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Electron spin-resonance studies of conduction electrons in phosphorus-doped silicon nanocrystals

Kazuaki Sumida, Keiichi Ninomiya, Minoru Fujii,^{a)} Kazuyoshi Fujio, and Shinji Hayashi

Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

Masafumi Kodama

The Graduate School of Science and Technology, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

Hitoshi Ohta

Department of Frontier Research and Technology, Headquarters for Innovative Cooperation and Development, Kobe University, Rokkodai, Nada, Kobe 657-8501, Japan

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The properties of conduction electrons in P-doped Si nanocrystals embedded in insulating glass matrices have been studied by electron spin-resonance spectroscopy. For heavily P-doped samples, a broad conduction electron signal is observed at low temperatures. The width of the signal is found to be much broader than that of P-doped bulk Si crystals. The temperature dependence of the signal intensity obeys the Curie law even when the P concentration is very high. This suggests that in P-doped nanocrystals donor levels do not merge into the conduction band even at very high P concentration, and also provides evidence that Si nanocrystals smaller than a certain threshold size do not become metallic, at least when they are prepared under an equilibrium condition. © 2007 American Institute of Physics. [DOI: [10.1063/1.2432377](https://doi.org/10.1063/1.2432377)]

I. INTRODUCTION

Si nanocrystals (Si-nc's) show strong luminescence in the visible range.¹⁻³ The luminescence arises from the recombination of electron-hole pairs confined in the zero-dimensional quantum confined system. The luminescence energy is changed from the band-gap energy of bulk Si crystals to the visible range by controlling the size.²⁻⁴ The luminescence property can be modified by shallow impurity doping.⁵⁻⁷ Doping of either *n*- or *p*-type impurities results in the quenching of the photoluminescence (PL) due to the efficient Auger interaction between photoexcited electron-hole pairs and carriers supplied by the impurity doping.^{7,8} The PL quenching is effectively suppressed when *n*- and *p*-type impurities are doped simultaneously because of the compensation of carriers in Si-nc's.^{6,7} The impurity codoped Si-nc's exhibit PL at energies lower than that of the bulk Si band gap, due probably to the transition between donor and acceptor states.⁷

The strong modification of PL spectra by impurity doping indicates that the electronic structure is modified. Electron spin resonance (ESR) is one of the powerful experimental techniques to investigate the electronic structure of semiconductors and has routinely been used to study the properties of conduction electrons in shallow-impurity-doped bulk Si crystals. The ESR spectra depend strongly on the doping level. In lightly P-doped bulk Si crystals ($\leq 10^{17} \text{ cm}^{-3}$), a hyperfine structure (splitting energy of 42 G) caused by the interaction between the donor electron spin and the P nucleus spin appears.⁹ In this doping level,

donor electrons are localized at the P donor sites and the donor level is well separated from the bottom of the conduction band. When the P concentration is increased, the hyperfine structure disappears and a conduction electron signal ($g=1.998$) appears. The signal obeys the Curie law when the donor concentration is in the 10^{16} – 10^{18} cm^{-3} range.^{10,11} In this P concentration range, donor electrons transfer between donor states via overlapped wave functions of P atoms.¹¹ When the P concentration is larger than $2 \times 10^{19} \text{ cm}^{-3}$, the Pauli paramagnetism appears, i.e., the integrated intensity of the conduction electron signal is independent of temperature due to the semiconductor-to-metal transition by the overlap of the donor band with the conduction band and the penetration of the Fermi level into the conduction band.¹¹⁻¹³

The hyperfine structure has also been observed in P-doped Si-nc's when the P concentration is moderate.¹⁴ However, the spectrum was much different from that of P-doped bulk Si crystals. The most significant difference was that in P-doped Si-nc's, the splitting energy is more than twice as large as that of bulk Si crystals. Furthermore, the splitting energy depends strongly on the size of Si-nc's. The spatial confinement of P atoms into the region smaller than the Bohr radius in bulk Si crystals is responsible for the enhancement of the hyperfine splitting.

The hyperfine structure is considered to be observed when, on average, one P atom is doped into one Si-nc. If more than two P atoms are doped, the interaction between the P atoms smears the structure and only a broad conduction electron signal appears. In fact, a broad signal with the g value of 1.998 has been observed for heavily P-doped Si-nc's at low temperatures.¹⁴ However, detailed studies on the conduction electron signal have not been made despite the importance of the knowledge on conduction electrons to realize

^{a)}Author to whom correspondence should be addressed; electronic mail: fujii@eedept.kobe-u.ac.jp

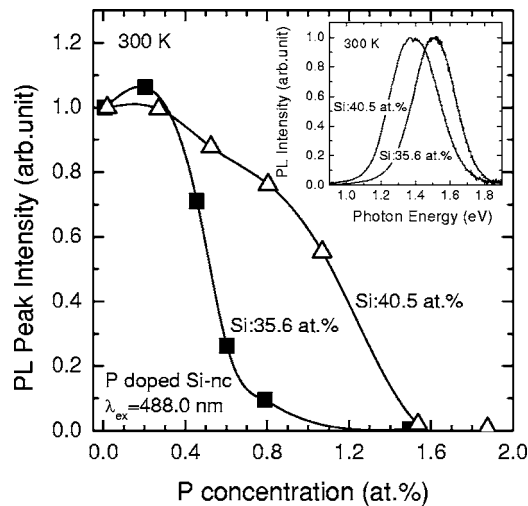


FIG. 1. PL peak intensities of P-doped Si-nc's as a function of P concentration. P concentration is changed from 0 to 1.9 at. %. In the inset, PL spectra of Si-nc's for the samples with the Si concentration of 35.6 and 40.5 at. % are shown.

Si-based optoelectronic devices. The purpose of this work is to study in detail the property of conduction electrons in heavily P-doped Si-nc's. We will show from the temperature and P concentration dependence of ESR spectra that the behavior of the conduction electron signal is significantly different from that of P-doped bulk Si crystals.

II. EXPERIMENT

Samples were prepared by the same method as used in our previous work.^{5-7,14} Small pieces of Si chips were placed on a phosphosilicate glass (PSG) sputtering target and they were simultaneously sputtered in Ar gas on a fused quartz substrate. The films were then annealed in a N₂ gas atmosphere for 30 min at 1150 °C to grow P-doped Si-nc's in PSG matrices. In the present samples, Si-nc's are isolated from others by PSG matrices and thus carrier transport between nanocrystals is prohibited. Si and P concentration in a whole film was determined by an electron probe microanalysis (JXA8900: JEOL). P concentration was changed from 0 to 1.9 at. %.

PL spectra were measured by using a single grating monochromator and a liquid N₂ 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 excitation source was a 488.0-nm line of an Ar ion laser. Continuous-wave X-band ESR was measured by a conventional ESR spectrometer (EMX 8/2.7: Bruker). The spectra were measured in the temperature range between 4.2 and 300 K in a continuous-flow He cryostat (Optistat: Oxford Instruments). The modulation frequency and modulation amplitude were 100 kHz and 2 G, respectively. A nuclear magnetic resonance Gauss meter with 10⁻⁶ G resolution was used for field monitoring.

III. RESULT

PL spectra for the samples with the Si concentration of 35.6 and 40.5 at. % are shown in the inset of Fig. 1. The PL

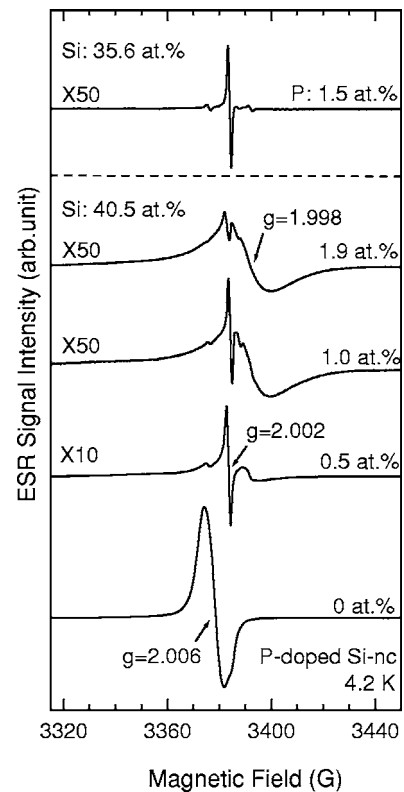


FIG. 2. ESR spectra of P-doped Si-nc's at 4.2 K. Lower part: Si concentration is 40.5 at. % and P concentration is changed from 0 to 1.9 at. %. Upper part: Si concentration is 35.6 at. % and P concentration is 1.5 at. %. For better comparison of the spectral shape, the spectra are scaled by the indicated multiplication factors.

arises from the recombination of electron-hole pairs confined in Si-nc's. The lower Si concentration results in higher PL peak energy because of the smaller size of Si-nc's and the stronger quantum confinement effect. In Fig. 1, PL peak intensity is plotted as a function of P concentration for two series of samples with the Si concentration of 35.6 and 40.5 at. %. For the sample with the Si concentration of 35.6 at. %, the PL peak intensity first increases with increasing the P concentration and then decreases very rapidly, while for that with the Si concentration of 40.5 at. %, it decreases monotonously.

Figure 2 shows ESR spectra of P-doped Si-nc's obtained at 4.2 K. P concentration is changed from 0 to 1.9 at. %, while Si concentration is fixed to about 40.5 at. %. For better comparison of the spectral shape, the spectra are scaled by the indicated multiplication factors. The ESR signal at $g=2.006$ for the sample without P doping is due to dangling bond defects at Si-SiO₂ interfaces.⁵ This signal becomes weaker by P doping. The P concentration dependence of the signal and the relation with the PL intensity have been discussed in detail in our previous papers.^{5,14} After the quenching of the $g=2.006$ signal, a signal with $g=2.002$ emerges. This signal can be assigned to an EX center characterized by involved hyperfine structure of 16 G splitting.¹⁵ By further increasing P concentration, the EX center is also quenched. This suggests that P doping softens the glass matrices and that stress at Si-SiO₂ interfaces is reduced.^{6,16} At the P concentration of 1.0 and 1.9 at. %, a broad signal with

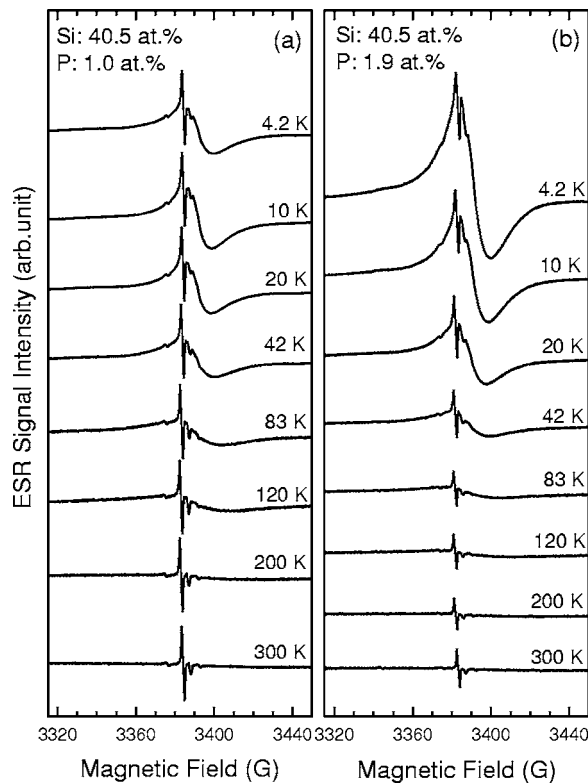


FIG. 3. Temperature dependence of ESR spectra. P concentration is (a) 1.0 and (b) 1.9 at. %. Si concentration is 40.5 at. %.

$g=1.998$ appears. The signal is assigned to conduction electrons in Si-nc's.¹⁷ In the case of the lower Si concentration sample (35.6 at. %), even at the highest P concentration (1.5 at. %), the conduction electron signal was not observed (upper part of Fig. 2).

Figures 3(a) and 3(b) show temperature dependence of ESR spectra for the samples with the P concentration of 1.0 and 1.9 at. %, respectively. Si concentration is 40.5 at. %. The conduction electron signal intensity depends on the temperature. In order to quantitatively discuss the temperature dependence of the intensity and linewidth, the spectra were fitted by the Lorentzian function. In Fig. 4, the linewidth (a) and the integrated intensity (b) obtained by the fitting are plotted as a function of temperature. For the sample with the P concentration of 1.0 at. %, the linewidth decreases slightly by raising the temperature up to 15 K and then increases, while for the sample with the P concentration of 1.9 at. %, it increases monotonously from 4.2 to 120 K. The solid line in Fig. 4(a) is the ESR linewidth obtained for P-doped bulk Si crystals.^{13,18} The linewidth of the present samples is significantly larger than that of bulk Si crystals. In Fig. 4(b), the intensity decreases with increasing the temperature in both samples except for a very low temperature range (<15 K) for the sample with the P concentration of 1.0 at. %.

IV. DISCUSSION

The integrated intensity of the ESR signal is proportional to the static susceptibility (χ). P-doped bulk Si crystals show the Curie or Pauli paramagnetism depending on the doping level. When the P concentration is in the 10^{16} – 10^{18} cm⁻³

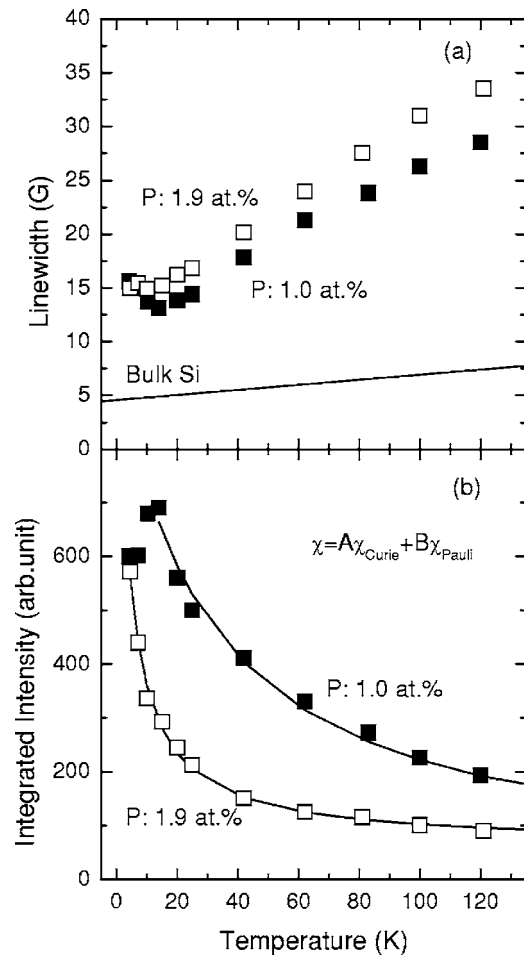


FIG. 4. (a) Linewidth and (b) integrated intensity of the conduction electron signal as a function of temperature. The solid line in (a) represents linewidth of a conduction electron signal in P-doped bulk Si crystals. The solid curves in (b) are the results of fitting by the weighted sum of Curie and Pauli paramagnetism.

range, the electrons stay at their nondegenerate states and electron transport is made by hopping. In this situation, the electron statistics are governed by the Maxwell-Boltzmann distribution and the total number is constant in a wide temperature range, showing a $\chi \propto T^{-1}$ behavior (Curie paramagnetism).^{10,13,19} On the other hand, when the P concentration is larger than 2×10^{19} cm⁻³, the paramagnetic susceptibility of the degenerated electrons at sufficiently low temperatures is temperature independent (Pauli paramagnetism).¹³ In the P concentration range of 10^{18} – 10^{20} cm⁻³, the temperature dependence of the ESR signal intensity is usually fitted by the sum of the Curie and Pauli paramagnetism.¹³

Following the procedure usually employed for P-doped bulk Si crystals, we attempt to fit the temperature dependence of the ESR signal intensity by the weighted sum of the Curie and Pauli paramagnetism, $\chi = A\chi_{\text{Curie}} + B\chi_{\text{Pauli}}$, where A and B are the fitting parameters. The solid curves in Fig. 4(b) show the results of the fitting. For the sample with the P concentration of 1.0 at. %, the intensity can be fitted only by the Curie paramagnetism, while for the sample with the P concentration of 1.9 at. % both the Curie and Pauli paramagnetism should be considered, although the contribution of the Pauli paramagnetism is very small [$B/(A+B)=0.016$].

If we assume that P is doped uniformly into the samples, i.e., uniformly doped in Si-nc's and PSG matrices, P concentration of 1.0 and 1.9 at. % corresponds to that of 5.0×10^{20} and $9.5 \times 10^{20} \text{ cm}^{-3}$, respectively, in Si-nc's. As described above, bulk Si crystals become metallic in these P concentration ranges; the donor states are overlapped with conduction bands and ESR signal intensity is almost independent of temperature. Therefore, the observed results are qualitatively different from that of P-doped bulk Si crystals.

In Si-nc's, the energy band structure is strongly modified from that of bulk Si crystals due to the quantum size effect. The modified energy band structure is considered to be responsible for the observed difference. The conduction band edge of Si-nc's is shifted to higher energy, while the energy of the donor states measured from the vacuum level is almost independent of the size of nanocrystals.^{20–22} Therefore, as the size decreases, the energy difference between the ground donor state and the conduction band edge, i.e., ionization energy, is increased, and thus the overlap of the conduction band and donor states is not realized even at very high P concentration. In other words, the P donor level in Si-nc's is no longer “shallow” but “deep.”²³ In this situation, the Curie paramagnetism is expected. Furthermore, even if the Fermi level is in the conduction band by heavy doping, the conduction band is quantized and electrons occupy the quantized levels. If the width of the quantized levels is very narrow, the Curie paramagnetism is also expected.²⁴

Another possible explanation of the Curie paramagnetism is that P concentration in Si-nc's is lower than the average P concentration in a whole film. In this work, Si-nc's are prepared by annealing Si-doped PSG. The as-deposited films are amorphous and during the annealing Si-nc's are grown; during the growth of Si-nc's P atoms are incorporated. Although doping of P into substitutional sites of Si-nc's is unambiguously demonstrated from previous ESR¹⁴ and IR absorption²⁵ measurements, it is not clear whether solid solubility of P in Si-nc's is the same as that in bulk Si crystals or not. It may be possible that the maximum possible P concentration in Si-nc's is lower than that of bulk Si crystals. In fact, the formation energies of P- or B-doped Si clusters are calculated to be much larger than those of pure Si clusters.²⁶ This may suggest that a part of P atoms are pushed out of nanocrystals during annealing and cooling the samples.

As described above, for the sample with the P concentration of 1.9 at. %, the Pauli paramagnetism is slightly contained. This probably arises from Si-nc's in the large end of the size distribution. In a previous paper,²⁷ we demonstrated that the size distribution becomes broader when P concentration is increased. This is because of the longer diffusion length of Si atoms during annealing due to the softening of glass matrices by P doping. The longer diffusion length makes Si-nc's larger and the size distribution broader. The present result seems to suggest that there is a threshold size of Si-nc's; nanocrystals larger than the threshold size can exhibit the Pauli paramagnetism when heavily doped, while others not.

In Fig. 4, below 15 K, the linewidth increases and the intensity decreases with decreasing temperature for the sample with the P concentration of 1.0 at. %. These proper-

ties can be explained by the localization of donor electrons. At low temperatures, the hopping of electrons between P sites is suppressed and the effect of motional narrowing reduces, resulting in the broadening of the spectra. The localization makes the spin-lattice relaxation time longer, which causes the saturation of the signal at relatively low microwave power. This effect appears as the decrease of the intensity at low temperatures. If the localization of donor electrons at P sites is suppressed by shortening the distance between P atoms by further increasing P concentration, these effects become small. In fact, for the sample with the P concentration of 1.9 at. %, the broadening and quenching of the signal at low temperatures are not observed.

V. CONCLUSION

The conduction electron signal in ESR spectra of P-doped Si-nc's was studied in detail as functions of P concentration and temperature. Despite very high P concentration, the intensity obeys Curie law, suggesting that Si-nc's do not become metallic by shallow impurity doping. The present results indicate that there is a threshold size of Si-nc's, below which they do not become metallic by shallow impurity doping. Therefore, similar studies for the samples with narrower size distribution of Si-nc's seem to be very interesting. Although the mechanism of Curie paramagnetism for heavily P-doped samples is not fully clarified, the most important conclusion obtained in this work is that Si-nc's do not exhibit semiconductor-to-metal transition even when they are annealed in the sea of P, i.e., in PSG.

In Si-nc's, carriers are confined in all three dimensions, and thus the quantum confinement effect appears most significantly. Since the properties of shallow impurities are expected to depend strongly on the confinement dimension, it is very interesting to compare the present results with those of one-dimensional Si nanostructures such as Si nanowires. The electronic properties of impurity-doped Si nanowires have been discussed based on the current transport measurements.²⁸ However, the diameter of nanowires studied so far was rather large (several tens to 100 nm) and in this size range, the quantum size effects are not expected. We believe that ESR studies of impurity-doped Si nanocrystals and nanowires with comparable sizes provide valuable information to fully understand the properties of conduction electrons in low-dimensional Si structures.

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