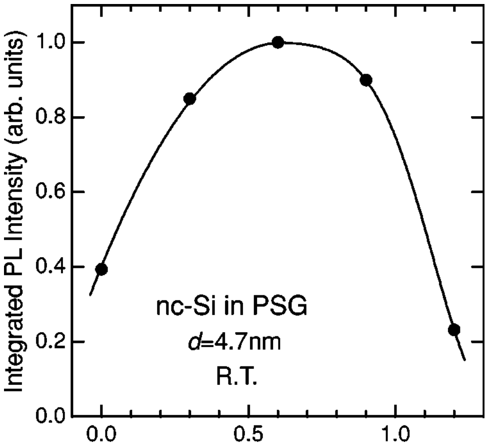

FIG. 2. Integrated PL intensity as a function of C_P. The solid curve is the guide to the eyes.

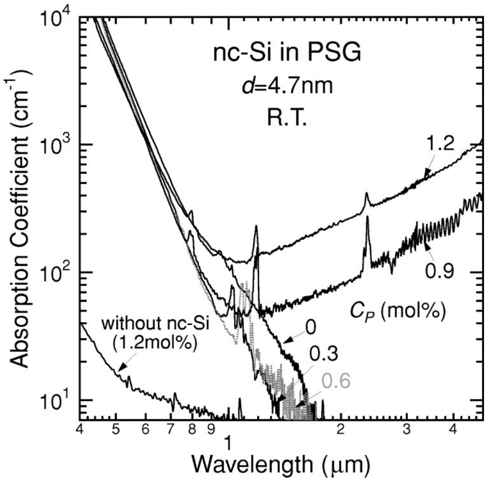

FIG. 3. Optical absorption spectra for nc-Si dispersed in PSG matrices with various C_P. For comparison purposes, an absorption spectrum of a PSG film (42 μm in thickness, $C_P = 1.2$ mol %) not containing nc-Si is shown.

In Fig. 3, optical absorption spectra for the samples with different C_P and a PSG film that does not contain nc-Si are shown. A few sharp peaks that can be assigned to the Si-H stretching overtones and combinations[15] are seen. These peaks are observed only for heavily P-doped samples because of the high moisture absorptivity of these samples. To obtain absorption coefficients of nc-Si (Ref. 16) the measured absorption spectra (absorbance) were divided by the film thickness and the volume fraction of nc-Si (25%). For the samples with $C_P \leqslant 0.6$ mol %, the absorption decreases monotonically to the infrared region. This absorption is due to the valence-to-conduction-band transitions in nc-Si and/or those related to band tails or defect levels. On the other hand, for the samples with $C_P > 0.6$ mol %, in addition to the absorption at the short-wavelength range, a smoothly rising absorption continuum appears in the infrared range. The infrared absorption increases together with the P concentration. It is important to note that the infrared absorption does not originate from PSG matrices. In fact, the PSG film that does not contain nc-Si is almost transparent in this spectral range (see Fig. 3).

A very similar absorption in the infrared range has been observed for n^+ bulk Si crystals.[17] In bulk Si, the infrared absorption has been assigned to free-electron absorption. The free-electron absorption is characterized by a monotonic, structureless, spectrum that grows as λ^p, where λ is the photon wavelength and the power p depends on the mode of scattering that occurs to conserve momentum during a transition of a free electron to a higher energy state within the same valley.[18] The Drude theory for the oscillation of an electron driven by a periodic electric field in a metal gives a damping (attenuation) that increases as λ^2. The collision with the semiconductor lattice, resulting in scattering by acoustic phonons, leads to an absorption increasing as $\lambda^{1.5}$, while that by optical phonons gives a dependence $\lambda^{2.5}$. Scattering by ionized impurities gives a dependence in λ^3 or $\lambda^{3.5}$, depending on the theoretical approximation used. In general, all three modes of scattering can occur and the resultant free-electron absorption is expected to be a weighted sum of all three processes. Therefore, the exponent p in the dependence λ^p can range from 1.5 to 3.5 depending on the ratio of the three scattering modes.

The similarity in the observed spectral shape to the free-electron absorption in the n^+ Si crystal implies that the observed infrared absorption is due to the intravalley transition of free electrons generated by P doping, i.e., free-electron absorption in *nc*-Si. We found that the observed infrared absorption can be well fitted with $\lambda^{1.7}$. This suggests that free-electron absorption in *nc*-Si is assisted mainly by acoustic phonon scattering. It should be noted here that in the present samples electrons generated by P doping are ‘‘free’’ only within each *nc*-Si crystal, and transport of electrons between adjacent *nc*-Si is prevented by thick PSG barriers.

The observed infrared absorption is a smooth spectral function. However, the intravalley transition spectrum of an individual nanocrystal should be discrete and consists of a series of peaks, because the allowed energy of an electron in the conduction band is expected to be discrete due to the quantum confinement effects. We believe that the discreteness is smeared out by the distribution of the degree of the quantization arising from the *nc*-Si size and shape variations.

The generation of free electrons in *nc*-Si is directly related to the observed PL quenching. If a free electron is supplied by an incorporation of a P atom into a substitutional site in *nc*-Si, the three-body Auger recombination process among the electron and a photoexcited exciton (*eeh* Auger process) becomes possible, i.e., the exciton recombination energy can be transferred to the electron with its following excitation to a higher energy level in the conduction band. The lifetime of the *eeh* Auger recombination process in a spherical Si crystallite has been calculated by Lannoo *et al.*, and depending on its size ranges between 0.1 and 1 ns.[19] This lifetime is several orders of magnitude shorter than the radiative lifetime of excitons in *nc*-Si. Therefore, the generation of free electrons results in a significant decrease in the PL efficiency. In the present samples, both the doped and undoped nanocrystals coexist. As C_P increases, the number of doped nanocrystals increases, so that the free-electron absorption increases and the PL comes to be quenched as a whole.

The high-energy shift of the PL peak with C_P (Fig. 1) can also be explained in the same manner. The PL bands observed are rather broad (full width at half maximum is about 270 meV) due to the size and shape variations of *nc*-Si. The PL signal at low-energy side of the peak comes from larger nanocrystals in the size distribution, while that at the high-energy side comes from smaller ones. If P atoms are uniformly distributed throughout a film, the probability that *nc*-Si is doped is higher for larger particles. Therefore, as C_P increases, PL quenching starts from the largest nanocrystals in the size distribution, and then proceeds to smaller nanocrystals with further increase of C_P. This implies that the PL quenching occurs from the low-energy side of the PL peak, thus resulting in the blue shift of the peak with C_P as can be seen in Fig. 1.

IV. CONCLUSION

Generation of excess electrons in *nc*-Si several nanometers in diameter by impurity doping was demonstrated by optical absorption spectroscopy in the infrared region. It was shown that heavily P-doped *nc*-Si shows absorption in the infrared region due to the intravalley transition of free-electrons supplied by P doping. It was also demonstrated that the generation of free electrons results in quenching of the exciton luminescence in *nc*-Si due to the nonradiative Auger recombination process among the free electron and a photoexcited exciton.

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*Author to whom correspondence should be addressed. Email address: fujii@eedept.kobe-u.ac.jp

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