PROC. 15TH INT. CONF. PHYSICS OF SEMICONDUCTORS, KYOTO, 1980
J. PHYS. SOC. JAPAN 49 (1980) SUPPL. A p. 173–180

D^- STATES IN GERMANIUM AND SILICON

Shin-ichiro Narita

Department of Material Physics
Faculty of Engineering Science
Osaka University
Toyonaka, Osaka 560
Japan

By means of long-wavelength photoconductivity, isolated D^- states and D^- complexes in Ge and Si have been investigated. The temperature-, uniaxial stress- and magnetic field-dependences of the photoconductivity spectra have clarified several types of the many valley effects and the electron- and spin-structures of the D^- states and D^- complexes.

I. Introduction

In 1958, Lampert [1] predicted the existence of D^- ion in semiconductors, in which two electrons are captured by a positively charged donor ion, like a hydrogen negative ion, H^-.

The binding energy of the second electron in H^- has been actively calculated variationally by many authors and the value has been found to converge to 0.0555Ry with increasing the variational parameters.

As the analogy with H^-, the predicted value of the D^- electron binding energy by Lampert was 0.055Ry* (effective Rydberg) for semiconductors, which corresponds to $\sim$0.54meV for Ge and $\sim$1.7meV for Si.

The first report of the observation of D^- center was published by Dean et al. [2] who found corresponding peaks in the emission spectra of Ge and Si. Their estimated energies of the second electrons in the D^- centers are $\sim$1.5meV for Ge and $\sim$4meV for Si, which are about three times as large as the predicted values.

The direct observations of the energies were done by Gershenzon et al. [3] using BWT for Ge and Si. They measured the submillimeter photoconductivities. Their obtained binding energies were also larger than the theoretical ones.

It was found afterwards that these large binding energies are associated with the complex-formation of the D^- center, so that the true value of the binding energy can be obtained only by preparing the isolated state of the D^- center using the sample with possibly smaller impurity concentration.

II. Isolated D^- States and Uniaxial Stress Effects

The long-wavelength photoconductivity measurements for isolated D^- state in P-doped Si were first performed by Norton [4] and our group [5] independently by using Michelson type and lameller grating type Fourier transform interferometers, respectively, and they first observed the reasonable spectral shape of the D^- state resembling that of H^-. They confirmed that the threshold of the photoconductivity spectra does not change at the impurity concentrations less than 1×10^{15} cm^{-3}P and concluded that the threshold energy of $\sim$1.7meV must be the second electron binding energy for the isolated D^- state in

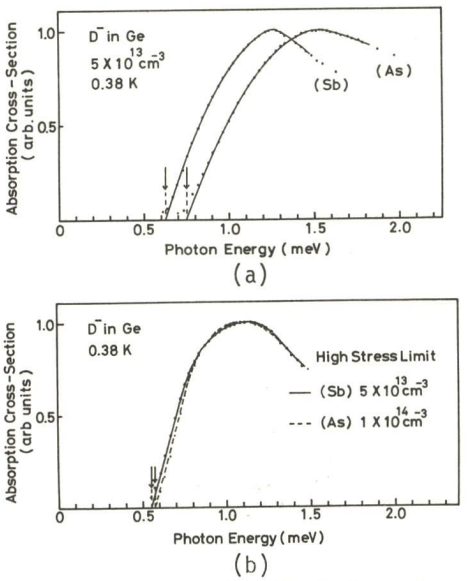

Fig.1 Long-wavelength photoconductivity spectra of D^- states in Sb- and As-doped Ge: (a) of stress free and (b) under high stress

P-doped Si.

On the other hand, it was supposed that the measurement of the very small binding energy of D^- electron in Ge ($\sim$0.54meV) is possible only at very low temperature with very small impurity concentration($<9\times10^{13}$ cm^{-3}). The long-wavelength photoconductivity experiments were done at 0.38K with the samples of $5\times10^{13}cm^{-3}$ Sb and As concentrations by using ^3He cryostat [6].

Figure 1(a) shows the photoconductivity spectra without stress. The threshold energies are appreciably smaller than those reported before and near the predicted value. The experimental values are 0.625meV for Sb and 0.75meV for As.

In the measurements for Si, similar chemical shift to the Ge case was found between P and As impurities: The threshold of the FIR photoconductivity of D^- state in As-doped Si was $\sim$2.0 meV, which is about 0.3meV larger than that in P-doped Si (see Fig.2).

The measurements for Ge under high [111]-uniaxial stress more than 2×10^9 dyn/cm^2 were done by a screw method [6] and gave the second electron binding energy of $\sim$0.55meV both for Sb and As impurities, as shown in Fig.1(b), which is in a good agreement with the predicted value for Ge.

The theoretical considerations on the D^- state in many valley semiconductors and those in the high stress limit have been done by Natori and Kamimura [7], taking the anisotropy of the orbits into account, but they neglected the electron-correlations. Therefore the calculation gave a little smaller binding energy than expected.

It is well known that a Si crystal behaves as a semiconductor with two valleys at the [100]-uniaxial stress limit. In our experiment [5] an appreciable shift of the photoconductivity threshold was observed with increasing the [100]-stress at 1.5K down to about 0.7meV and in a recent experiment at very low temperature, it was confirmed that the finite value at 0.35K under high stress of about 2×10^9 dyn/cm^2 is $\sim$1.1meV both for P- and As-doped Si and $\sim$1.5meV for Li-doped Si as shown in Fig.2.

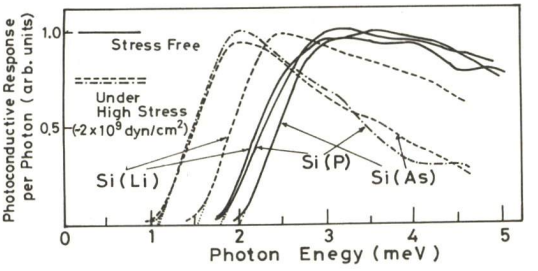

Fig.2 Long-wavelength photoconductivity spectra of D^- state in P- , As- and Li-doped Si of stress free (solid curves) and under [100]-stress of $\sim2\times10^9$ dyn/cm^2 (broken curves)

To understand the curious energy shifts of the thresholds down to about a half of the predicted value in Si, Larsen [8] gave a theory including the following assumption: i) The central cell correction due to the short range core-pontential is limited to the inner orbit. ii) The effect of the stress on the population of

the electrons in the valley-orbits is stronger for the outer orbit compared with the inner orbit. iii) An isotropic mass tensor for the orbits is assumed. He caluculated the D^- electron binding energy for P- and As-doped Si as a function of the [100]-stress using the spherical envelope function of Chandrasekhar [9] given by

$$[\exp(-\alpha r_1-\beta r_2) + \exp(-\alpha r_2-\beta r_1)](1+c|r_1-r_2|). \quad (1)$$

In his calculation, the binding energy of the second electron in D^- state in P- and As-doped Si is reduced to about 40% of the initial value and recovers to more than 90% of the initial one at the high stress region. The reduction may be larger for As-doped Si and smaller for Li-doped Si compared with P-doped Si, because of the difference of the valley orbit interactions in these dopants. These theoretical results can well explain the experimental results of the stress effects on the shift of the threshold for P-, As- and Li-doped Si. Similar reduction of the binding energy by applying stress was observed for isolated A^+ states in B-doped Si [10].

III. Magnetic Field Effects

i) Single valley case

The D^- state is frequently compared with H^-. Because of the isotropic nature of the electron mass in H^-, various calculations for H^- have been done more actively than for D^-. Two electrons captured by a proton are known to be in the spin-singlet state and H^- has only one bound state in the absence of magnetic field.

The analogy with H^- is probably well applicable to the highly [111]-stressed Ge with small impurity concentration. Since the measurements are done at very low temperature for Ge and the spins of the electrons in the isolated donors and the conduction band are strongly polarized in the magnetic field, the probability of two electrons being in the D^- state, the density of the D^- center, n_{D^-}, is largely reduced by the application of the following formula [11, 12]:

$$n_{D^-} = \frac{N_D}{2+\sqrt{\Lambda}} - \frac{N_A}{2}, \qquad \text{with} \quad \Lambda = \frac{\sigma^+ g}{\sigma_0 (1-P_0^2) G}, \qquad P_0 = \tanh\left(\frac{g^* \mu_0 H}{2kT}\right), \quad (2)$$

where N_D and N_A are the densities of donors and acceptors, G and g the rates of the photo-excitations from the neutral donor, D_0, and the D^- state to the conduction band, respectively, σ^+ and σ_0 the recombination cross-sections of D^+ and D_0 for the conduction

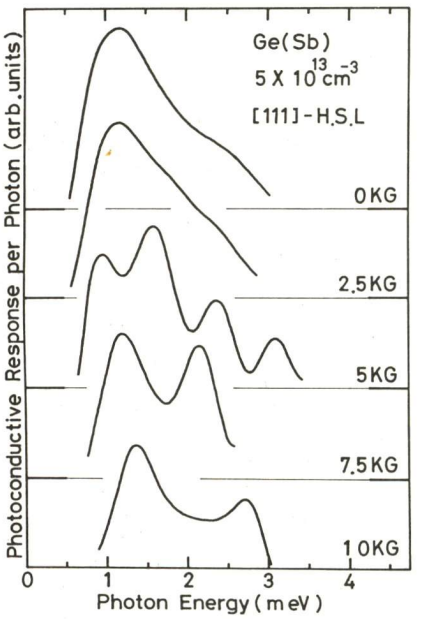

Fig.3 Magnetic field dependence of long-wavelength photoconductivity spectra of isolated D^- state in Sb-doped Ge under sufficiently high [111]-stress at 0.35K (H// I// [111])

electrons, and g* the effective g-value.

The experiments have been performed using Ge samples with 5×10^{13} cm^{-3}Sb. We used a specially designed ^{3}He cryostat with Helmholtz-type superconducting solenoid [11]. The results of the long-wavelength photoconductivity are shown in Fig.3, (H// I// [111]). With increasing the magnetic field, the photoconductivity intensity decays according to eqs.(2) and the threshold shifts to higher energies. At higher magnetic fields than ∿5kG, the main peak at 0kG splits into several peaks and the spacings between adjacent peaks are found to accurately coincide with the Landau level splittings of the conduction band, $\hbar\omega_c$, calculated by using the transverse mass, $m_t=0.082m_0$ (m_0: the free electron mass). In this case the first peak from the low energy side is largest among the observed peaks.

The theoretical investigations on D^- state in magnetic fields in a variational approximation have been done by Natori and Kamimura [13] and by Larsen [14]. The magnetic freeze-out effect was calculated for the spin-singlet state assuming a spherical energy surface. Natori and Kamimura used the YKA type trial functions and Larsen assumed the Chandrasekhar type envelope function (1) for his special calculation method. The experimental shift of the binding energy was compared with the theoretical one and the former was seen to be almost parallel to the latter.

They also theoretically studied the excited states of D^- in magnetic fields and found that the higher the magnetic field becomes, the more excited states are bound, including the spin-triplet states etc. They assumed a spherical energy surface as in H^-. The experiments of D^- state in sufficiently high magnetic fields up to 8T were performed with Ge samples with 5×10^{13} cm^{-3} Sb under high [111]stress. However, we could not observe the signal due to the spin-triplet state, probably being disturbed by the large magneto-resistance.

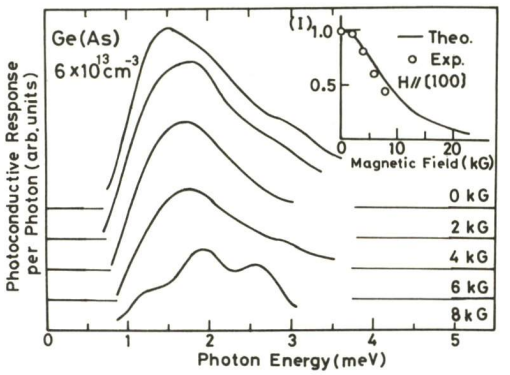

Fig.4 Magnetic field dependence of long-wavelength photoconductivity spectra of isolated D^- state in As-doped Ge of stress free (many valleys) at 0.35K (H// I// [100]). In the inset the theoretical and experimental decays of the photoconductivity are shown, wehre g* is chosen to be 1.56. The photoconductivity intensities are normalized by the aid of 1s-C.B. excitation spectra of the donor

ii) Many valley case

In the experiments, the directions of the magnetic field and the photocurrent must be parallel to the [100]-crystal axis, because the four valleys in Ge should be equivalent in the measurements.

Figure 4 shows the magnetic field dependence of the long-wavelength photoconductivity in a Ge sample of stress free with 6×10^{13} cm^{-3}As at 0.35K. At high magnetic fields you can also see the peak splittings. In this case, the photoconductivity intensity also decays with increasing the magnetic field, as in the case of stressed Sb-doped Ge, according to eqs.(2). The inset of Fig.4 shows the comparison of the decay aspects between the theoretical result and the experimental one.

On the other hand, the photoconductivity in Sb-doped Ge sample of stress free with the impurity concentration of 5×10^{13} cm^{-3} does not show any remarkable change

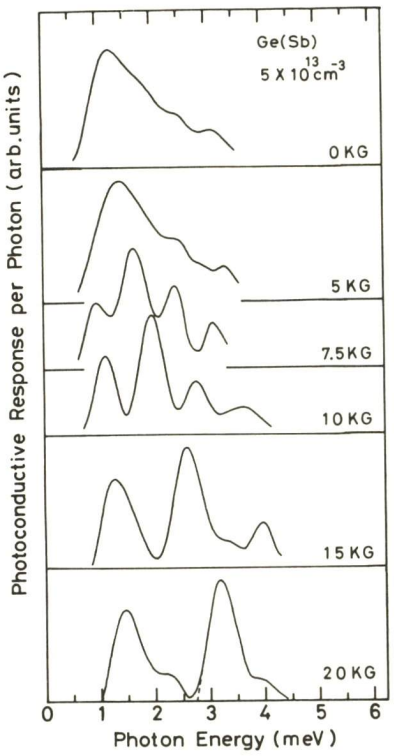

Fig.5 Magnetic field dependence of long-wavelength photoconductivity spectra of isolated D^- state in Sb-doped Ge of stress free (many valleys) at 0.35K (H// I// [100])

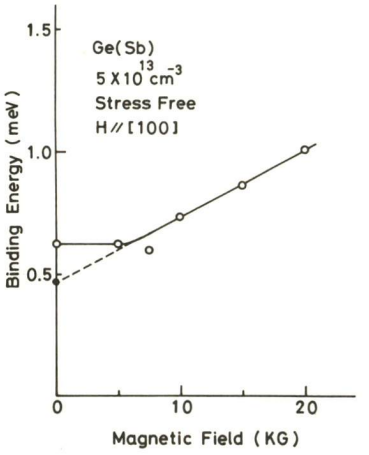

Fig.6 Spin-singlet to triplet transition

with the magnetic field in the configuration of H// I// [100] as shown in Fig.5. Also in this case, the main peak clearly splits into several peaks at higher magnetic fields than ∿7.5kG. The spacings between the peaks just coincide with $\hbar\omega_c$, if we use the mass derived from the curvature of the conduction band energy surface in the [100]-direction ($0.135m_0$). However the highest peak in this case is the second peak from the low energy side.

The difference of the spectral behavior of the D^- state in Ge of stress free in magnetic fields between Sb- and As-doped crystals is supposed to be ascribed to the difference of the valley-orbit interaction effect on the D^- center between Sb and As.

In many valley semiconductors even in the absence of magnetic field the bound state is not necessarily limited to the single one. In other words, several excited states including spin-triplet states may be bound as suggested by Natori and Kamimura [7]. Supposing from the one-electron state of donors, the valley orbit interaction in the D^- electron in As-doped Ge must be so strong that the spin-triplet ground state is appreciably high from the spin-singlet ground state.

On the contrary, in the case of Sb-doped Ge of stress free, the valley-orbit interaction is small enough that the spin-triplet state is also bound and located at just above the spin-singlet state even at zero magnetic field. By applying strong magnetic field the lowest state alternates from the spin-singlet state to the spin-triplet one. Then non-decay of the photoconductivity can be observed.

Figure 6 shows the change of the long-wavelength photoconductivity threshold obtained from Fig.5. The bending point at about 6kG may be interpreted as the spin-singlet to triplet transition point. The extrapolation of the triplet line to 0kG gives the location of the triplet state at zero magnetic field (∿0.155meV above the spin-singlet state).

The assumption of the direct transition from the lowest D^- state to the conduction band-Landau levels may well

explain the peak splittings having accurate coincidences with $\hbar\omega_c$.

In the case of Ge samples of stress free (many valleys), we have found in Fig.5 that the second peak in the spectra is largest, compared with all other peaks observed. This experimental fact can be explained considering the selection rules [11, 15] for the e_+, e_- and e_z excitations of the electrons from the D^- ground state to the Landau levels of the conduction band, where e_+ and e_- mean the excitations by the right and left handed circularly polarized light and e_z by the z-direction polarized light. In the experiments the pointing vector of the incident light was directed to the z-direction and perpendicular to the magnetic field. On the other hand, in the case of [111]-stressed samples, the largest peak was the first one from the low energy side as seen in Fig.3. In this case we must take into account that the D^- wave-function is almost confined into the plane perpendicular to the magnetic field by the stress.

IV. D^- Complexes

What kind of variations in the long-wavelength photoconductivity spectra of the D^- state can be observed with increasing the impurity concentration? Figures 7 and 8 show the impurity concentration dependences of the spectra of Sb-doped Ge at 0.38K and those of P-doped Si at 1.5K. Both the spectra shift to higher energies with increasing the concentration, though the changes seem to occur by steps at their beginnings; that is, the lower energy peak gradually decreases as the higher energy peak increases. Considering the behaviors of the spectra, the phenomena cannot be understood by a mechanism of a continuous change [12].

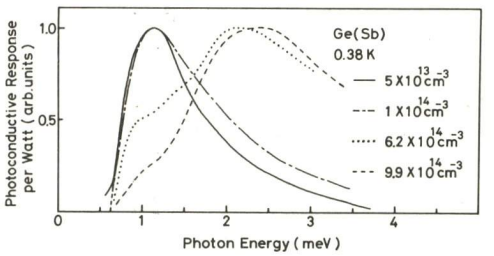

Fig.7 Impurity concentration dependence of the photoconductivity spectra of D^- states in Sb-doped Ge at 0.38K

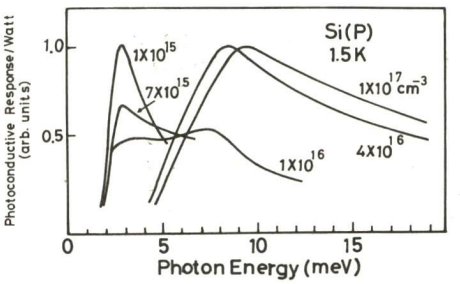

Fig.8 Impurity concentration dependence of the photoconductivity spectra of D^- states in P-doped Si at 1.5K

Norton at first assumed D_2^- formations in P-doped Si [16], in which D_2^- means an electron state bound to two neutral donors. On the other hand, Aleksandrov et al. proposed a mechanism for the change of the spectra of A^+ states in B-doped Si [17]. For convenience in the present discussion, we replace the A^+ state in their paper with D^- state. In their model, a D^- electron may move up to a neutral donor, D_0, nearest to a D^+ center by hopping, then the binding energy of the D^- electron increases by the Coulomb field due to the D^+ center.

In order to clarify the mechanism of D^- complex formation at the first stage, we performed two kinds of experiments: the temperature dependence and magnetic field effect of D^- complex spectra [18, 11].

i) Temperature dependence:

The samples used for this experiment are classified into two groups. The impurity concentrations of the first group-samples

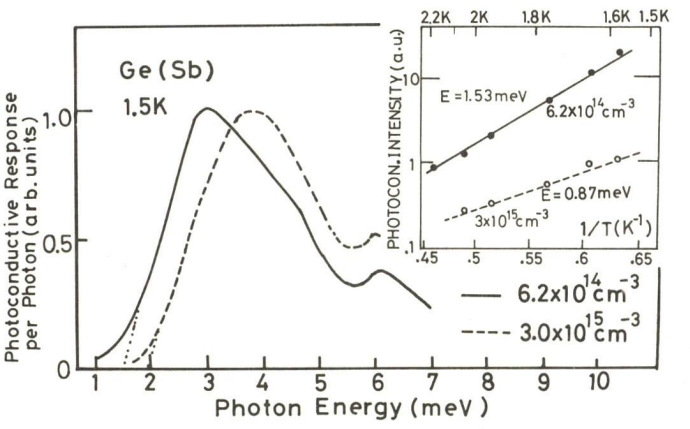

Fig.9 Long-wavelength photoconductivity spectra of D^- complexes in Ge samples with 6.2×10^{14} cm^{-3} and 3.0×10^{15} cm^{-3} Sb. In the inset, the photoconductivity intensity vs. reciprocal temperature curves represent the apparent thermal activation energies are in the range of $4\sim9\times10^{14}$ cm^{-3}Sb. Around the concentration of 4×10^{14} cm^{-3}Sb the D^- states begin to form D^- complexes judging from the results in Fig.7. The concentrations of the second group are more than 1×10^{15} cm^{-3} Sb. The thermal activation energy obtained from the photoconductivity intensity vs. reciprocal temperature curve for one of the samples of the first group agrees well with the threshold energy of the photoconductivity spectra as shown in Fig.9, while for a sample of the second group, the apparent thermal activation energy becomes appreciably smaller than that of the first group, though the threshold shifts to a higher energy as shown in the figure.

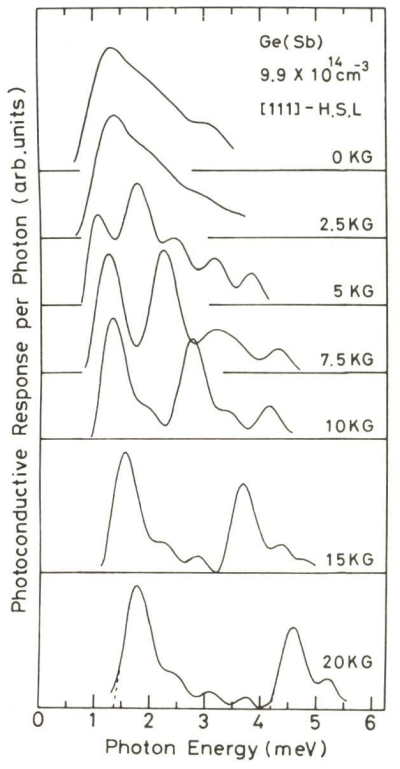

Fig.10 Magnetic field dependence of the photoconductivity spectra of D^- complexes in Sb-doped Ge under high [111]-stress (single valley) at 0.35K (H// I// [111])

It can be easily shown from the rate equation of the recombination of the D^- electron to a D^+ center that the apparent activation energy becomes smaller than the true value of the activation energy, if the direct recombinations of D^- electrons to D^+ centers occur, and the agreement of the thermal activation energy with the threshold energy gives a strong evidence for few recombination probabilities of D^- electrons to D^+ centers [18]. Therefore, this result denies the dominant existence of D^--D^+ pairs in the crystals at the first stage of the D^- complex formation.

ii) Magnetic field Effects:

Figure 10 shows the magnetic field dependence of the long-wavelength photoconductivity spectra of Sb-doped Ge with a relatively high impurity concentration of 9.9×10^{14} cm^{-3} under sufficiently high [111]-stress at 0.35K, (H// I// [111]). (This concentration belongs to the first group under high [111]-stress).

In this case, the photoconductivity intensity does not show any remarkable decay with increasing the magnetic

field. The decay was seen in the isolated D^- state under high [111] -stress as shown in Fig.3. Similar result was obtained for As-doped Ge of stress free with 6×10^{14} cm^{-3} impurity concentration.

Assuming the model proposed by Aleksandrov et al. the photoconductivity intensity must decrease with increasing the magnetic field, because, in the D^--D^+ structure, the two electrons in the D^- center must be also in the spin-singlet state. This is not the case of the present experiment shown in Fig.10. Therefore, at least, in the first stage of complex formation, D^--D^+ pairs as Aledsandrov et al. advocated can not be dominantly formed, and the model of D_2^- state seems to be preferable. However, one question arises considering the analogy with H_2^-. In the case of H_2^-, the energy stabilization by forming the molecule is about 20% of the initial binding energy of H^-, while in the experiment of D^- complex, the threshold shift of the D^- state in Sb-doped Ge with increasing the impurity concentration from 5×10^{13} cm^{-3} to 9.9×10^{14} cm^{-3} is appreciably large; that is, from 0.55meV to $\sim$1.2meV (see the threshold of the large peak in Fig.7). Similar large shift is seen in P-doped Si as shown in Fig.8 (from 1.7meV to 3.8meV). To explain these large discrepancies, we may present a speculative model of the many valley effect on the D_2^- state; that is, the three electrons captured by two positively charged donor ions are stabilized in energy by belonging to three different valleys.

Considering the above results, for the impurity concentrations over 2×10^{15} cm^{-3} in Sb- or As-doped Ge, (or over 1×10^{17} cm^{-3} in P-doped Si), D^+ centers seem to have a great effects on the structure of D^- complex. In large impurity concentrations, we must take more complicated model for the D^- complexes, including the assembly of D^+ centers and D_n^- centers, etc.

The author would like to express his sincere thanks to his cooperators in this study; M. Taniguchi, M. Kobayashi, M. Hirano, N. Sugimoto, T. Okamoto, N. Hasegawa and T. Shinbashi.

References

1) M.A. Lampert: Phys. Rev. Lett. 1 (1958) 540.
2) P.J. Dean, J.R. Haynes and W.F. Flood: Phys. Rev. 161 (1967) 711.
3) E.M. Gershenzon, C.N. Gol'tsman and A.P. Mel'nikov: Pis'ma Zh. Eksp. Teor. Fiz. 14 (1971) 281 (JETP Lett. 14 (1971) 185).
4) P. Norton: Phys. Rev. Lett. 37 (1976) 164.
5) M. Taniguchi and S. Narita: Solid State Commun. 20 (1976) 131.
6) M. Taniguchi and S. Narita: J. Phys. Soc. Japan 43 (1977) 1262.
7) A. Natori and H. Kamimura: J. Phys. Soc. Japan 43 (1977) 1270.
8) D.M. Larsen: private communications.
9) S. Chandrasekhar: Astrophy. J. 102 (1945) 395.
10) N. Sugimoto, S. Natita, M. Taniguchi and M. Kobayashi: Solid State Commun. 30 (1979) 395.
11) M. Taniguchi and S. Narita: J. Phys. Soc. Japan 47 (1979) 1503.
12) M. Taniguchi, S. Narita, N. Hasegawa and M. Kobayashi: J. Phys. Soc. Japan 45 (1978) 545.
13) A. Natori and H. Kamimura: J. Phys. Soc. Japan 44 (1978) 1216.
14) D.M. Larsen: Phys. Rev. Lett. 42 (1979) 742.
15) A. Natori and H. Kamimura: J. Phys. Soc. Japan 47 (1979) 1550.
16) P. Norton: J. Appl. Phys. 47 (1976) 308.
17) V.N. Aleksandrov, E.M. Gershenzon, A.P. Mel'nikov, R.I. Ravinovich and N.A. Serebryakova: Pis'ma Zh. Eksp. Teor. Fiz. 22 (1975) 573. (Soviet Physics-JETP Letters 22 (1975) 282).
18) M. Taniguchi, M. Hirano and S. Narita: Phys. Rev. Lett. 35 (1975) 1095.