

Fine Structure Due to Donor–Acceptor Pair Luminescence in Compensated Si

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A fine structure on the higher energy side of donor–acceptor (DA) pair luminescence at 4.2K has been analyzed in compensated Si involving P donors and B acceptors. We calculated the density distribution of DA pairs against photon energy from the number of pairs as a function of the transition energy of respective pairs. A close agreement was obtained between the density curve and the observed spectral structure using the generally accepted values of energy gap and P donor and B acceptor ionization energies. This allows us to conclude that the structure is due to discrete DA pair recombination. © 2010 The Japan Society of Applied Physics

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Donor–acceptor (DA) pair luminescence is one of the most well-defined recombination processes in semiconductors.^{1,2)} A characteristic discrete line structure was observed on the higher energy side of the DA pair luminescence band, and the structure was beautifully explained by the discrete Coulombic energy term caused by the DA pair separation. The DA pair luminescence with the fine structure has been investigated in detail in many semiconductors, such as GaP, CdTe, SiC, and others. However, very little work has been performed on the DA pair luminescence from Si,³⁾ and the fine structure has not yet been reported. The main reason for this is that Si crystals for electronic devices have very low residual impurities, resulting in low compensation ratio. For the observation of DA pair luminescence, impurity levels on the order of 10^{15} – 10^{17} cm⁻³ are necessary for both donor acceptor impurities, as was the case for GaP and other semiconductors.

Recently the use of less pure Si materials, called “solar-grade Si (SOG-Si)”, has been urgently needed for the mass production of solar cells to cope with current energy and environmental issues. The concentrations of the residual donor and acceptor impurities in the SOG-Si are on the order of 10^{15} – 10^{17} cm⁻³, leading to a heavy compensation between donors and acceptors. This situation is suitable for the observation of DA pair luminescence. It should be pointed out that the concentration range is difficult to handle for conventional impurity characterization techniques. Resistivity measurement is ineffective for compensated samples. The photoluminescence⁴⁾ (PL) and infrared absorption⁵⁾ methods for quantitative impurity analysis are not applicable to a concentration range higher than 10^{15} cm⁻³. Secondary ion mass spectroscopy, glow discharge mass spectroscopy and inductively coupled plasma mass spectroscopy become erroneous as the concentration is decreased to the order of 10^{15} cm⁻³. The purpose of this paper was to make a detailed investigation of DA pair luminescence in compensated Si, and we believe the refined information we have gleaned contributes greatly to the accurate characterization of donor and acceptor impurities in compensated Si, which is crucial in the fabrication of high-quality and low-cost solar cells.

The sample used for the present study was a Si wafer from an ingot grown by the Czochralski method with B and P doping. The B and P concentrations were, respectively, determined to be 4.0×10^{16} and 2.9×10^{16} cm⁻³ from the

method described in ref. 6 and 1.4×10^{16} and 3.0×10^{15} cm⁻³ from the Hall effect measurement: The comparison between the two methods will be discussed in a forthcoming paper. We also measured various compensated Si crystals with B and P concentrations on the order of 10^{15} – 10^{17} cm⁻³. They were grown either by the Czochralski method or unidirectional solidification method in three groups in different countries. Essentially the same fine structure was observed from most of the samples, which will be reported in a separate paper.

The sample was immersed in liquid He in a quartz cryostat for PL measurements. We excited the sample with the 532 nm line of second harmonic generation of a Nd:YVO₄ laser with a beam diameter of about 3 mm. The incident power on the sample surface was 35 and 0.7 mW for high and low excitation conditions, respectively. Emission from the sample was analyzed with a monochromator ($f = 0.32$ m) with 300 and 600 grooves·mm⁻¹ gratings blazed at 1.2 μm and detected by a cooled InGaAs photodiode array. The spectral resolution was about 0.25 and 0.125 meV, depending on the grating used.

PL spectra from the sample under the low and high excitation conditions are shown in Figs. 1(a) and 1(b), respectively, where the spectral resolution was 0.25 meV. Three bands appeared under the low excitation condition with a similar shape having a tail on the high-energy side. The spacing between the highest and middle bands and that between the highest and lowest bands are in good agreement with the transverse acoustic (TA) phonon energy (19 meV) and the transverse optical (TO) phonon energy (58 meV). This allows us to conclude that the highest, middle and lowest bands are a no-phonon (NP) band and its TA and TO phonon sidebands, respectively. The peak positions of the three bands shifted equally to the high-energy side under the high excitation condition; this is characteristic of DA pair luminescence.^{1,2)} The peak positions of the three bands agree with the P-donor and B-acceptor pair (P–B pair) luminescence reported by Enck and Honig.³⁾ Based on these facts we conclude that the observed band is due to P–B pair luminescence. Two sharp lines at 1.1500 and 1.0920 eV and three broad bands at 1.145, 1.087 eV and vaguely at 1.125 eV can be observed under the high excitation condition in Fig. 1(b). They are assigned as the NP and TO bands of P-bound excitons,⁷⁾ denoted P_{NP}(BE) and P_{TO}(BE), and the NP, TO, and TA bands of the luminescence due to impurity associated localized carriers⁸⁾

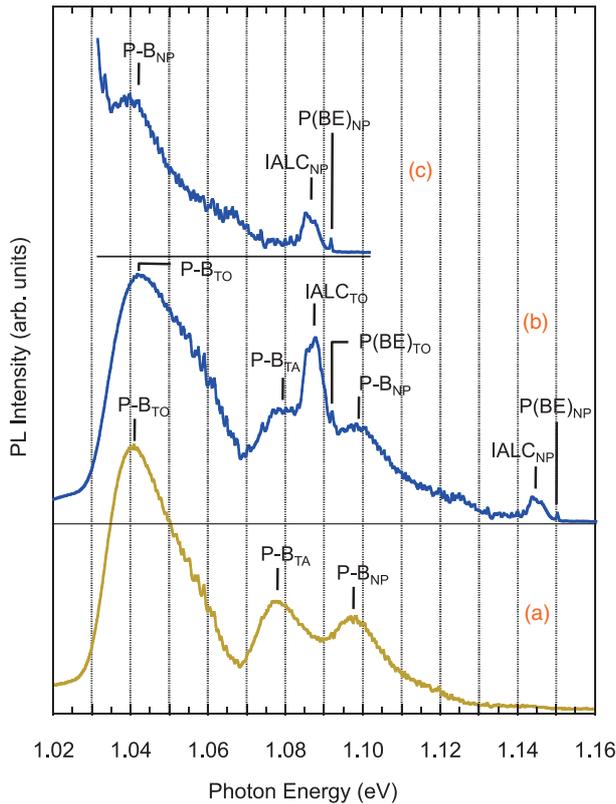


Fig. 1. PL spectra of compensated Si involving P donors and B acceptors at 4.2 K under (a) low and (b) high excitation condition. (c) NP band in (b) was shifted toward the lower energy side by TO-phonon energy (58 meV) and enlarged vertically by a factor of 1.5.

(IALC), respectively, from their peak positions. These bands will not be discussed further, since this is outside the scope of the present paper.

Now we focus on the fine structure in the high-energy tail of the NP and TO bands of the P–B pair luminescence. The shape of the structure of the NP bands, as clearly demonstrated by the comparison between Figs. 1(b) and 1(c), where the NP band in (b) was shifted toward the lower energy side by the amount of TO phonon energy and was enlarged vertically by a factor of 1.5 in (c). The structure appeared also under the low excitation condition in the NP and TO bands, as shown in Fig. 1(a). Figure 2(a) is an enlarged illustration of the high-energy side of the NP band in Fig. 1(b). Many narrow discrete bands are observable. The discrete line structure in the high-energy tail of the DA pair band is well explained by the theoretical spectrum, first in GaP¹⁾ and later on in many semiconductors²⁾ except for Si. We calculated the number of DA pairs in Si by analogy with GaP.¹⁾

The recombination energy of DA pair luminescence is given by

$$h\nu = E_G - (E_D + E_A) + \frac{e^2}{4\pi\epsilon_0\epsilon_r r} - \frac{a}{r^6}, \quad (1)$$

where E_G is the energy gap, E_D and E_A are the donor and acceptor ionization energy, ϵ_r is the low-frequency relative dielectric constant (11.7 for Si), and r is the DA pair separation. The last term in eq. (1) is the Van der Waals (VdW) interaction and a is a constant for a given DA pair.

The theoretical spectrum of DA pair luminescence is deduced as the number of possible DA pairings as a function of the transition energy given by eq. (1). Si has a diamond structure consisting of two interpenetrating fcc lattices, offset from one another by $(1/4, 1/4, 1/4)$, where we use the ordinate unit of a lattice constant. DA pairs within the same fcc lattice denote type I pairing, while those within the different fcc lattice type II pairing. The pair separation r for the two types of DA pairs is given by

$$r = \begin{cases} \left(\frac{1}{2}m\right)^{1/2} a_0 & \text{(type I),} \\ \left(\frac{1}{2}m - \frac{5}{16}\right)^{1/2} a_0 & \text{(type II),} \end{cases}$$

where m is a shell number for indexing the pair, the nearest neighbor pair having $m = 1$, the second nearest pair $m = 2$, and so on, and a_0 is a lattice constant (0.543 nm for Si).¹⁾ Number of pairs is calculated as a function of m for type I and type II. The DA pair is classified into type I and type II in compound semiconductors, depending on the substitutional sites of impurities. However, such classification is meaningless in the diamond structure, since the basis of the lattice consists of identical atoms. Therefore, the theoretical spectrum of DA pair luminescence in Si is the sum of the type I and type II spectra. The obtained theoretical spectrum is shown in Fig. 2(c), where the italicized numbers above several lines indicate m for type I. In the figure we adjusted the $[E_G - (E_D + E_A)]$ value and neglected the VdW term in eq. (1), which will be discussed in the next paragraph. The distribution of pairs is very dense. This is due to the mixture of type I and type II spectra and the small value of $(E_D + E_A)$ as a result of shallow levels, where only the distant pairs with large m contribute to the emission spectrum.

The widths of discrete narrow bands in Fig. 2(a) were on the order of 0.25–0.5 meV. We measured the spectrum under the twice-higher spectral resolution of 0.125 meV, but did not observe any substantial spectral narrowing, indicating that the observed curve reflected the real spectral shape at 4.2 K. Therefore, we could not make a one-to-one correspondence between the theoretical lines and the observed discrete bands as in the case of GaP. In order to make a realistic comparison between the theoretical and observed spectra we totalled the number of pairs in every 0.5 meV interval of photon energy, as shown in Fig. 2(b). The envelope curve of the bar graph corresponds to the pair density distribution against photon energy. Then, we were able to fit the theoretical graph to the observed spectrum by using the $[E_G - (E_D + E_A)]$ value as an adjustable parameter. Actually, the spectrum in Fig. 2(b) is the best-fitted one under the condition of

$$E_G - (E_D + E_A) = 1.0800 \text{ (eV)}. \quad (2)$$

The fine structure in the observed spectrum coincides with the theoretical curve as indicated by arrows, where we took into account the deviation due to the VdW term in eq. (1): The observed spectrum shifted to the lower energy side and the amount of the shift became larger for smaller m . Analysis of the systematic shift enables us to determine the constant a in the VdW term, which will be reported in a forthcoming paper. We could recognize a little discrepancy between the theoretical and observed spectra. Possible

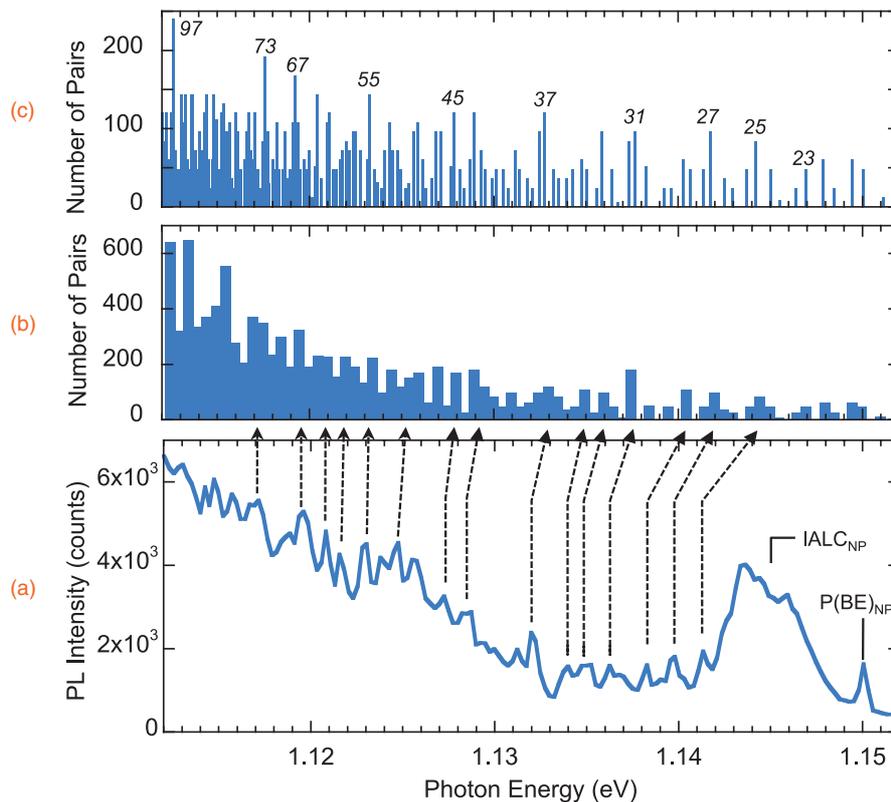


Fig. 2. Match between the observed fine structure of DA pair luminescence and theoretical distribution of DA pairs. (a) Higher energy side of P-B pair luminescence spectrum at 4.2 K under high excitation condition. (b) Density distribution of DA pairs against photon energy calculated from theoretical line spectrum in (c). (c) Distribution of DA pairs as a function of the transition energy of separated pairs. Numbers above several lines indicate the shell number, m for type I pairs. Theoretical spectra in (b) was best fitted to the observed spectrum in (a) under the condition of $E_G - (E_D + E_A) = 1.0800$ eV.

sources of the discrepancy are the disregard of the dependence of the transition probability on the DA pair separation, the difference in the density between the possible DA pair sites and the actual DA pair distribution, and the higher order complexity, such as inequivalent sites in a given m shell and the transition from excited states. The condition in eq. (2) is consistent with the generally accepted values of P donor, B acceptor ionization energies,⁹⁾ and band gap energy¹⁰⁾ ($E_D = 45$ meV, $E_A = 45$ meV, and E_G (0 K) = 1.1700 eV).

In conclusion, we have analyzed the fine structure observed in the higher energy side of P-B pair luminescence and identified its origin as being due to the discrete DA pair distribution. The successful observation of the discrete DA pair luminescence enables us to assign the species of donor and acceptor impurities accurately and to obtain their ionization energies. This also leads us to suggest the possibility of quantitative analysis of donor and acceptor impurities from the spectral shape analysis, considering that the pair distribution is dependent on the donor and acceptor concentrations. We believe that the observation of discrete DA pair luminescence will provide a great deal of useful

information for impurity analysis in the concentration range between 10^{15} and 10^{17} cm⁻³, which is important for the characterization of SOG-Si.

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Note added in proof—Since the acceptance of the present paper, one of the authors (MT) has noticed that sharp lines due to DA pairs involving deep In acceptors had been reported in the literature [U. O. Ziemelis and R. R. Parsons: *Can. J. Phys.* **59** (1981) 784]. He is grateful to Professor M. L. W. Thewalt for advising him of the reference.