

PHOTOLUMINESCENCE OBSERVATION OF DONOR PAIRS IN SILICON

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The asymmetric broadening with a tail on the lower energy side and the peak shift to lower energies are observed in the luminescence band due to bound excitons in silicon crystals which contain phosphorus impurities below the critical concentration for semiconductor-metal transition (8×10^{16} – $3 \times 10^{18} \text{ cm}^{-3}$). These behaviors are understood in terms of an exciton bound to a donor pair in silicon.

IN THIS LETTER we report observation of impurity associated recombination radiation from silicon which contains phosphorus impurities below the critical concentration for semiconductor-metal transition. As the impurity concentration is increased, it is found that the tail of luminescence band due to bound excitons appears on the lower energy side and the peak position shifts to lower energies. These characteristic properties of bound exciton luminescence are well understood by the model of pairing or clustering of donor impurities. Pairing and clustering of donors in silicon were firstly observed by electron paramagnetic resonance (EPR) measurements [1]. However, there have been no reports on pairing or clustering effects of donor atoms on luminescence, that is, a single exciton bound to a pair or cluster of donor impurities in silicon except for Nishino and his coworkers' recent suggestion [2] that a broad luminescence band observed in the same impurity concentration region might be due to excitons bound to impurity clusters.

The samples used were silicon single crystals grown by the Czochralski method with phosphorus concentration in the range 7×10^{15} – $3 \times 10^{18} \text{ cm}^{-3}$. Photoluminescence measurements were carried out at 4.2 K with a Parkin-Elmer E-1 type grating spectrometer, detected with an RCA 7102 S-1 photomultiplier tube cooled by dry ice. A continuous argon ion laser with a maximum output of 1 W at 5145 Å was used as an excitation light source. The laser light irradiated the sample over a spot 5–10 mm in diameter and the intensity was decreased by a neutral filter to avoid generating electron-hole droplets which were observed under high excitation.

Figure 1 shows typical spectra of luminescences due to annihilation of excitons (BE) bound to neutral donor impurities with simultaneous emission of transverse optic (TO) phonon for various samples. TO phonon side bands which have the largest luminescence efficiency are shown here, though no-phonon lines also

have the similar shapes. Below the impurity concentration of $1 \times 10^{16} \text{ cm}^{-3}$, the peak position and the half width of the BE_{TO} luminescence do not change even by varying the impurity concentration. Around $8 \times 10^{16} \text{ cm}^{-3}$, the tail of the peak appears in the longer wavelength region and becomes larger with the increase in phosphorus concentration. Above $1 \times 10^{17} \text{ cm}^{-3}$, the peak position begins to shift to lower energies and the line shape tends to become more symmetrical as the concentration is increased.

As the excitation intensity is increased, the luminescence due to electron-hole droplets appears and rapidly grows up as shown in Fig. 2. The line shape with the tail of BE_{TO} component does not seem to be changed by the variation of the excitation intensity.

Figure 3 shows the peak positions of the bound exciton, BE_{TO} , and the electron-hole droplets, EHD_{TO} , against the phosphorus concentration. In this figure, the luminescence intensity ratio of the no-phonon (NP) band to the TO side band is also plotted as a function of the impurity concentration. It is interesting that the relative intensity of the NP band decreases with the increase in the phosphorus concentration in the range where the tailing and the peak shift of the BE line are observed. When excitons are tightly bound to impurities and are localized in the real space, it is well known that the transition probability without phonon emission is strong and that the nitrogen center in GaP is a typical example of this effect [3]. The decrease of the relative intensity of the NP line observed here, therefore, suggests that the exciton tends to be delocalized from the impurity site in this concentration region.

The two characteristic properties of the BE line, i.e. the asymmetrical broadening with a tail on the lower energy side and the peak shift to lower energies, are discussed here based upon a model of pairing of donor impurities. From EPR studies [2], it is known that at low concentrations the donor electrons are

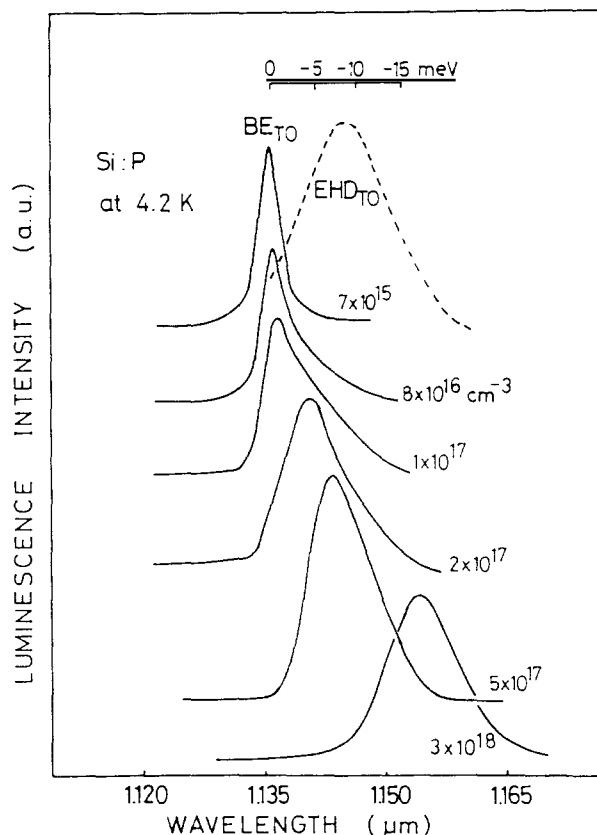


Fig. 1. Luminescence spectra due to annihilation of excitons (BE) bound to neutral donor impurities with simultaneous emission of transverse optic (TO) phonon for various samples. The spectrum due to electron-hole droplets observed at lower concentration and under high excitation is also shown as comparison.

localized on the donor atoms without interacting each other, so that they give rise to two hyperfine lines due to P^{31} nuclei. When the donor concentration is above $6 \times 10^{16} \text{ cm}^{-3}$, the exchange-coupled pair lines appear between the two lines. With the increase in the donor concentration various kinds of clusters become to be formed, which results in the formation of other discrete lines and also a broad asymmetric line superimposed over the lines in the EPR spectrum. The fact that the impurity concentration region where the tailing and the peak shift are observed in the luminescence spectrum corresponds well to the EPR result suggests that they have some correlation with the formation of pairs and clusters of donor impurities.

As for donor levels, it is well established [4] that when a pair of donor atoms are considered, this pair can be treated as a hydrogen-like molecule and bonding and antibonding states are formed in the analogical sense of the molecular orbital theory. The bonding gives rise to the increase of the ionization energy of donors. This fact enables us to conjecture that the pairing of donor

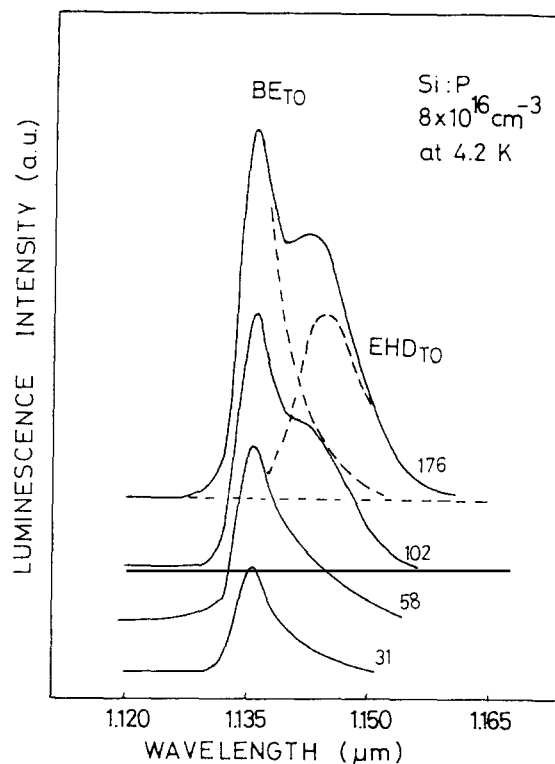


Fig. 2. The excitation intensity dependence of the luminescence spectra of the sample with phosphorus impurities of $8 \times 10^{16} \text{ cm}^{-3}$. Figures stand for the relative intensity of excitation light.

atoms also causes the increase of binding energy of excitons. In the system consisting of two neutral donors and an exciton, the exciton can be transferred between paired donor atoms if the distance between donor impurities are sufficiently small. Due to this transferring effect, the binding energy of the exciton is increased in the analogous way to the impurity band conduction [5]. The transfer energy increases as the separation between donors decreases. As will be shown by Narita in the following paper [6], the formation probability of pairs with energies of several meV is not small in the impurity concentration region where the band tail and the peak shift of the BE luminescence are observed. So, it is likely that the band tail is due to pairing of donor atoms and that the peak position of the BE line shifts to lower energies when the impurity concentration is high enough and the amount of pairs becomes large. The theoretical and quantitative discussion on this model will appear in detail in the following paper [6].

Transferring between paired impurities means that the exciton becomes to be loosely bound to impurities compared with the normal exciton bound to isolated donors at low impurity concentration and is delocalized from one donor site. This is consistent with the fact that the ratio of the NP band to the TO side band decreases

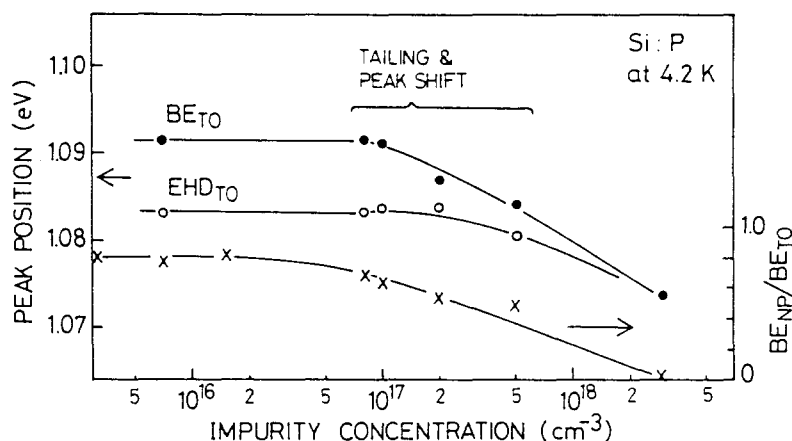


Fig. 3. Peak positions of bound excitons (●) and electron-hole droplets (○), and relative intensity of no-phonon (NP) band to the TO side band (×) of bound excitons as functions of impurity concentration.

in this phosphorus concentration region. The formation of clusters of three or four donor impurities which are also observed by EPR measurements [2] is more favorable to the tailing and the peak shift of the BE luminescence line.

Kukimoto and his co-workers [7] report that the binding energy of excitons of CdS in the same donor impurity concentration region, i.e. below the Mott transition, decreases with the increase in the impurity concentration and that the emission line due to bound excitons shows asymmetric broadening with a tail extending to lower energies at high donor concentration. They explain these properties in terms of screening effect of donor electrons and Stark effect due to charged impurities on excitons. In the case of bound excitons in silicon, however, the emission line shifts to lower energies, which is opposite to that of CdS, and the compensation ratio which is a very important and sensitive factor for Stark effect is much smaller in silicon than in CdS. So, it is very difficult to explain the properties of bound excitons in silicon by the same model for CdS.

The luminescence at the critical concentration $n_c \approx 3 \times 10^{18} \text{ cm}^{-3}$ for the semiconductor-metal transition differs from other samples in several ways. First of all, the line shape does not change when the excitation intensity is varied by several orders of magnitude, while other samples show the change of line shape due to the generation of electron-hole droplets. The peak position shifts to higher energies as the excitation intensity is increased. The energy shift is about 1.5 meV when the intensity is changed by three orders of magnitude. The luminescence intensity linearly increases as a function of excitation intensity, while the electron-hole droplets increases super-linearly in other samples. Moreover, the NP line is hardly observed at this concentrations. As for the origin of this luminescence, it

should be pointed out that the pairing model cannot be applicable any more in this concentration region, since donors are not isolated and the impurity band is formed. The fact that the NP line is not observed suggests that excitons are not localized at impurity sites and it is consistent with the formation of the impurity band. Parsons and his co-workers [8] say that this luminescence is also due to electron-hole droplets in doped silicon crystals. However, the peak shift and the linearity of the excitation dependence indicate that this luminescence is rather due to the transition of electrons in the impurity band to the valence band as proposed by Martin and Sauer [9]. More precise experiments are necessary to clearly identify the luminescence.

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