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THE UNIVERSITY OF CHICAGO
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THE JAMES FRANCK INSTITUTE
5640 South Ellis Avenue
Chicago, Illinois 60637

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Prepared by

A

H. FRITZSCHE,
Principal Investigator
Tel. (312) 753-8221

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1. ABSTRACT OF RESEARCH GOAL

Superior GaAs material is in great demand for high frequency and high speed GaAs devices such as Impatt diodes, Gunn diodes, field effect transistors, and avalanche photodiodes. The quality and control of impurities in GaAs material is much less advanced than in elemental semiconductors such as Si. This is partly because substitutional dopants can occupy either Ga sites or As sites and they tend to associate and cluster. We intend to develop a new method for preparing homogeneous and well controlled GaAs material. This method is nuclear transmutation doping. It has yielded superior Si and Ge semiconductor device material and should be even more successful in the case of GaAs because of the larger neutron capture cross sections and shorter radioactive decay times involved. We intend to study the doping characteristics of bulk and epitaxial layers of GaAs using nuclear transmutation doping and the resulting electrical characteristics.

II. SUMMARY OF RESULTS AND ACCOMPLISHMENTS

Nominally pure and Cr-doped semi-insulating GaAs crystals as well as very pure epitaxially-grown GaAs were exposed to thermal neutron fluences between 10^{17} and 2×10^{18} neutrons/cm². We established by conductivity and Hall effect measurements that transmutation doping is successful in GaAs. The concentration of donors produced by thermal neutron capture and subsequent nuclear transmutation agrees with the theoretically expected value to within the 10% experimental error. Transmutation doping is found to be 1000 times more efficient in GaAs than in Si because of the larger abundances and capture cross sections of the Ga and As isotopes. High quality epitaxial GaAs can be transmutation doped with great control of the concentration and homogeneity of the resulting donors. The recoil damage associated with transmutation doping can be removed by annealing at 600°C without protective Si₃N₄ encapsulation. Low quality GaAs and Cr-doped semi-insulating GaAs on the other hand, requires annealing at 800°C and hence Si₃N₄ encapsulation to remove the recoil damage. This is because a large residual impurity concentration retards the diffusion of interstitial recoil atoms and leads to defect complexes. The electrical transport properties of transmutation-doped GaAs were studied between 1.4 and 450K. The nonmetal-metal transition was observed at a critical donor concentration of 3×10^{16} cm⁻³ in uncompensated samples. The critical concentration increases with compensation. The electron mobility was found to be higher in transmutation doped GaAs than in non-irradiated samples of similar electron concentration. The reason for this is the absence of compensating acceptors in the transmutation doping process.

III. INTRODUCTION

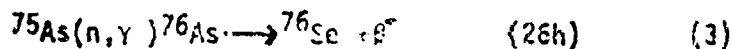
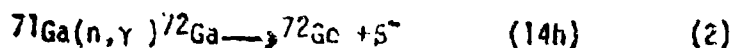
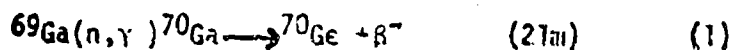
Thirty years ago, Cleland, Lark-Horovitz and Pigg¹ carried out the first transmutation doping and showed that it is a convenient and highly reproducible method for introducing a homogeneous distribution of dopants into certain semiconductors. This work was continued by Fritzsche et al.,² Cuevas,³ and others⁴ who made a detailed investigation of the electronic transport properties of transmutation doped Ge down to He temperatures. The method was applied to Te by Kuehnel et al.⁵ and is now widely used in the manufacture of Si devices.

Besides a brief study by Mirianashvili et al.,⁶ no detailed investigation of transmutation doping has been carried out on GaAs. This is quite surprising in view of the importance of GaAs as device material and the difficulties encountered with dopants in III-V compounds with regard to impurity and vacancy complexes and the question whether Ge or other impurities are on Ga or As sites.

We report here a study of the resistivity ρ and the Hall coefficient R of GaAs exposed to thermal neutron fluences between 10^{17} and 2×10^{18} n/cm². Three kinds of GaAs crystals were used, undoped and semi-insulating (Cr-doped) crystals, and a high purity epitaxial layer.⁷ R , ρ , and the Hall mobility R/ρ were measured between 1.4 and 450K.

IV. DOPING EFFICIENCY

In contrast to Si and Ge, all naturally occurring isotopes of Ga and As participate in transmutation doping with the reactions



The capture cross sections for thermal neutrons are 1.68, 4.86 and 4.3 barn and the natural abundances 60, 40, and 100% for the Ga and As isotopes in the reactions (1), (2), and (3), respectively. If the resultant Ge atoms are located on Ga sites and the Se atoms on As sites, then all end products will act as shallow donors. In this case one expects to find a nuclear transmutation doping efficiency of

$$N_D = 0.16 \phi t \quad (4)$$

which is three orders of magnitude higher than that in Si. Here ϕ is the thermal neutron flux ($n/\text{cm}^2\text{sec}$) and t the irradiation time (sec).

V. RECOIL DAMAGE AND ANNEALING

After GaAs samples have been irradiated by thermal neutrons and the induced radioactivity has been allowed to decay, the samples have very high resistivities. This is due to deep lying electronic states from radiation damage defects. These defects arise predominantly from atoms displaced by the recoil energy associated with the γ -decay and β^- -decay processes of reactions (1) to (3). The recoil energies from the β^- and γ -emissions are

$$E_R(\gamma) = E_\gamma^2 / 2Mc^2$$

$$E_R(\beta^-) = E_\beta (E_\beta + 2m_0c^2) / 2Mc^2$$

where M is the mass of the recoiling nucleus, m_0 is the electron rest mass, and E_γ and E_β are the energies of the γ - and β^- -particles, respectively. The recoil energies cover a range of values

because various decay channels are possible. Decay with the highest γ -energy $E_\gamma \approx 7.5$ MeV occurs with low probability (1%). The most probable decay proceeds by emission of two or three photons of lower energy. In the following table we list the (improbable) maximum recoil energy involving one photon, the most probable recoil energy associated with emission of two photons and the minimum recoil energy resulting from emission of three photons. The range of recoil energies associated with β -decay depends on the correlation between the emitted neutrino and β particle. The table lists the maximum and most probable values $E_R(\beta \text{ max})$ and $E_R(\beta)$, respectively.

Table: Recoil Energies of Decay Reactions in eV.

| | $E_R(1\gamma)$ | $E_R(2\gamma)$ | $E_R(3\gamma)$ | $E_R(\beta \text{ max})$ | $E_R(\beta)$ |
|------------------|----------------|----------------|----------------|--------------------------|--------------|
| ^{70}Ga | 457 | 228 | 152 | 33 | 16 |
| ^{72}Ga | 444 | 222 | 148 | 100 | 50 |
| ^{76}As | 375 | 187 | 125 | 83 | 40 |

Since the energy needed to create a vacancy-interstitial pair is only about 9eV in the Ga-sublattice and about 10eV in the As-sublattice, a considerable number of defects are produced by the recoil processes. In elemental semiconductors annihilation of such defect pairs by annealing causes little problem. In GaAs, however, the transmuted Ge and Se atoms may end up either on a Ga or an As lattice site. Whether the transmuted Ge atom acts as a donor or as an acceptor depends on this choice. The doping efficiency calculated in the previous section was based on the assumption that all Ge atoms are situated on the Ga sublattice after annealing. Any Ge atom misplaced on the As sublattice acts as a compensating acceptor. Moreover, it forces a displaced As atom to choose a Ga lattice site (antisite defect) to remain an interstitial atom. At higher transmutation densities interdiffusion between locally damaged regions may be expected to increase the number of transmuted atoms misplaced on wrong sublattices.

If the Ge atoms end up on Ga and As lattice sites with equal probability the doping efficiency of Eq. (4) will be reduced by about 20%. The Ge atoms on As sites act as acceptors and will in that case produce a compensation ratio of $N_A/N_D \approx 0.25$. Our present experimental results presented below suggest that transmutation doping of epitaxially grown GaAs yields a compensation ratio of approximately this magnitude. The residual impurity concentration in melt grown GaAs does not permit a conclusive quantitative analysis of the compensation ratio.

VI. EXPERIMENTAL DETAILS

The undoped and Cr-doped, semi-insulating crystals were melt-grown and purchased from Laser Diode Lab., Inc. Bridge-shaped samples with three electrode arms on each side and enlarged pads for current contacts were ultrasonically cut from 0.1 cm thick wafers. The undoped crystal had an excess electron concentration of $2-3 \times 10^{16} \text{ cm}^{-3}$. The Cr-doped crystal had $\rho > 10^7 \text{ ohm cm}$ at 300K. The epitaxially grown crystal⁷ was a square platelet $0.5 \times 0.5 \times 0.02 \text{ cm}$. The samples were irradiated at the Research Reactor Facility at the University of Missouri in a thermal neutron flux of $\phi = 5 \times 10^{11} \text{ n/cm}^2\text{sec}$. Annealing of the recoil and radiation damage was carried out at 800°C for 4.5-10.5 hours in an inert gas atmosphere after pyrolytic Si_3N_4 encapsulation to prevent As evaporation. The epitaxial layer was annealed at 600°C .

VII. RESULTS

Table I lists the values of the Hall coefficient R , resistivity ρ as well as of the electron density $n = 1/R_e$ and the Hall mobility $\mu_H = R/\rho$ measured at 300K before and after transmutation doping for the undoped GaAs samples. From measurements at 450K we estimate that errors due to carrier freeze-out are less than 10 percent.

Table I. Characteristics at 300K of Undoped GaAs Samples Before and After Transmutation Doping

| Sample No.: | 0 | 1 | 3 | 4 | 5. | |
|-------------------------------|--------------------------------------|-------|-------|-------|--------|--------|
| Before irradiation | $R(\text{cm}^3/\text{C})$ | 263 | 216 | 254 | 249 | 245 |
| | $\rho(\text{ohm-cm})$ | 0.07 | 0.06 | 0.072 | 0.07 | 0.068 |
| | $n(10^{16}\text{cm}^{-3})$ | 2.37 | 2.89 | 2.46 | 2.5 | 2.55 |
| | $\mu_H(10^3\text{cm}^2/\text{Vs})$ | 3.78 | 3.60 | 3.53 | 3.56 | 3.60 |
| After irradiation + annealing | $\phi t(10^{17}\text{n/cm}^2)$ | 0 | 1.0 | 3.125 | 9.37 | 18.75 |
| | anneal time (h) | 10.5 | 5 | 10.5 | 4.5 | 4.5 |
| | $R(\text{cm}^3/\text{C})$ | 193 | 131 | 101 | 37.5 | 19.2 |
| | $\rho(\text{ohm-cm})$ | 0.044 | 0.035 | 0.024 | 0.0094 | 0.0055 |
| | $n(10^{16}\text{cm}^{-3})$ | 3.23 | 4.75 | 6.2 | 16.7 | 32.5 |
| | $\mu_H(10^3\text{cm}^2/\text{Vs})$ | 4.35 | 3.71 | 4.19 | 3.97 | 3.47 |
| | $\Delta n(10^{16}\text{cm}^{-3})$ | 0.86 | 1.86 | 4.8 | 14.2 | 30 |
| | $0.16 \phi t(10^{16}\text{cm}^{-3})$ | 0 | 1.6 | 5.0 | 15 | 30 |

In order to test the quality of the Si_3N_4 encapsulation, sample No. 0, which received no irradiation was measured before and after annealing at 800°C for 10.5 hours. Evaporation of As atoms is known to produce deep electron traps and would therefore result in a reduction in n and μ_H . Instead we observe a small increase in carrier concentration and an improvement in mobility. It appears that annealing removes some low lying acceptor states initially present in the material. Unfortunately, this was discovered after the other samples had been irradiated. One therefore may have to correct the final Δn results by subtracting a value which probably is proportional to the anneal time. The last two rows in Table I compare the measured change in carrier concentration Δn with that expected from Eq. (4) and the irradiations ϕt (listed in row 5).

The close agreement between the measured and calculated values of the donor concentration introduced by transmutation doping shows that most Ge atoms are indeed on Ga sites.

A comparison of the last two rows of Table II which lists the data of Cr-doped samples after transmutation doping is less conclusive. However, since the difference $0.16 \phi t - n$ increases monotonically with ϕt , we believe that the major cause for this difference is that Cr-doping delays complete annealing or creates As vacancies which can capture Ge atoms which have been displaced from their normal lattice sites by the recoil energy.

Table III shows preliminary results on a high purity epitaxial layer. The values for the donor and acceptor concentrations were calculated from the mobility at 77K using the master curve of Wolfe et al.⁸ One finds that N_D has increased by $1.1 \times 10^{15} \text{cm}^{-3}$ which agrees within 10% with the value expected from Eq. (4) even though the sample was annealed for only one hour at 600°C. In impure samples, a much higher anneal temperature of 800°C was needed because the impurities tend to trap the diffusing species. Further anneal studies on this epitaxial sample are needed to see whether the increased N_D value is caused by remaining radiation or by Ge on As sites.

Figs. 1-3 show the temperature dependencies of R , ρ and μ_H , respectively, for the samples listed in Table I and II. The non-irradiated sample is labelled (00) before annealing and (0) after annealing. Attention is drawn to the following features in the figures. The maxima in the Hall curves near 80K mark the transition from dominant band conduction at higher temperatures to impurity conduction in a band of states formed by the shallow donors, at lower temperatures. The critical donor concentration N_c at which the

Table II. Characteristics at 300K of Cr-Doped GaAs ($\sim 9 \times 10^{16} \text{Cr/cm}^3$) Samples After Transmutation Doping and Annealing at 800°C for 4.5 hours.

| Sample No.: | 1C | 2C | 3C | 4C |
|---------------------------------------|-------|-------|-------|-------|
| $R(\text{cm}^3/\text{C})$ | 560 | 323 | 111 | 40.2 |
| $\rho(\text{ohm-cm})$ | 0.235 | 0.143 | 0.043 | 0.014 |
| $\mu_H(10^3 \text{cm}^2/\text{Vs})$ | 2.38 | 2.25 | 2.56 | 2.97 |
| $n(10^{16} \text{cm}^{-3})$ | 1.10 | 1.72 | 5.63 | 15.5 |
| $0.16 \phi t(10^{16} \text{cm}^{-3})$ | 7.5 | 9.0 | 15.0 | 30.0 |

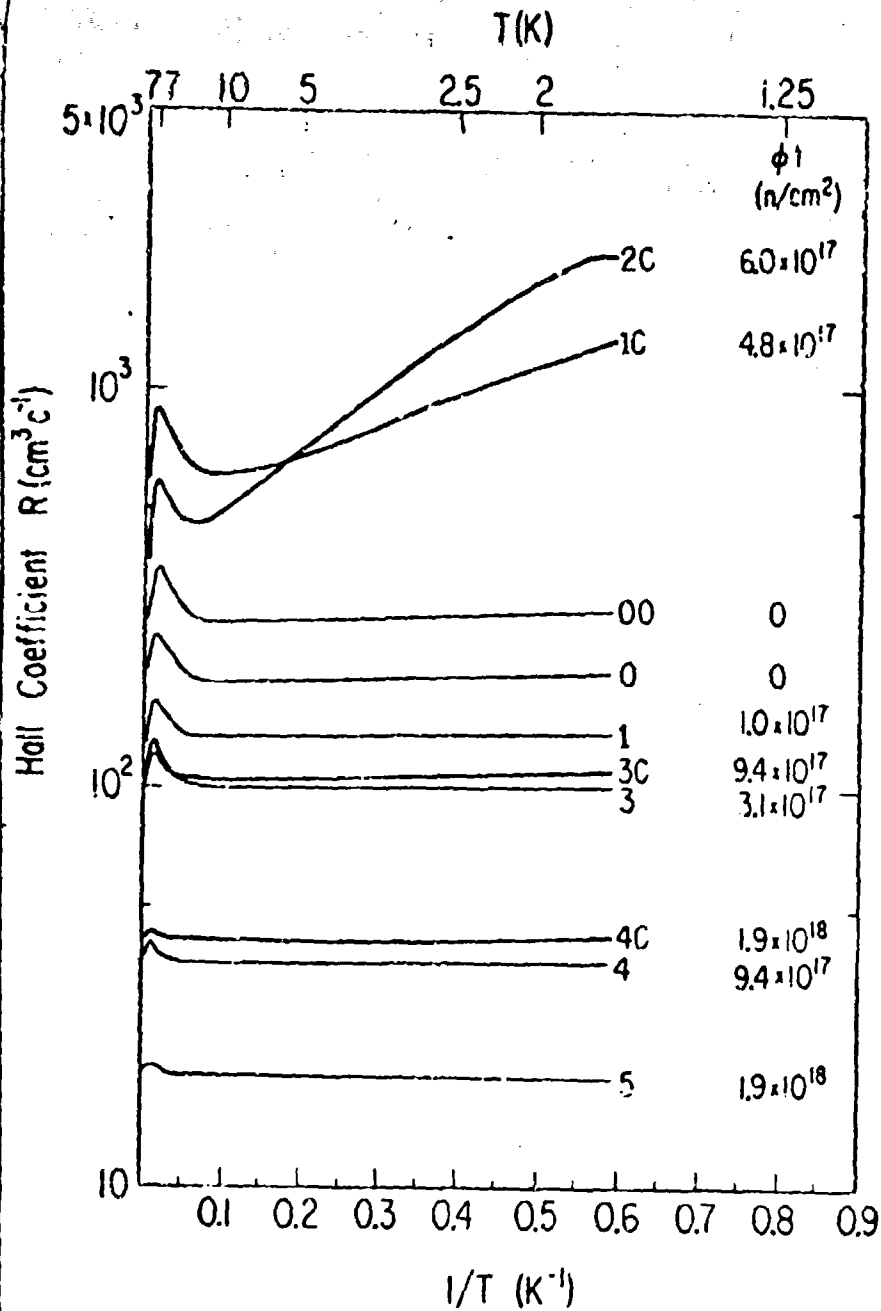


Fig. 1. Temperature dependence of the Hall coefficient of GaAs samples after various amounts of neutron transmutation doping. The characteristics of these samples are listed in Tables I and II.

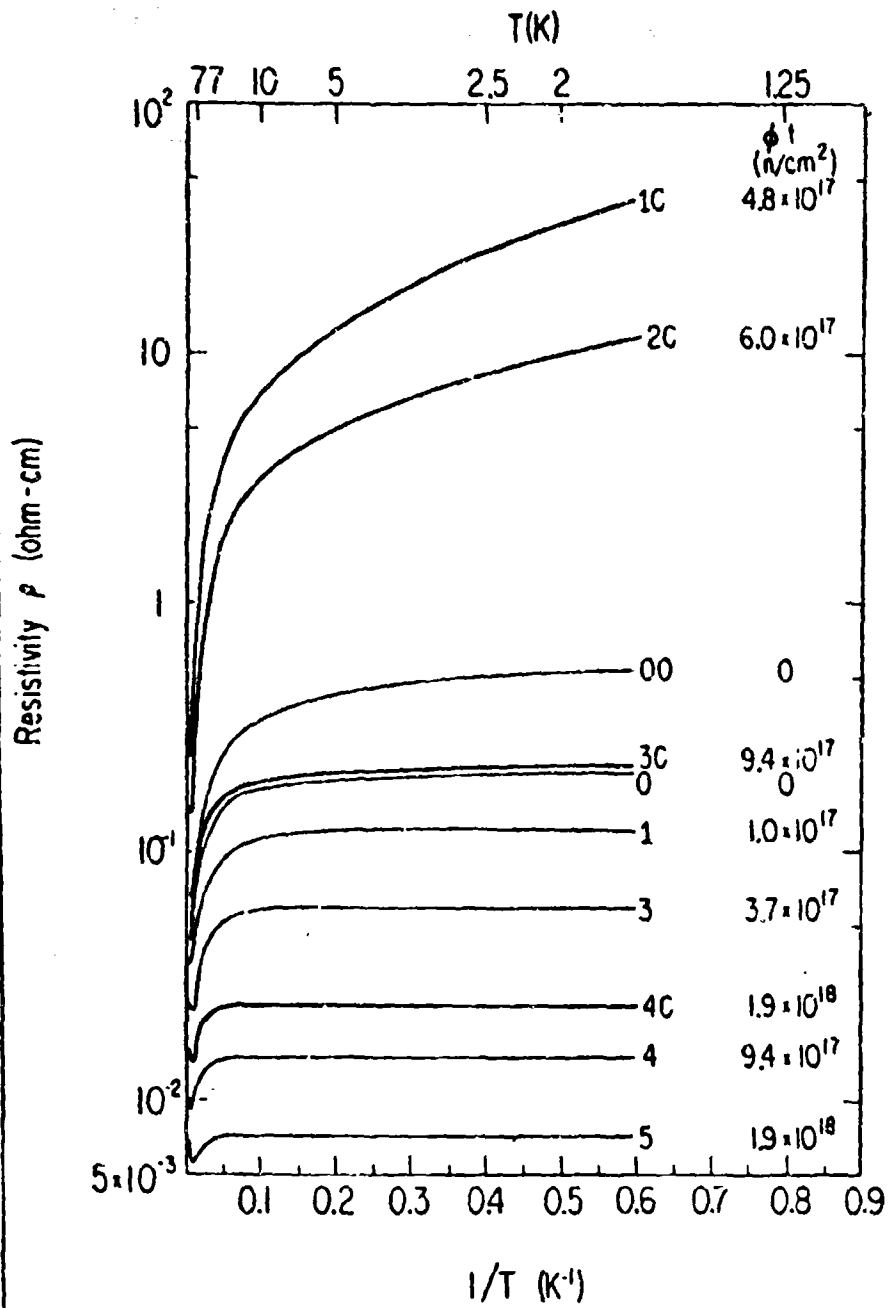


Fig. 2. Temperature dependence of the resistivity of the samples of Figure 1.

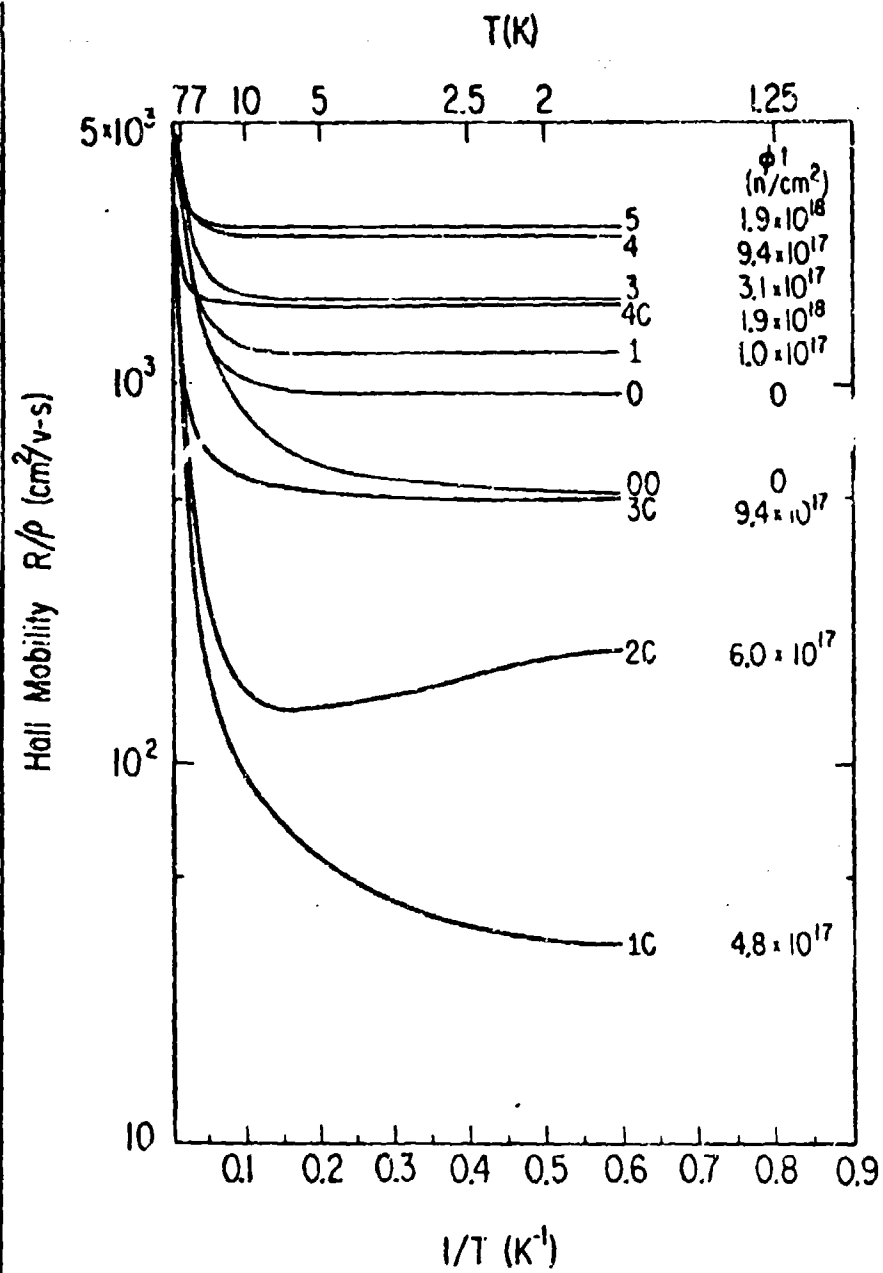


Fig. 3. Temperature dependence of the Hall mobility of the samples shown in the previous two figures.

Table III. Characteristics at 300K of Epitaxial GaAs Before and After Transmutation Doping. $0.16 \mu t = 1.2 \times 10^{15} \text{cm}^{-3}$. Anneal: 1 hour at 600°C .

| | R (cm^3/C) | ρ (ohmcm) | μ_H (cm^2/V_s) | n (cm^{-3}) | N_D (cm^{-3}) | N_A (cm^{-3}) |
|--------|---------------------------------|-------------------|---|---------------------------|-------------------------------|-------------------------------|
| Before | 39,800 | 5.18 | 7,690 | 1.57×10^{14} | 2.1×10^{14} | 5.7×10^{13} |
| After | 7,820 | 1.01 | 7,770 | 7.98×10^{14} | 1.3×10^{15} | 4.7×10^{14} |

nonmetal-metal transition occurs is about $3 \times 10^{16} \text{cm}^{-3}$ for the undoped samples.⁹ R of these samples is therefore temperature independent at low T. Samples 1C and 2C which are partially compensated by Cr-doping have a temperature activated Hall coefficient at low T. The nonmetal-metal transition occurs at a somewhat higher concentration than that of sample 3C. We estimate $n_C = 6 \times 10^{16} \text{cm}^{-3}$ and $N_C = 1.5 \times 10^{17} \text{cm}^{-3}$ for this sample series. Such increase of the critical concentration with compensation has also been observed in Ge.¹⁰ It is at variance with Mott's criterion for N_C at the metal-nonmetal transition.¹¹

The resistivity curves of Fig. 2 show two activation regimes. The larger activation ϵ_1 at higher T is due to excitation of carriers into the conduction band. The smaller low temperature activation energy ϵ_2 decreases to zero as the nonmetal-metal transition is reached. For the metallic samples ϵ_1 is still finite which means electronic transport takes place in a band of donor states below the conduction band. This is supported by the fact that the Hall mobility increases with donor concentration even for the metal-like samples (Fig. 3). Similar results have been observed in Ge above the nonmetal-metal transition.¹² We believe the increase of mobility with donor concentration is caused by the increased overlap of the donor state wave functions. The low temperature Hall mobility of the partially compensated samples is lower than that of the uncompensated ones because of the random disorder potentials of the compensating acceptor ions.

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