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Uniaxial Stress Effect on the Electron Affinity of the D^- State in Germanium

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Long-wavelength (submillimeter plus millimeter) photoconductivity measurements in doped germanium have been performed under uniaxial compressive stress along the [111] crystal direction. The electron affinity estimated from newly observed spectra is smaller than that in a previous measurement without stress and is consistent with the theoretical prediction for the D^- state. The larger electron affinity of the D^- state without stress is ascribed to a many-valley effect.

Though many experimental results[1-6] associated with the impurity states in semiconductors have been ascribed to the D^- (or A^+) states, conclusive evidence of the existence of the D^- (A^+) state has not been reported. In the submillimeter photoconductivity measurements on Ge,[6] the experimental electron affinity of the shallow trapping state, which has been supposed to be the D^- state, was about 3 times larger than the theoretical value[7] estimated by a simple analogy to H^-.[8] Moreover the spectral shape of the photoconductivity does not agree with the theoretical one. Even if the existence of the D^- state in Ge (or Si) is assumed, the complete analogy of it with H^- would not hold, because the conduction band in Ge (Si) has many-valley structure with anisotropic energy surfaces.

In this Comment we wish to report a stress experiment on the long-wavelength (submillimeter plus millimeter) photoconductivity in Ge, performed in order to reduce the many-valley structure to the single-valley one. By this experiment, we have confirmed that the mentioned discrepancy between experiment and the theory comes mainly from the effect of the many-valley structure in Ge, and we believe our results to be the first conclusive evidence for the existence of the D^- states in semiconductors.

The present photoconductivity measurements are performed on Sb-doped germanium crystals under uniaxial compressive stress along the [111] crystal direction by the use of a lamellar grating spectrometer and extending the wavelength range from submillimeter to millimeter. By applying a [111] stress, the four conduction-band valleys in germanium become inequivalent in energy; that is, the energy of the valley with the principal axis of the energy ellipsoid parallel to the [111] stress direction is lowered, while the other three valleys are equally elevated in energy. Thus, under sufficient stress, the electrons in the four valleys are accumulated into the lowest [111] valley and the crystal behaves as a semiconductor with a single conduction-band valley.

The energy separation between the bottom of the conduction band of the [111] valley and those of the other three valleys is given by

$$\Delta E_c = \tfrac{4}{9} X s_{44} \Xi_u , \qquad (1)$$

where X is the magnitude of stress, s_{44} is the reciprocal of the rigidity, and Ξ_u is the shear-deformation-potential constant. By using the values of the parameters for Ge, $s_{44} = 1.454\times 10^{-12}$ cm^2/dyn [9] and $\Xi_u = 19.3$ eV,[10] we know that an energy separation of 1 meV between the valleys is obtained by applying a stress of 0.8×10^8 dyn/cm^2.

Figure 1 shows long-wavelength photoconductivity spectra of Sb-doped germanium under a uniaxial stress of $(0-1)\times 10^9$ dyn/cm^2 along the [111] crystal direction at 1.5 K. The measured relative photoconductive responses are calibrated for the spectral distribution of the light source. As previously reported,[6] the submillimeter photoconductivity spectra of Ge without stress have maximum near 3 meV and were ascribed to the excitation of electrons from the trapping state to the conduction band (curve a in Fig. 1).

By the application of very small stress ($\sim 9\times 10^7$ dyn/cm^2) to the crystal, the photoconductivity maximum shifts a little to the lower energy side, ~2.7 meV (curve b), and further application of stress brings an appearance of a new photoconductivity maximum in the low-energy region, ~1.1 meV (curve c, $X \simeq 2\times 10^8$ dyn/cm^2). With increasing stress, the ratio of the height of the photoconductivity maximum at ~1.1 meV to that in the higher-energy region (2.2–3 meV) increases, and the high-energy maximum slightly shifts to the low-energy side, becomes smaller, and vanishes (curves d, e, and f).

We reported in a previous Letter[6] that the electron affinity of the trapping state could be estimated by the extrapolation of the low-energy slope of the main photoconductivity spectral peak and the energy obtained agreed well with the value determined from the temperature dependence of the photoconductive response, 1.56 meV. By applying this extrapolation method to the newly observed photoconductivity spectral peak in the low-energy region, we estimate the electron affinity of the trapping state under sufficient stress ($\sim 8\times 10^8$ dyn/cm^2) to be ~0.54 meV as shown in Fig. 2.

According to the 24-parameter result of the variational calculation by Hylleraas and Midtdal,[11] the electron affinity of the negative hydrogen ion H^- can be represented by 0.055 45$\mathcal{R}$, and in the present case of the D^- state in Ge, the value of $\mathcal{R}$ must be replaced by the 1s donor-state energy from effective-mass theory, 9.81 meV.[12] Thus the theoretical value is calculated to be 0.544 meV, very close to the present experimental value.

Let us consider two electrons bound to an ionized-donor, D^- state, in germanium. Without stress, the probability that the two electrons are associated with different valleys is expected to be considerably greater than with the same valley, for the reason to be described later. How-

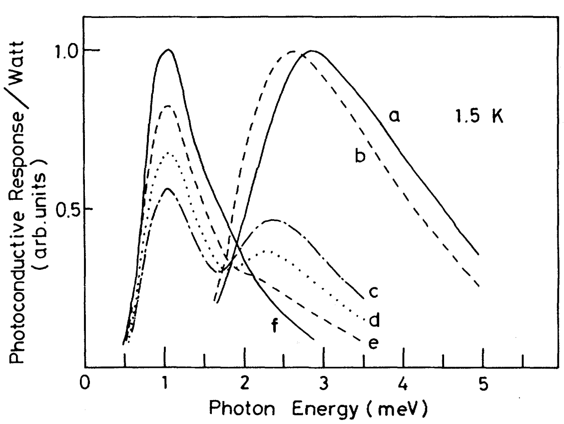

FIG. 1. [111] compressive stress dependence of long-wavelength photoconductivity spectra of Sb-doped germanium. All the spectra are normalized so that the sum of the heights of the high-energy peak and the low-energy peak in each curve becomes unity. In the determinations of the heights, the high-energy tailings of the low-energy peaks are taken into account. The magnitudes of stress (in units of dyn/cm^2) are, for curve a, 0; b, $\sim 9\times 10^7$; c, $\sim 2\times 10^8$; d, $\sim 3\times 10^8$; e, $\sim 4\times 10^8$; and f, $\sim 6\times 10^8$.

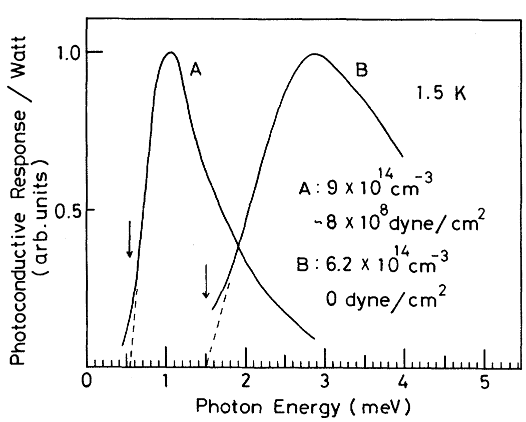

FIG. 2. Determination of the electron affinities of the D^- states in Sb-doped Ge by extrapolation of the low-energy slopes of the photoconductivity peaks.

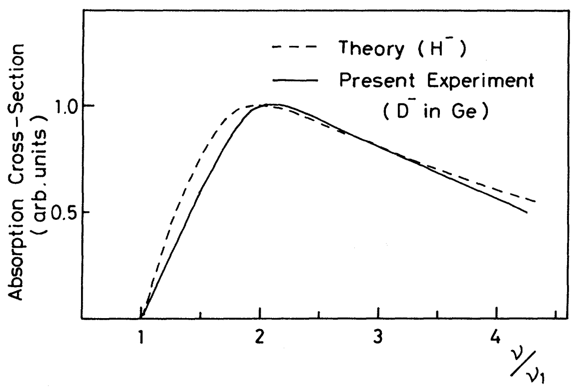

FIG. 3. Comparison of the experimental absorption cross sections of the D^- state in sufficiently uniaxial-stressed Sb-doped Ge with the theoretical absorption cross sections of H^-. Experimental cross sections are derived from the photoconductivity per photon. The frequency ν divided by the threshold frequency ν_1 is chosen as the abscissa and the maximum heights of both the peaks are normalized to unity.

ever, by applying stress to the crystal, the [111] valley becomes lower in energy compared with the other three valleys and the probability that the two electrons are associated with the same [111] valley increases and exceeds that for different valleys. Under sufficient stress $X > \sim 5 \times 10^8$ dyn/cm^2, which corresponds to energy separations $\Delta E_c > \sim 6$ meV, two bound electrons are only found in the [111] valley. By this explanation, the variation of the spectra in Fig. 1 can be well understood.

It is very interesting to compare the spectrum of the relative photoconductivity per photon for the D^- state in Ge under sufficient stress ($\sim 8 \times 10^8$ dyn/cm^2) with the spectrum of the theoretical absorption cross section for H^- calculated by Chandrasekhar,[13,8] who used the wave function by Henrich.[14] The comparison is shown in Fig. 3, where the frequency ν divided by the threshold frequency ν_1 is chosen as the abscissa, and both the spectral maxima are normalized to unity. The agreement of the spectral shape between theory and experiment is fairly good.

It is known from the present experiment that many-valley structures in semiconductors give an interesting effect on the D^- state. In semiconductors with a single valley of isotropic energy surface, the two electrons in the D^- state are supposed to occupy the same orbit with antiparallel spins and this state is completely analogous to H^-. On the other hand, in many-valley semiconductors the two electrons prefer to stay at different valleys, because they are stabilized in energy by a considerable reduction in the Coulomb repulsion energy, especially in the valleys with appreciably anisotropic energy surfaces (Ge). The effect of the [111] stress is to squeeze the two electrons into the [111] valley with antiparallel spins, realizing an effective analogy between the D^- state and H^-. Thus the larger electron affinity of the D^- state in Ge without stress is ascribed to a many-valley effect of the conduction band.

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