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Galvanomagnetic Effects in Boundary Layer of Germanium Bicrystals

Yoshihiro HAMAKAWA AND Jiro YAMAGUCHI
Faculty of Engineering, Osaka University
Higashinoda, Miyakojima, Osaka, Japan

The reduced resistivity and associated galvanomagnetic effects along the grain boundary layer in *n*-type grown bicrystals have been measured in the temperature range between 2.8∼300°K. Results obtained from the samples of misfit angle 12° show that the Hall coefficient has a steep maximum at about 25°K and a slope of the log (ρ_s/t) *vs* $1/T$ changes at this temperature, and in the temperature range below 10°K, log (ρ_s/t) becomes almost constant, and at the same time a large negative magnetoresistance is observed. These behaviors are similar to those of impurity conduction found in highly doped semiconductors. The dislocation acceptor levels, the ionization energies and the dislocation line densities in the grain boundary layer are estimated, and magnetoresistance anomalies are discussed on the basis of several tentative models.

1. Introduction

In recent years, low temperature anomalies of carrier transport property in highly doped semiconductors have been precisely investigated as a problem of the impurity conduction[1)-3)]. It has been suggested that at high impurity concentrations conduction takes place in the impurity band formed as a result of overlapping of the wave function of neighboring impurity atoms, and at relatively low concentrations the banding does not occur and the conduction takes place by hopping of carriers from occupied to unoccupied localized impurity states.

The effect of dislocations on the impurity conduction has recently been studied by Fritzsche[4)], and he has concluded that the dislocations, which were introduced by neutron irradiation, do not affect the impurity conduction for densities up to $10^4/cm^2$.

On the other hand, the dislocation density related to the unpaired dangling bond in the medium angle grain boundary has been estimated to be $10^{11}/cm^2$ or larger[5)] which acts essentially as acceptor center in *n*-type germanium. Mataré[6)] has observed the temperature-independent behavior of conduction in the grain boundary layer at low temperatures. Recently, Kobayashi *et al.*[7)] have reported an occurrence of impurity conduction on germanium surfaces cleaned by heat-treatment.

From these facts it may be expected that high density of dangling bond states in the grain boundary layer should cause a kind of impurity conduction at low temperatures. The purpose of this paper is to search for the grain boundary conduction along this prospect from the measurement of galvanomagnetic effects.

2. Preparation of Samples and Measurements

The grain boundaries used in this study were grown by the Czochralski method with bicrystal seeds symmetrically tilted about [100] axis[8)], with the misfit angle 12°. A mother crystal was antimony doped *n*-type germanium of about 15∼20 ohm-cm resistivity. Rectangular form samples of about 6×4×2 mm³ were prepared as shown in Fig. 1.

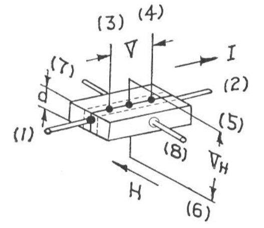

Fig. 1. Arrangement of the leads of the sample. Solid circles denote ohmic contacts to grain boundary, and open circles to *n*-type bulk.

Ohmic contacts to grain boundary plane (solid circles in the figure) were accomplished by indium alloying, and those to *n*-type bulk (circles in the figure) were made by soldering with gold plated copper wires. To eliminate the surface effect, the sample mounted with nonmagnetic lead wires was contained in a

Pyrex glass tube evacuated at about 10^{-3} mm Hg.

The measurements of grain boundary conductance and associated galvanomagnetic effects were made by usual d.c. techniques, the pertinent voltages being read by an electronic potentiometer. The cryogenic apparatus and the method of sample mounting in the dewar used in this experiment are the same as those described in the previous paper[5].

3. Experimental Results and Discussions

The voltage-current characteristics of the grain boundary layer are ohmic in all cases for electric fields below 40 volts/cm, therefore the boundary layer current of 100μA or less (corresponding fields not higher than 3 volts/cm) has been used in the following measurements.

Figs. 2 and 3 show the temperature dependence of reduced resistivity (ρ_s/t) and Hall coefficient (R_H/t) along the grain boundary layer with the misfit angle of 12°, in which suffices $\parallel$ and $\perp$ denote the direction of current parallel and perpendicular to the dislocation arrays respectively.

The sign of Hall voltage shows a nature of ***p***-type conduction as reported elsewhere[9], and no change in its sign is observed at all temperatures measured.

As is seen from Figs. 2 and 3, the Hall curves exhibit a sharp maximum at about 25°K, and at the same time the slope of log (ρ_s/t) plots decreases, and at about 10°K the reduced resistivities have a maximum, and a

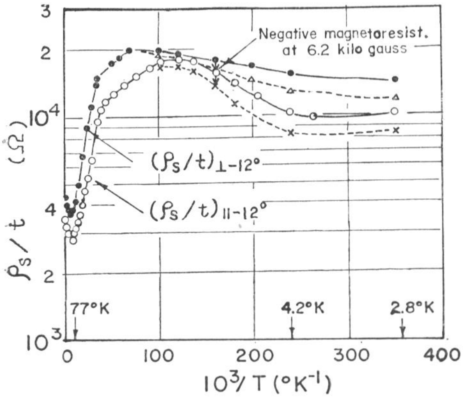

Fig. 2. Reduced resistivity along the germanium grain boundary layer as a function of $1/T$ for the samples of the misfit angle 12°.

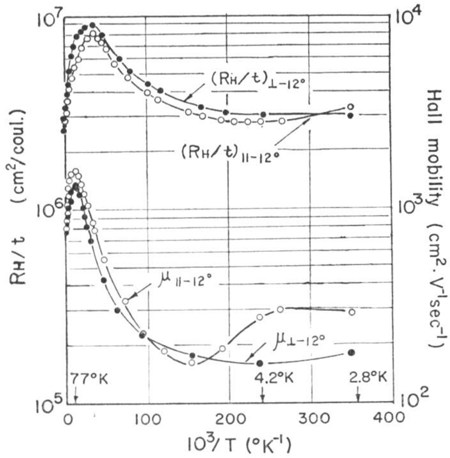

Fig. 3. Reduced Hall coefficient and Hall mobility along the grain boundary layer as a function of $1/T$ for the sample of the misfit angle 12°.

large negative transverse magnetoresistance appears in the lower temperature region. General behaviors of these properties are similar to those of impurity conduction in highly doped semiconductors. It has been suggested from the work on the impurity conduction that the Hall curve maximum occurs at the temperature at which the contribution to the conduction in the normal band is equal to that in the impurity band.

The Hall mobility in the grain boundary layer conduction is defined as the ratio of the reduced Hall coefficient to resistivity *i.e.*, $\mu=(R_H/t)/(\rho_s/t)=(R_H/\rho_s)$, and its temperature dependence obtained from the data in Figs. 2 and 3 is also plotted in Fig. 3. As mentioned in our paper[5], this boundary layer mobility in the normal band conduction region is mainly restricted by the potential well scattering due to the space charge around the grain boundary and by the dislocation scattering, and is expressed by the form $\mu^{-1}=\mu_{ls}^{-1}+\mu_d^{-1}$. It is estimated from Dexter and Seitz's theory[11] in the dislocation scattering region (80∼20°K) that the dislocation line density was 4.6×10^{11} lines/cm² for $\theta_m=12°$. Moreover, the carrier concentration of 3.8×10^{17} cm^{-3} or larger is calculated from the Hall coefficient in the exhaustion region (at 250°K) by assuming the width of boundary layer to be 1000Å. This high carrier concentration in the grain boundary also implies the possibility of impurity conduction at low temperatures. If this be true, decreasing of slope of the log ρ_s/t *vs* $1/T$ curves at the temperature corresponding to the peak value of (R_H/t) has an important meaning.

According to the theory of impurity conduction, the impurity resistivity ρ_i is given by $A\cdot\exp(-\varepsilon_i/kT)$, where ε_i is the activation energy. Analyzing the slope in Fig. 3, we obtain ε_i of about 6.5×10^{-4} eV which may be corresponding to the ε_2 or ε_3 after Fritzche's notation[2]. The ionization energy is nearly equal for both of the samples $\parallel$ and $\perp$, but the temperature of the Hall curve peak and the onset temperature of negative magnetoresistance in the perpendicular case are slightly high as compared with that in the parallel case. On the other hand, the activation energy from the valence band to the dislocation acceptor level (ε_1) can be estimated from the temperature dependence of Hall coefficient in the normal band conduction region, to be (0.006 ± 0.002) eV and (0.010 ± 0.002) eV for the samples (12-$\parallel$-18) and (12 $-\perp-$18) respectively.

Fig. 4 shows a magnetic field dependence

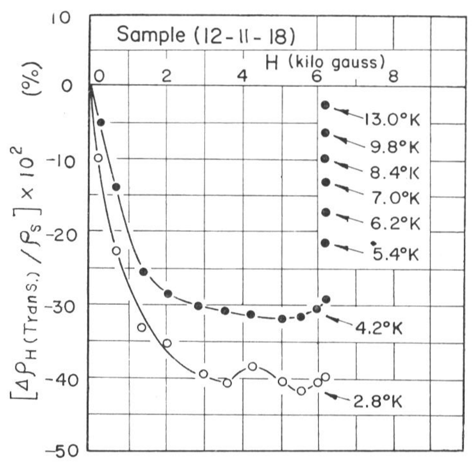

Fig. 4. Magnetic field dependence of the transverse magnetoresistance at low temperatures for the sample (12-||-18).

of transverse magnetoresistance with a parameter of temperature. As is evident from the figure, a large negative magnetoresistance is observed, and the value increases with decreasing temperature or with increasing magnetic field. Moreover, oscillatory component appears at the lower temperature. At about 13°K the negative magnetoresistance vanishes, and above this temperature positive magnetoresistance which may be due to normal band conduction is observed. Whereas, the longitudinal magnetoresistance of this sample changes from positive to negative with increasing magnetic field as shown in Fig. 5. Similar results of the magnetoresistance effects were obtained in the two other samples of the same misfit angle, but the oscillatory characteristics in the transverse magnetoresistance varied from sample to sample.

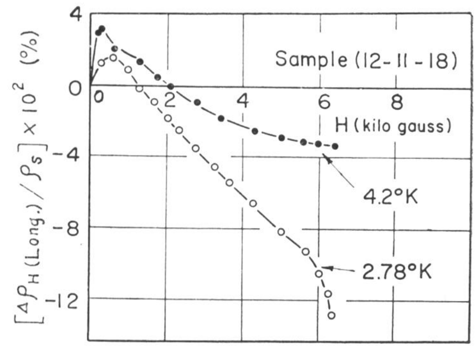

Fig. 5. Magnetic field dependence of the longitudinal magnetoresistance at low temperatures for the sample (12-||-18).

Although the underlying physical basis concerning these anomalous galvanomagnetic effects is very complex, several possible causes will be enumerated and briefly discussed as follows;

(i) *de Haas-van Alphen effect*: In a highly degenerate system, the electronic properties are quite sensitive to the density of states near the Fermi level. When the magnetic field increased, the Landau level separation $\hbar\omega$ becomes greater, and oscillatory carrier transport properties are produced as a result of the Landau levels passing through the Fermi surface.

In order to examine the degeneracy of electronic state in the samples, the magnetic field dependence of Hall coefficient was checked, and the representative data are shown in Fig. 6. It is seen that the reduced Hall coefficients in the normal band conduction region are practically independent of magnetic field strength, but that at lower temperatures decrease slightly with increasing magnetic field for strengths above 4 kilo gauss. In a previous work on the impurity conduction, a large decrease in magnitude of the Hall coefficient with increasing magnetic field has been observed in both *p*- and[13] *n*-type[14] germanium at low temperatures. Besides, negative and oscillatory magnetoresistance has been detected in highly doped germanium[15], indium antimonide[16] and lead telluride[12].

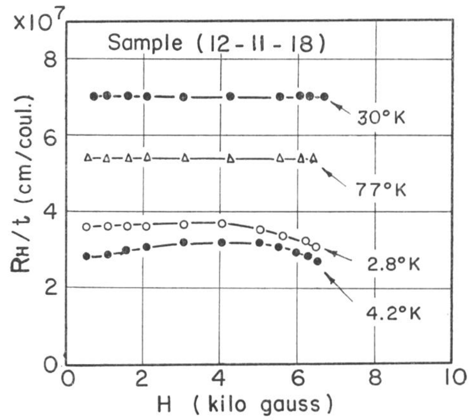

Fig. 6. Magnetic field dependence of the reduced Hall coefficient (R_H/t) in various temperatures for the sample (12-||-18).

An oscillatory effect may occur when the following conditions are satisfied: (a) $\omega\tau>1$, (b) $E_f>\hbar\omega$ and (c) $\hbar\omega>kT$, where E_f is the Fermi energy, and τ is the carrier relaxation time. Apart from condition (b) and (c), the critical magnetic field for the beginning of the cyclotron motion is examined by condition (a). From Fig. 3, the carrier mobility at 4.2°K is about 300 cm^2/volt. sec. and the ratio of effective mass to cyclotron mass (m^*/m_c) is assumed to be 4, and $\omega\tau=\mu\cdot H\cdot c^{-1}\ (m^*/m_c)$, thus we obtain the value of the critical field strength to be 83 kilo gauss or larger. Since the magnetic field strength of the experiment is about one order smaller than this critical field, the de Haas-van Alphen oscillation cannot be expected so long as the above values of mobility and (m^*/m_c) are adopted.

(ii) *The spin-dependent scattering*: A theoretical interpretation of the negative magnetoresistance based on the spin dependent scattering[17] has been given by Toyozawa[18]. According to his theory, the magnetoresistance should relate to quadratic magnetic field, *i.e.*, $\Delta\rho_H/\rho_s=-S\cdot H^2$. The coefficient S is a quantity quadratically proportinal to the susceptibility of the localized spins, and the value of $S^{-1/2}$ at 4.2°K obtained from the data of Sb doped germanium[15] was 2×10^4 (gauss). In our case, $S^{-1/2}$ is estimated to be 2.3×10^3 (gauss) for weak field region at 4.2°K.

(iii) *Galvanomagnetomorphic effect*: An another case considerable in this respect is a galvanomagnetomorphic effect caused by the thin grain boundary. An anomalous carrier conduction and oscillatory magnetoresistance in metallic films have been observed, and the generalized theory for the galvanomagnetic effects was carried out by Sondheimer[19] for metals and by Friedman and Koenig[20] for semi-metals. In the case of the grain boundary layer, the width of the boundary layer t can be changed by controlling the electric field around the grain boundary. The slope of the energy band near the top of valence band may depend on the square root of bias voltage applied across the grain boundary.

Fig. 7 shows a magnetic field dependence of grain boundary resistivity ρ_H (long.) in a longitudinal magnetic field at various bias voltages applied across the grain boundary.

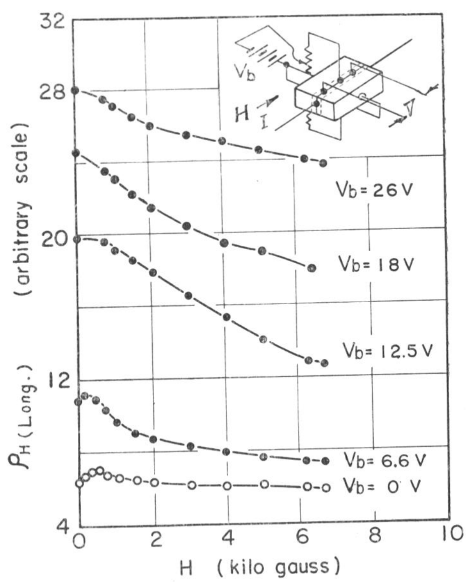

Fig. 7. Magnetic field dependence of the grain boundary layer resistivity at 4.2°K with a parameter of bias voltages applied across the grain boundary in the case of the magnetic field parallel to current flow (longitudinal case).

The decrease in ρ_H (long.) with increasing magnetic field may be caused by decrease of the cyclotron radius with the increase of magnetic field, and the increase of ρ_H (long.) in the absence of a magnetic field with increasing the bias voltage may be due to the effects from change of the scattering process and of the occupancy of the electronic state in the grain boundary. By a simple calculation, the carrier mean free path at 3°K obtained from Fig. 3 is the same order of the width of the grain boundary layer t which was estimated by Mataré[6]. These behaviors are indicative of the galvanomagnetomorphic effect found in thin metallic films.

Additional measurements and their analyses are now being carried out and the detailed discussion on the mechanism of conduction at low temperatures will be reported in the near future.

4. Conclusions

Carrier transport properties along the boundary layer of germanium bicrystal have been investigated from the measurements of the reduced resistivity and associated galvanomagnetic effects.

The general picture of the properties at low temperatures—a steep maxium in the log (R_H/t) *vs* $1/T$ curves, a change in slope in log (ρ_s/t) *vs* $1/T$ and the negative magnetoresistance etc.—may imply the possibility of the dangling bond level conduction.

The activation energy ε_1 of the dislocation acceptor level and the ionization energy ε_i for impurity conduction are estimated to be $(0.06\sim0.01)$ eV and 6.5×10^{-4} eV respectively.

The galvanomagnetomorphic effects are observed, but the evidence is not conclusive because of lack of experimental informations about the data at stronger magnetic fields.

Acknowledgements

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DISCUSSION

Elbaum, C.: I wonder whether you took into account the segregation of impurities to the grain boundary. And if so, how did you compute the corresponding effect?

Hamakawa, Y.: The effect of impurities was not taken into account in analysing the data reported here. Because the donor concentrations doped in the bulk were less than 2×10^{14} cm^{-3}, so I think that these small impurity concentrations do not contribute to the observed effects.

Queisser, H.: The situation seems to be quite different from the one observed at silicon grain boundaries. The electrical behavior of the dislocations in Si boundaries is very strongly dependent upon the impurity atmospheres surrounding the dislocations. (Paper II C-9 of this conference).*

* *Proc. Int. Conf. Cryst. Latt. Def. (1962)*: J. Phys. Soc. Japan **18** Suppl. III (1963).