The Density of States Spectrum for the Impurity Band in Highly-Compensated Heavily Arsenic-Doped n-Type Germanium

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The density of states spectrum for the impurity band is obtained by adopting a rigid band picture and measuring the temperature dependence of the resistivity and the Hall effect for highly- compensated heavily arsenic-doped n-type germanium crystals with initial donor concentrations per cm^3 of 3.24 x 10^{18}, 3.32 x 10^{18} and 5.20 x 10^{18} and with various degrees of compensation realized by thermal-neutron irradiation and isochronal anneals. Obtained density of states decreases exponentially towards the inside of the energy gap, and the density of states spectrum is essentially independent on the initial donor concentration.

KEYWORDS: density of states spectrum, impurity band, arsenic-doped germanium, thermal-neutron irradiation, isochronal anneal

1. Introduction

The effect of compensation on impurity conduction in heavily doped n-type germanium has been studied extensively by the use of thermal-neutron-irradiation and isochronal-annealing method which enable to change the degree of compensation without changing donor concentration.[1)] Being adopted a picture that the donor band is rigid, that is, the density of states as a function of energy does not change it shape by the change of the degree of compensation, and a certain number of electrons fill up the band by stepwise anneals, the density of states spectrum for the impurity band has been obtained. The impurity band tail extends to as deep as -50 meV in the forbidden gap.

This work is intended to obtain the more precise density of states spectrum for the impurity band especially in the energy region near the conduction band edge. Preliminary results have been reported for the impurity band spectrum for two highly-compensated heavily-doped n-type germanium crystals with initial arsenic donor concentrations of 3.32 x 10^{18} cm^{-3} and 5.20 x 10^{18} cm^{-3}.[2)] For both samples, the Hall mobility at 4.2 K recovers monotonically with successive isochronal anneals up to about 250 °C, and then, decreases towards a minimum value at an annealing temperature of about 320 °C. This reverse annealing in Hall mobility recovery at the annealing stage around 290 °C has been interpreted as being due to dissociation of vacancy-arsenic complexes formed in the preceding process.[3)] Applying a rigid band picture to this annealing stage around 290 °C is thought to be inappropriate.

In this paper, the density of states spectrum for the impurity band is obtained by adopting a rigid band picture and analyzing the temperature dependence of the resistivity and the Hall effect for highly-compensated heavily arsenic-doped n-type germanium crystals with various degrees of compensation realized by thermal-neutron irradiation and isochronal anneals at temperatures below 250 °C.

2. Experimental

Single crystals of arsenic-doped germanium with initial donor concentrations of 3.24 x 10^{18} cm^{-3}, 3.32 x 10^{18} cm^{-3} and 5.20 x 10^{18} cm^{-3} were irradiated with thermal neutrons at a total flux of about 10^{19} cm^{-2} at room temperature. Thermal-neutron irradiation on germanium crystals causes nuclear reaction between germanium nuclei and thermal neutrons, in which Ga, As and Se atoms are produced in the ratio 30:10:1.2,[4)] accompanied by β-ray emissions of about 1 MeV. Some of the lattice defects produced by the β-rays, such as vacancies and

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interstitial-arsenic complexes, act as acceptors in n-type materials.[1)] The concentrations of donors and accepters such as As, Se and Ga produced by the nuclear reactions are estimated to be much lower than both the initial donor concentration and the concentration of the acceptors produced by the β-rays. Therefore, the thermal-neutron irradiated germanium crystals are substantially those irradiated by β-rays rather than thermal neutrons.

Annealing was done very gradually by isochronal anneals for 60 min in pure helium gas at temperatures above 100 °C with intervals of 5 °C or 10 °C. After each isochronal anneal, the temperature dependence of the resistivity and the Hall coefficient were measured over the temperature range between 1 K and 300 K.

3. Results

Figure 1 shows the variation of the resistivity ρ versus temperature T curve by the isochronal anneals for the arsenic-doped germanium sample with the initial donor concentration of 3.24 x 10^{18} cm^{-3}, and Fig. 2 shows the variation of the Hall coefficient R_H versus temperature T curve for the same sample. Curves shown in both figures are for five steps after annealing at temperatures T_A indicated, and not for all annealing steps measured. As can be seen from these figures, acceptors are annealed out and electrons which were captured by these acceptors are restored to the donors or the conduction band. The acceptors which are annealed out are vacancies and interstitial-arsenic complexes produced by the β-rays. The electron concentration n, which is assumed equal to the Hall concentration $1/eR_H$ at room temperature, where e is the electron charge, is also indicated in Figs. 1 and 2.

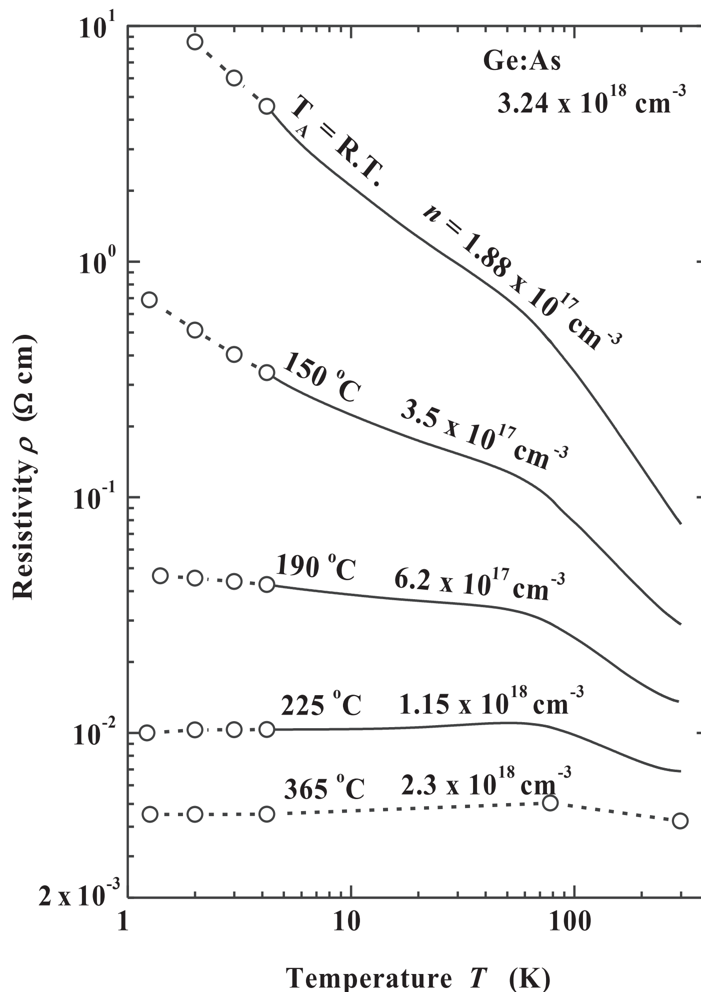

Fig. 1. Variation of the resistivity ρ versus temperature T curve by the isochronal anneals for the arsenic-doped germanium sample with the initial donor concentration of 3.24 x 10^{18} cm^{-3}. Curves are for five steps after annealing at temperatures T_A. Solid lines are continuously measured data. The electron concentration n for each step is also indicated

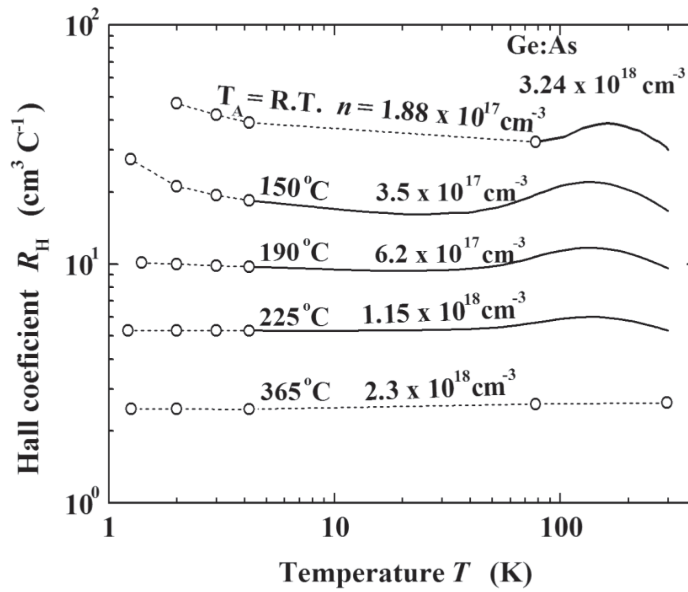

Fig. 2. Variation of the Hall coefficient R_H versus temperature T curve by the isochronal anneals for the arsenic-doped germanium sample with the initial donor concentration of 3.24 x 10^{18} cm^{-3}. Curves are for five steps after annealing at temperatures T_A. Solid lines are continuously measured data. The electron concentration n for each step is also indicated.

Variations due to isochronal anneals of ρ-T and R_H-T curves for the three samples are similar to each other, though the ρ-T and R_H-T curves for the as-irradiated samples differ between them. The ρ-T and R_H-T curves for the as-irradiated sample with the initial donor concentration of 3.32 x 10^{18} cm^{-3}, in which the electron concentration is 5.2 x 10^{17} cm^{-3}, are similar to the curves after annealing at 190 °C in Figs. 1 and 2. The ρ-T and R_H-T curves for the as-irradiated sample with the initial donor concentration of 5.20 x 10^{18} cm^{-3}, in which the electron concentration is 1.50 x 10^{18} cm^{-3}, are similar to the curves for the sample after annealing at 225 °C in Figs. 1 and 2. The samples with nearly the same electron concentration show similar ρ-T and R_H-T curves. Thus, the behavior of the ρ-T and R_H-T curves does not depend on the annealing temperature T_A, but mainly on the electron concentration n.

In the ρ-T curve such as curves in Fig. 1, an activation energy is observed in a temperature range from 80 K to 300 K. In the case of uncompensated n-type germanium crystals with these electron concentrations, a positive temperature coefficient of resistivity is observed over a temperature range from 200 K to 300 K in the ρ-T curves,[5)] indicating perfect depletion of electrons from donor sites into the conduction band. The activation energy observed in the ρ-T curve such as curves in Fig. 1 means that the electrons are not perfectly depleted but are staying in low mobility states lying in the forbidden band. Since the electrons in these states are mobile as shown from the observed conductivity at 4.2 K and the conduction is carried by a drift motion of electrons shown from the Hall effect at 4.2 K, these states in the forbidden band are forming a band, that is, the impurity band.

The density of states of the impurity band is obtained by adopting a rigid band picture and analyzing the measured data for annealing steps below 250 °C. The position of the Fermi level for each annealing step is supposed as lying below the conduction band edge by the energy equal to an activation energy observed in the ρ-T curve such as curves in Fig. 1. The number of electrons contained in the impurity band is assumed equal to the Hall concentration $1/eR_H$ at room temperature. With these assumptions, the electron concentration n in the impurity band is given as a function of the Fermi level ε_F as shown in Fig. 3. The derivative of this function n (ε_F) with ε_F is the density of states D (ε_F). Here, for each pair of annealing steps, i-th step and (i+2)-th step, by dividing the difference of the electron concentration $\Delta n_i = n_{i+2} - n_i$ by the difference of the Fermi level energy $\Delta \varepsilon_{F\,i} = \varepsilon_{F\,i+2} - \varepsilon_{F\,i}$, the density of states $D(\frac{\varepsilon_{F\,i} + \varepsilon_{F\,i+2}}{2}) = \Delta n_i / \Delta \varepsilon_{F\,i}$ is obtained for the three samples, and is shown in Fig. 4.

Figure 5 shows the Hall mobility $\mu_H = R_H / \rho$ at 4.2 K as a function of the Fermi level ε_F.

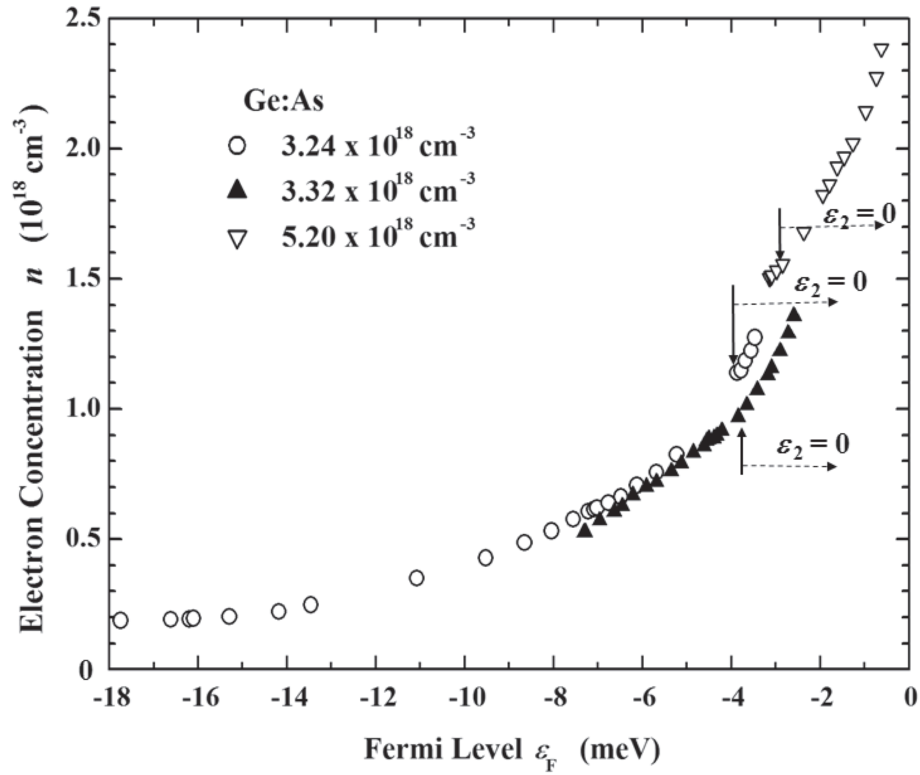

Fig. 3. The electron concentration n versus the Fermi level ε_F. Solid-line arrows indicate the Fermi levels where the activation energy in the liquid helium temperature region ε_2 becomes zero and the metal-nonmetal transition occurs.

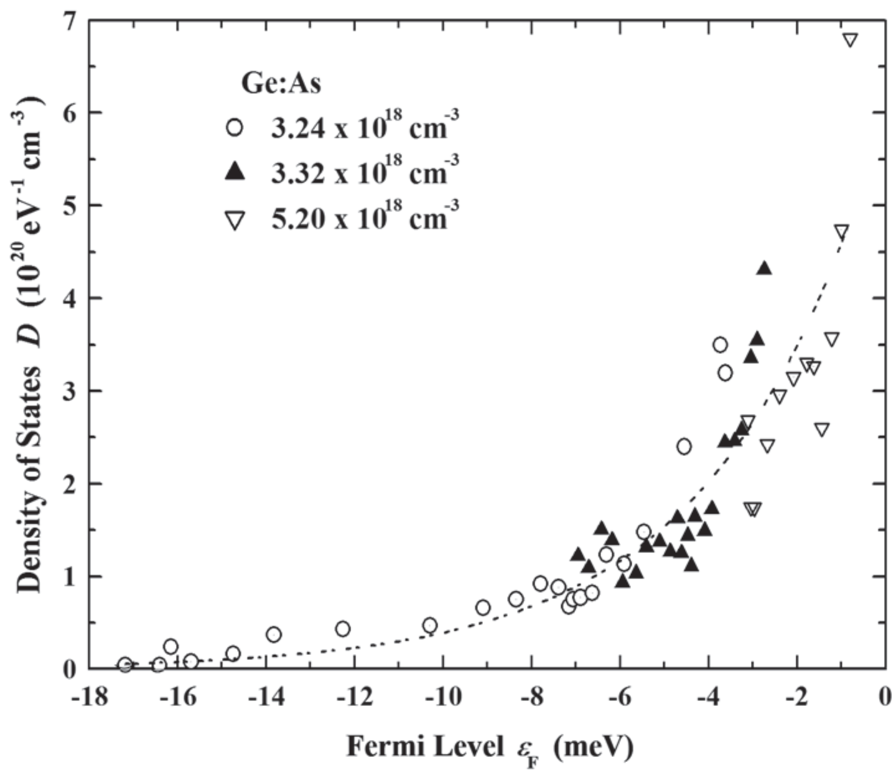

Fig. 4. The density of states D for the impurity band. The broken line is an exponential fitting curve.

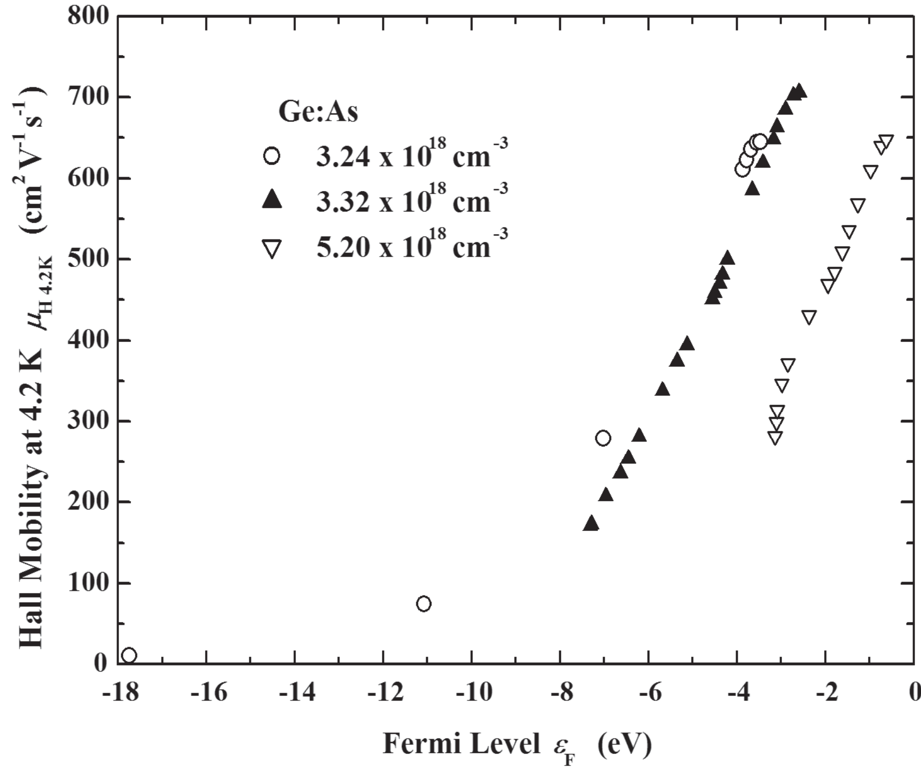

Fig. 5. The Hall mobility $\mu_H = R_H/\rho$ at 4.2 K versus the Fermi level ε_F.

4. Discussion

Obtained density of states shown in Fig. 4 decreases exponentially towards the inside of the energy gap, and the density of states spectrum is essentially independent on the initial donor concentration. The broken line in Fig. 4 is an exponential fitting curve.

The Hall mobility at 4.2 K shown in Fig. 5 becomes higher monotonically with increasing Fermi level energy through successive isochronal anneals, which is considered due to decreasing concentration of charged acceptors. The Hall mobility for the sample with initial donor concentration of 5.20 x 10^{18} cm^{-3} is lower than the ones for the samples with initial donor concentrations of 3.24 x 10^{18} cm^{-3} and 3.32 x 10^{18} cm^{-3} at the same Fermi levels. This is considered due to the higher concentration of charged acceptors which act as scatterers for the sample with the initial donor concentration of 5.20 x 10^{18} cm^{-3} at the same Fermi levels where electron concentrations for the three samples are nearly equal as shown in Fig. 3.

For the upper three curves in Fig. 1, an activation energy ε_2 is observed in the liquid helium temperature region and the conduction is the intermediate-concentration type, while for the lower two curves, no activation energy is observed in the liquid helium temperature region and the conduction is metallic. The Fermi levels where ε_2 becomes zero and the metal-nonmetal transition occurs are indicated by solid-line arrows in Fig. 3 for the three samples. The electron concentration n, the compensation ratio K and the Fermi level energy ε_F where ε_2 becomes zero and the metal-nonmetal transition occurs are shown in Table I. The electron concentrations corresponding to the metal-nonmetal transition for these compensated samples are higher than the one for uncompensated antimony-doped germanium crystals, which is 2 x 10^{17} cm^{-3}.[6)] This is considered due to the effect of charged acceptors repulsing the electrons in the compensated samples.

Table I. The electron concentration n, the compensation ratio K and the Fermi level ε_F, where ε_2 becomes zero and the metal-nonmetal transition occurs.

	n	K	ε_F
Ge : As 3.24 x 10^{18} cm^{-3}	1.15 x 10^{18} cm^{-3}	0.65	-3.9 meV
Ge : As 3.32 x 10^{18} cm^{-3}	0.97 x 10^{18} cm^{-3}	0.71	-3.8 meV
Ge : As 5.20 x 10^{18} cm^{-3}	1.56 x 10^{18} cm^{-3}	0.70	-2.8 meV

5. Conclusions

The density of states spectrum for the impurity band was obtained for highly-compensated heavily arsenic-doped n-type germanium crystals with initial donor concentrations of 3.24 x 10^{18} cm^{-3}, 3.32 x 10^{18} cm^{-3} and 5.20 x 10^{18} cm^{-3}. Obtained density of states decreases exponentially towards the inside of the energy gap, and the density of states spectrum is essentially independent on the initial donor concentration.

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