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D^- STATE IN SILICON

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D^- state in phosphorus-doped silicon has been studied by means of long-wavelength (submillimeter plus millimeter) photoconductivity measurements. The concentration dependence of the D^- state spectra indicates the transition from an isolated D^- state to a state of an electron bound to more than one neutral donors, D_n^-. A [100] stress experiment reveals the effect of the donor core potential on the D^- state.

D^- (or A^+) states in semiconductors have recently attracted strong interest among semiconductor researchers, associated with various properties of the impurity states. We have studied the D^- states in Ge by measuring the long wavelength photoconductivities in doped Ge in a spectral region from 100 μm to 3 mm, and in the experiments of Sb-doped Ge under [111] stress, we obtained an indisputable evidence of the existence of D^- states in Ge.[1,2] The present experiments have been performed to extend the above method to the study of D^- states in Si.

The submillimeter photoconductivity in doped Si was first measured by Gershenzon *et al.*[3,4] who used backward wave tubes, and recently studied by Norton using a Michelson type Fourier transform spectrometer.[5] According to Gershenzon[4] the photoconductivity spectrum of P-doped Si has the maximum at about 2.3 meV. In his paper, the impurity concentration is not accurately described, though it is indicated in the figure caption as 10^{14}–10^{15} cm^{-3}. On the other hand, Norton measured the photoconductivity in Si with 4×10^{16} cm^{-3} P and estimated the electron binding energy of the D^- state to be 3.7 meV which is very close to that found by Dean *et al.*,[6] and he also suggested that the D^- state energy must asymptotically approach to ~ 2 meV with decreasing concentration.

In the present experiments, we measure long-wavelength photoconductivities of P-doped Si samples with various impurity concentrations at 1.5–4.2 K. According to the spectral region, we employ alternatively a lamellar grating Fourier transform spectrometer and a Michelson type one.

Figure 1 shows the submillimeter photoconductivity spectrum for P-doped Si with a small donor concentration of 1×10^{15} cm^{-3} at 1.5 K.

We have determined electron affinities of D^- states in Ge by the following three methods.

(i) The first one by measuring the temperature dependence of the intensity of the photoconductive response was applied to relatively pure Ge samples without stress.[1]

(ii) The second one by extrapolating the low energy slope of the photoconductivity peak was employed for the relatively pure Ge without stress[1] and under stress.[2]

(iii) The third one by fitting the photoconductivity per photon curve of the D^- state to the theoretical absorption cross section curve of H^- calculated by Chandrasekhar[7] was used for relatively pure Ge under stress.[2]

These three methods gave results consistent with one another, so that the second method has been employed for the electron affinity determination of the D^- state in Si giving the energy to be ~ 1.7 meV for 1×10^{15} cm^{-3} P. The curve fitting mentioned above as the third method is shown in the inset of Fig. 1, where the threshold is assumed to be 1.73 meV. However, it is to be noticed that there exist a many valley effect in the D^- state of Si without stress.[2] Therefore, it is not obvious whether the analogy of the D^- state to the H^- can hold in this case or not.

The upper part of Fig. 2 shows the concentration dependence of the photoconductivity spectra in P-doped Si. With increasing the donor concentration [(a) 1×10^{15} cm^{-3} to (b) 7×10^{15} cm^{-3}], the higher energy component of the spectrum increases, and further increase of the concentration results in an appearance of the photoconductivity maximum at the higher energy region [(c) at ~ 8 meV], and then the spectra shift to the higher energy side for concentrations above 4×10^{16} cm^{-3} (d and e). The spectrum for the small donor concentration (1×10^{15} cm^{-3}) is believed to correspond to isolated D^- states, because further decreases in donor concentrations does not change the spectrum of a. The spectra, b, c, may be explained by the assumption of the coexistence of D^- states and D_n^- states. The latter implies the state of an electron bound to n neutral donors ($n \geqq 2$). The coexistence can be verified by the measurement of the temperature dependence of the spectrum c, as shown in the lower part of Fig. 2. In the figure, all the spectral curves are normalized at the maxima of the curves. With increasing temperature from 1.5 to 2.1 K the lower energy component decreases and vanishes.

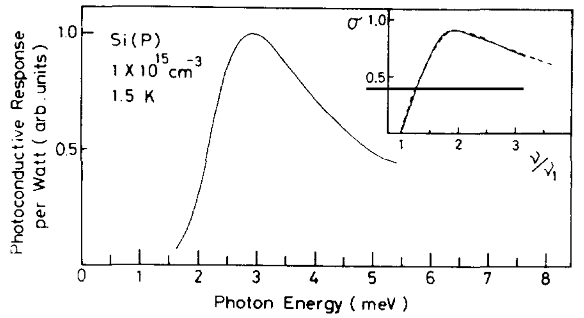

Fig. 1. Submillimeter photoconductivity spectrum of P-doped Si of low impurity concentration. The inset shows the comparison of the photoconductivities per photon (solid curve) with the theoretical absorption cross sections of H$^-$ (dotted curve), where the frequency ν divided by the threshold frequency ν_1 is chosen as the abscissa and the maximum heights of both the curves are normalized to unity.

This result may be interpreted as follows. The quasi-Fermi level of the electrons is situated right below the D^- state and therefore the electron population in the D^- state is strongly affected by the temperature change, while that of the deep D_n^- state is almost unchanged.

Uniaxial compressive stress experiments are carried out for the study of the many valley effect on the isolated D^- state in Si. By applying stress parallel to the [100] crystalline axis, the six conduction band valleys become inequivalent in energy; that is, the energy of the two valleys with the principal axis of the energy-ellipsoid parallel to the [100] stress is lowered, while the other four valleys are equally elevated in energy. Thus, the conduction electrons are accumulated into the two [100] valleys.

The energy separation between the bottoms of the two [100] conduction bands and those of the other conduction bands is given by

$$\Delta E_c = X(s_{11} - s_{12})\Xi_u, \qquad (1)$$

where X is the magnitude of stress, s_{ij} are the elastic compliance constants and Ξ_u is the shear deformation potential constant. By using the known parameters for Si, we see that the energy separation of 1 meV is brought by applying stress of 1.13×10^8 dyn/cm^2. The upper part of Fig. 3 shows the uniaxial stress dependence of the photoconductivity spectra in Si with 1×10^{15} cm^{-3} P, where X is changed from 0 to 2.1×10^8 dyn/cm^2 at 1.5 K. With increasing stress, the photoconductivity maximum shifts a little to the lower energy side while the intensity of the photo-response decreases. The estimated electron affinity of the D^- state at $(1-2.1) \times 10^8$ dyn/cm^2 is ~0.8 meV and above 2.5×10^8 dyn/cm^2, the photo-response becomes too small to be detected. Though this spectral change indicates the many valley effect in Si, it is quite different from that in Sb-doped Ge under the [111] stress as shown in the lower part of Fig. 3. The behavior of the D^- state in Si under stress corresponds to that in Ge at the high energy region, and the appearance of a new photoconductivity maximum at low energy region with increasing stress observed in Ge never occur in P-doped Si. The lack of the appearance of low energy maximum in Si means that under a sufficient stress, the bound state of an electron at a neutral donor, D^- state, cannot exist or the state is too shallow to be detected by the present means of detection. The chemical shift of the donor ground state in P-doped Si is very large compared with Sb-doped Ge.

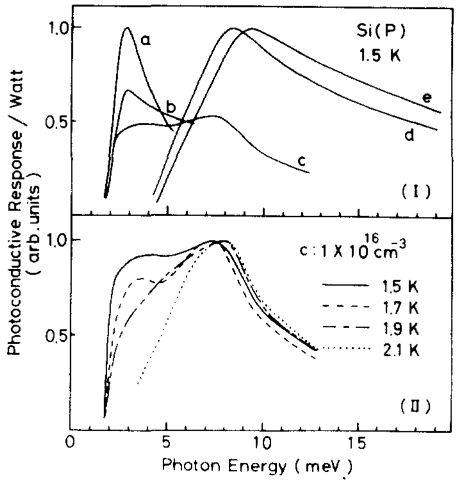

Fig. 2.(I) The concentration dependence of the submillimeter photoconductivity spectra of P-doped Si. The donor concentrations are (a) 1×10^{15} cm^{-3} (b) 7×10^{15} cm^{-3} (c) 1×10^{16} cm^{-3} (d) 4×10^{16} cm^{-3} and (e) 1×10^{17} cm^{-3}. (II) The temperature dependence of the spectrum c in (I).

Assuming a single band for simplification, the effective mass Hamiltonian of the donor ground state and the D^- state are given by

$$H_D = -\frac{\hbar^2}{2m^*}\nabla^2 - \frac{e^2}{\kappa r} + \Delta V, \qquad (2)$$

$$H_{D^-} = -\frac{\hbar^2}{2m^*}\nabla_1^2 - \frac{\hbar^2}{2m^*}\nabla_2^2 - \frac{e^2}{\kappa r_1} - \frac{e^2}{\kappa r_2} + \frac{e^2}{\kappa r_{12}} + \Delta V_1 + \Delta V_2 \qquad (3)$$

where m^* is the effective mass, κ is the static dielectric constant, subscripts in equation (3) denote the coordinates of the two electrons and ΔV is the core potential. The electron affinity of the D^- state can be defined as the difference between the donor ground state energy E_D and the D^- state energy E_{D^-}:

$$J = E_D - E_{D^-}. \qquad (4)$$

In the case of $\Delta V = 0$, which can hold approximately

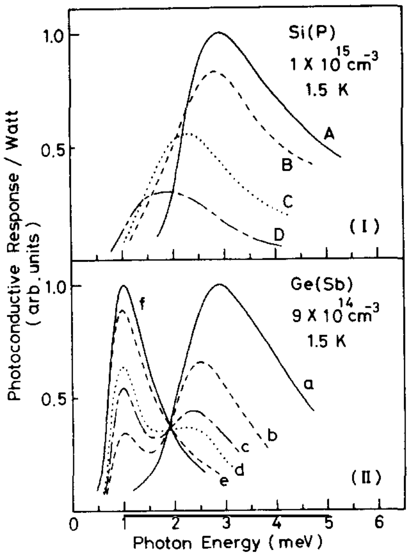

Fig. 3 (I) [100] compressive stress dependence of long-wavelength photoconductivity spectra of P-doped Si. The magnitudes of stress in units of dyn/cm^2 are (A) 0, (B) $\sim 0.4 \times 10^8$ (C) $\sim 1.1 \times 10^8$ and (D) $\sim 2.1 \times 10^8$. (II) [111] stress dependence of long-wavelength photoconductivity spectra of Sb-doped Ge for comparison. The magnitudes of stress in units of dyn/cm^2 are (a) 0, (b) $\sim 1.3 \times 10^8$ (c) $\sim 1.8 \times 10^8$ (d) $\sim 2.5 \times 10^8$ (e) $\sim 3.7 \times 10^8$ and (f) $\sim 6.0 \times 10^8$.

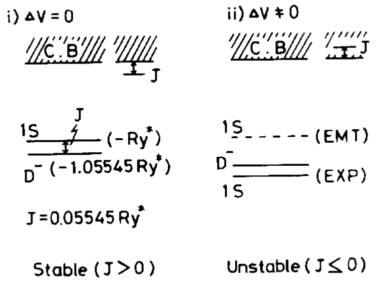

Fig. 4. Schematic energy diagrams of D^- states. (i) The core potential is very small. (ii) The core potential is considerably large.

in Sb-doped Ge, the donor ground state energy, $-$Ry*, and the lowest energy of the D^- state, $-$1.05545 Ry*[8] are obtained from equations (2) and (3) without ΔV, where Ry* is the effective Rydberg. The left hand side of Fig. 4 shows schematically the energy relation in this case. However, when the effect of the donor core potential cannot be ignored, as in P-doped Si, the donor ground state is situated at a considerably lower energy than that by the effective mass theory, while the D^- state energy may be a little larger than or not largely differ from that calculated without the core potential, because the effective radius of the electrons in the D^- state must be larger compared with that of the donor ground state. Therefore, the electron affinity of the D^- state in P-doped Si becomes negative or nearly zero, which means that the bound state of the D^- state cannot exist or is extremely shallow. This energy relation is shown in the right hand side of Fig. 4. Thus, the disappearance of the photoconductivity maximum at the low energy region with increasing stress is well explained.

In conclusion, the D^- state in P-doped Si is stable only by the many valley effect and becomes unstable when the electrons are confined into the [100] valleys by applying stress to the crystal. The spectrum of the D_n^- state in P-doped Si at the impurity concentration of $4 \times 10^{16}\,cm^{-3}$ [(d) in Fig. 2 (I)] corresponds consistently with those reported by Norton.[5] On the other hand, the maximum and shape of the D^- state spectrum in P-doped Si reported by Gershenzon[4] differ considerably from our results for the sample with $1 \times 10^{15}\,cm^{-3}$ P, though the energy obtained by extrapolating the low energy slope of the peak in his data is almost equal to that in our experiment.

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