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Strain-Induced Change in Conductivity in Antimony- and Arsenic-Doped Germanium

Akio KOBAYASHI, Koichi SUGIYAMA AND Takahiro INAMURA
Electrical Communication Laboratory
Musashino, Tokyo, Japan

Hall coefficient, piezoresistance, magnetoresistance and negative magnetoresistance in antimony- and arsenic-doped germanium have been observed under [111] compression over the range 1°K to 300°K. The valley-orbit splitting energy of arsenic donor is calculated from Hall measurement to be 3.9 meV. Piezoresistance, magnetoresistance and negative magnetoresistance in the range of impurity conduction show large anisotropy with the axis of rotation along [111]. The ratio of piezoresistance parallel to [111] to the value perpendicular to [111] is 5~6. Under compression the activation energy ε_3 of impurity conduction for antimony-doped samples does not vary, on the other hand the value for an arsenic-doped one decreases. Magnetoresistance in [111] magnetic field increases with stress, while that in the field perpendicular to [111] stress decreases. Negative magnetoresistance appears in both n- and p-type germanium with stress. These characters are discussed in terms of modification of wave functions of impurity atoms by strain.

1. Introduction

Kohn and Luttinger[1] analysed that the hydrogen-like 1s levels of group V donors in germanium are splitted into a singlet ground state and triplet excited states by valley-orbit perturbation. This 1s splitting energy is called the valley-orbit splitting and will be referred to as 4Δ in the remainder of the paper. 4Δ is different for the species of donors. When the crystal is subjected to stress, some valleys of the conduction band go up and the others go down giving rise to the change in population of carriers in the valleys.

By the use of this effect 4Δ can be obtained. Fritzsche[2] has obtained 4Δ for As- and Sb-doped germanium from the analysis of stress dependence of piezoresistance.

A part of the present paper is concerned with 4Δ which has been obtained from temperature dependence of Hall effect under the [111] compression.

In the impurity conduction region Fritzsche[3] has observed the tremendous change in resistance in n-type germanium as a function of stress. He has found that in arsenic- and phosphorus-doped germanium, [111] compression decreases the activation energy ε_2 and increases the critical impurity separation from non-metallic to metallic conduction and that in antimony-doped germanium the opposite is observed. The results have been explained from the modification of overlapping of donor wave functions between neighboring donors with strain.

We have studied strain-induced change in activation energy ε_3 of impurity conduction in arsenic- and antimony-doped germanium using uncompensated and heavily compensated samples. Further, we have investigated anisotropy of piezoresistance, magnetoresistance and negative magnetoresistance under [111] compressive stress.

2. Experiments

Single crystals of germanium doped with antimony and arsenic as majority impurity and with gallium as compensating minority impurity were used. Donor concentrations were of order 10^{16} to $10^{17}\,cm^{-3}$ and compensation ratios were zero to 0.75. The crystals were pulled in the [111] direction by zone leveling method. The geometry of samples was a rectangular bar having $1\times1\,mm^2$ in cross section and 15~20mm in length along [111] and the side faces were $(1\bar{1}0)$ and $(11\bar{2})$. The surfaces of the specimens were well polished, etched in CP-4 and rinsed in deionized water. After electrical contacts were soldered, light etching again was employed to prevent surface contamination. Electrodes of $1\times5\,mm^2$, which served for measuring resistivity perpendicular to the [111] axis, were attached to the side faces of the bar by soldering or by evaporation of solder followed by heat-treatment.

Piezoresistance was measured along [111] and [1$\bar{1}$0] (or [11$\bar{2}$]) to obtain the anisotropy at temperature range 1~300°K. The largest compressive stress applied along [111] by a beam balance was kept at 2×10^9 dynes/cm^2 to avoid breakage. Magnetoresistance and Hall effect were observed with and without stress at magnetic field up to 9kOe. Anisotropy of magnetoresistance was also measured.

3. Results and Discussions

(A) *Valley-Orbit Splitting Energy*

Fig. 1 shows an energy diagram of the four valleys of the conduction band and of the 1s-like levels of group V donor in germanium as a function of [111] compression. The 1s-like donor states are composed by the triplet states and the singlet ground state. In the figure, 4Δ which is called valley-orbit splitting energy for the 1s-like levels depends on the donor elements. $-\varepsilon_0$ is the lowest energy eigenstate of the effective mass Hamiltonian.

When the crystal is subjected to the [111] compression, the degeneracy of the conduction band valleys is destroyed and the shift of the valleys is given by the deformation theory. According to Price's theory[4], the 1s-like states also are modified due to strain as shown in Fig. 1. Thus the ionization energy of the donor $\varepsilon_0+4\Delta$ is depressed by 3Δ at the stress limit. Therefore, when we measure temperature dependence of Hall effect at high stress,

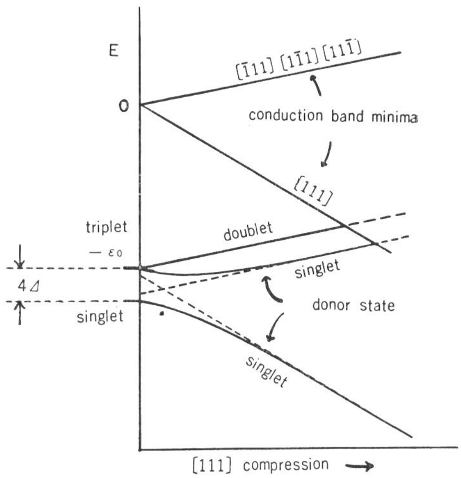


Fig. 1. Energy diagram of the valleys of the conduction band and of the 1s-like levels of group V donor as a function of [111] compression.

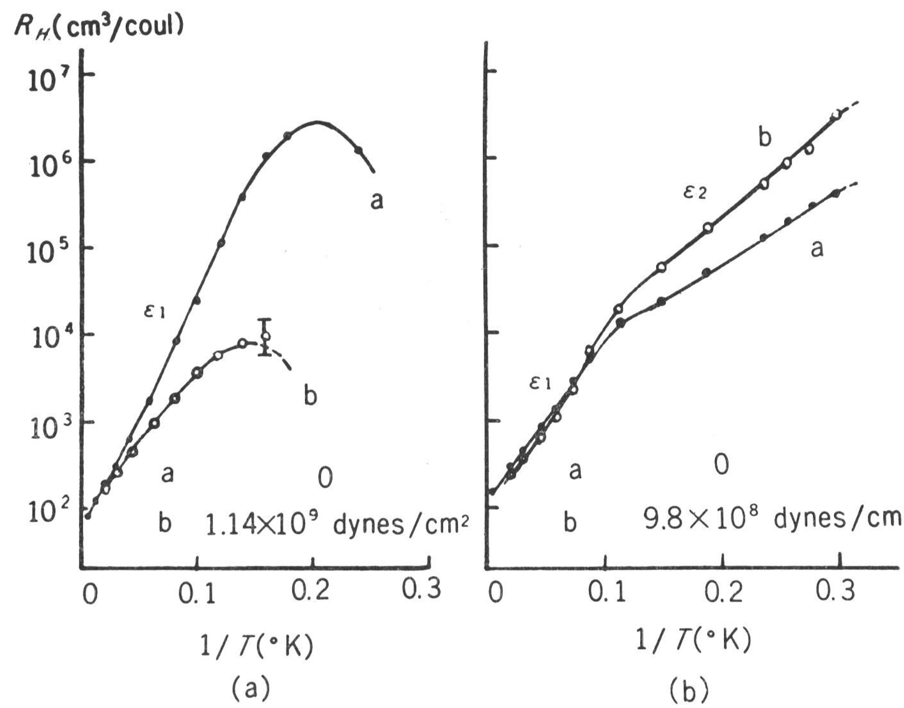


Fig. 2. (a) Hall coefficient with and without stress in arsenic-doped germanium of concentration 8.3×10^{16} cm^{-3}. (b) Hall coefficient with and without stress in antimony-doped germanium of 5.0×10^{16} cm^{-3}.

Table I. ε_3: Activation energy of impurity conduction in heavily compensated germanium.

Donor	ε_3 at zero stress (eV)	ε_3 at 10^9dynes/cm^2 (eV)	Concentration of donor, N_D(cm^{-3})	Compensation ratio, $K=N_A/N_D$
Sb	3.1×10^{-4}	3.2×10^{-4}	1.35×10^{17}	0.38
As	5.6×10^{-4}	3.9×10^{-4}	2.20×10^{17}	0.45

we can observe the depressed ionization energy $\varepsilon_0+\Delta$. Then we obtain 4Δ by simple arithmetic.

Hall coefficient with and without stress was observed for an arsenic-doped germanium of concentration of 8.3×10^{16} cm^{-3} as a function of reciprocal temperature as shown in Fig. 2 (a). In this figure Curves "a" and "b" refer to measurements without and with stress respectively. We obtain the activation energy of 4.80 meV at zero stress and the value of 1.88 meV at stress of 1.14×10^9 dynes/cm^2. If the difference between them is equated with 3Δ, then we have 3.9 meV for 4Δ of the arsenic donor. This value agrees well with the value of 4.15 meV obtained by Fritzsche.[2]

Fig. 2 (b) shows Hall measurement with and without stress for antimony-doped germanium of 5.0×10^{16} cm^{-3} in concentration. Because 4Δ of the antimony donor is less than 1 meV, we can not find the depression of the ionization energy by stress in this figure.

(B) *Activation Energy ε_3 of Impurity Conduction.*

When large stress was applied on arsenic-doped germanium at low temperatures below 10°K, we observed decrease in activation energy of conductivity in the ε_3 region of impurity conduction. On contrast to this, we could not find such change in activation energy ε_3 in antimony-doped germanium. Table I shows the change in ε_3 at zero stress and at stress of 10^9 dynes/cm^2.

The decrease in ε_3 can be interpreted by strain-induced expansion of the Bohr orbit of the ground state donor wave function as follows. The ground state donor wave function is made of the sum of four pancake-shaped wave functions each of which originates from the individual valleys as it is shown in the upper part of Fig. 3 (a). When the crystal is subjected to the [111] compression, shear strains modify the donor wave functions and result in only one pancake-like wave function originating from the [111] valley as shown in the lower part of Fig. 3 (a).

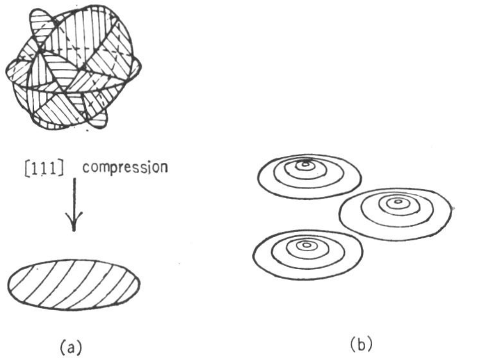


Fig. 3. (a) Ground state wave function made of four pancake-like wave functions is modified by shear strains resulting in one pancake-like wave function originating from [111] valley. (b) Pancake-like wave functions cause anisotropy of overlap.

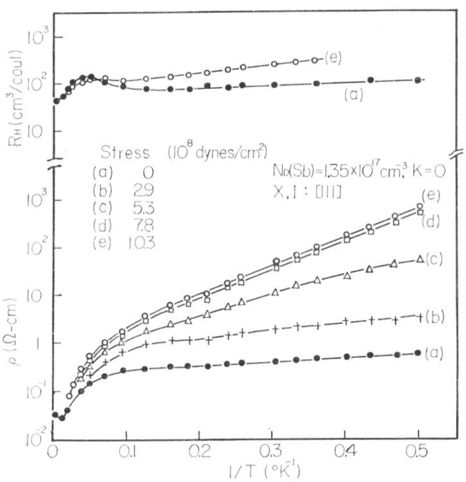
The effective Bohr radius at zero stress is given by

$$a=a_{\text{eff. mass}}(\varepsilon_0/\varepsilon_0+4\Delta)^{1/2},$$

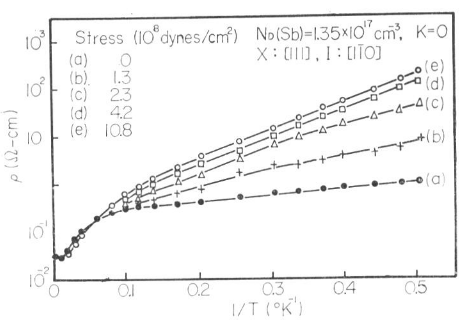
where $a_{\text{eff. mass}}$ is the Bohr orbit calculated from the effective mass Hamiltonian. At zero stress the ground state orbit of arsenic donor is about 17% smaller than its effective mass value, because of the large valley orbit splitting 4Δ. The orbit increases with stress as the ionization energy decreases with stress. It is well explained by many authors[5] that at lower concentration of donor, impurity conduction in the ε_3 range is caused by hopping mechanism due to the overlap between neighboring donor wave functions and its activation energy is determined by the potential fluctuation with the compensating impurity ions. If we assume this is true in higher concentration range as the present case, we can explain the decrease in ε_3 with stress because of the increase in overlap of neighboring donor wave functions. In antimony-doped germanium, strain-induced change of the Bohr orbit is negligible because of the small valley orbit splitting. This is the reason why ε_3 in antimony-doped one does not change with uniaxial compression.

(C) *Anisotropy of Piezoresistance.*

Figs. 4 (a) and (b) show temperature dependence of resistance in [111] and [1$\bar{1}$0] directions under [111] compression for an antimony-doped specimen. We have the ratio of resistivity parallel to the stress direction to the value perpendicular to that to be 5~6 at 10^9 dynes/cm^2 for both the uncompensated and compensated samples doped with antimony. This anisotropy can be explained by the anisotropy of overlap of neighboring pancake-like donor wave functions as it is easy to see from Fig. 3 (b).



(a)

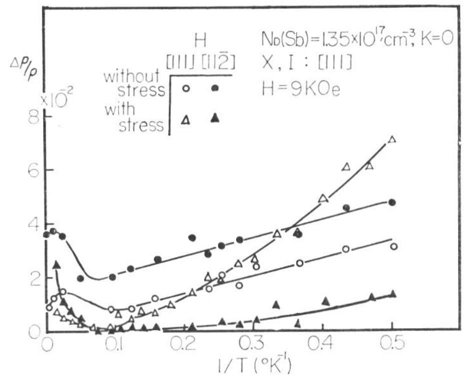


(b)

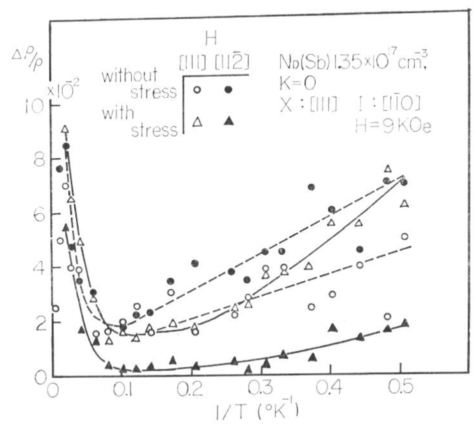
Fig. 4. (a) Piezoresistance in [111] direction under [111] compression in antimony-doped germanium of concentration 1.35×10^{17} cm^{-3}. (b) Piezoresistance in [1$\bar{1}$0] direction under [111] compression in the same sample.

(D) *Anisotropy of Magnetoresistance.*

Fig. 5 shows longitudinal and transverse magnetoresistance in the current along [111] and [1$\bar{1}$0] in the antimony-doped sample at zero stress and at a stress of 10^9 dynes/cm^2. Similar characteristics have been obtained in the arsenic-doped sample.



(a)



(b)

Fig. 5. (a) Longitudinal magnetoresistance in [111] direction in the same sample as that of Fig. 4. Stress 10^9 dynes/cm^2. (b) Transverse magnetoresistance in [1$\bar{1}$0] current direction.

In impurity conduction region the difference between longitudinal and transverse magnetoresistance in the magnetic field parallel or perpendicular to [111] is not so large, but at high stress the magnetoresistance in magnetic field parallel to the stress direction becomes larger and independent of current directions. In contrast to this, the magnetoresistance in the magnetic field perpendicular to the stress direction becomes very small.

The [111] magnetic field shrinks the orbit of the pancake-shaped ground state donor wave function with the axis of rotation along [111] and gives rise to the depression of overlap between neighboring donor wave functions as it is discussed by Sladek and Keyes[6]. Since the shrinkage of overlap in the ε_3 region causes the decrease in transition probability of electrons from a donor wave function to neighbor one, *i.e.*, decrease in current, we can understand that the largest magnetoresistance is observed in the magnetic field parallel to the [111] stress direction.

Further we have observed anisotropy of negative magnetoresistance in *n*- and *p*-type germanium subjected to stress. The detail will be published in the near future[7].

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DISCUSSION

Becker, J. H.: Would you care to comment on the explanation of the negative magnetoresistance which was observed?

Kobayashi, A.: The negative magnetoresistance in germanium and silicon are not yet explained, but it is somewhat similar to negative magnetoresistance in copper doped with manganese. The latter effect has been well explained by *s-d* interaction between the spin of a conduction electron and the spin of a manganese *d*-electron. Recently Toyozawa presented a theory in which he assumed the existence of two kinds of impurity conduction electrons, one of which acts as a localized electron such as a *d*-electron in the dilute alloy, but this theory can not explain our results. Our results show that the largest negative magnetoresistance independent of current directions is observed in the magnetic field along the stress direction which is [111] in the case of *n*-type and [100] in the case of *p*-type respectively.

Donor wave function under [111] stress is a pancake-shaped oblate spheroid along [111] and acceptor wave function under [100] stress is a cigar-shaped prolate spheroid along [100]. And there might be spin-orbit interaction. At low temperatures neighboring spins might couple with each other in antiferromagnetic way due to the overlapping of the wave functions. Since magnetic field destroys the antiparallel order of spins, it may give rise to decrease in scattering of electron by different spins and may result in the negative magnetoresistance.