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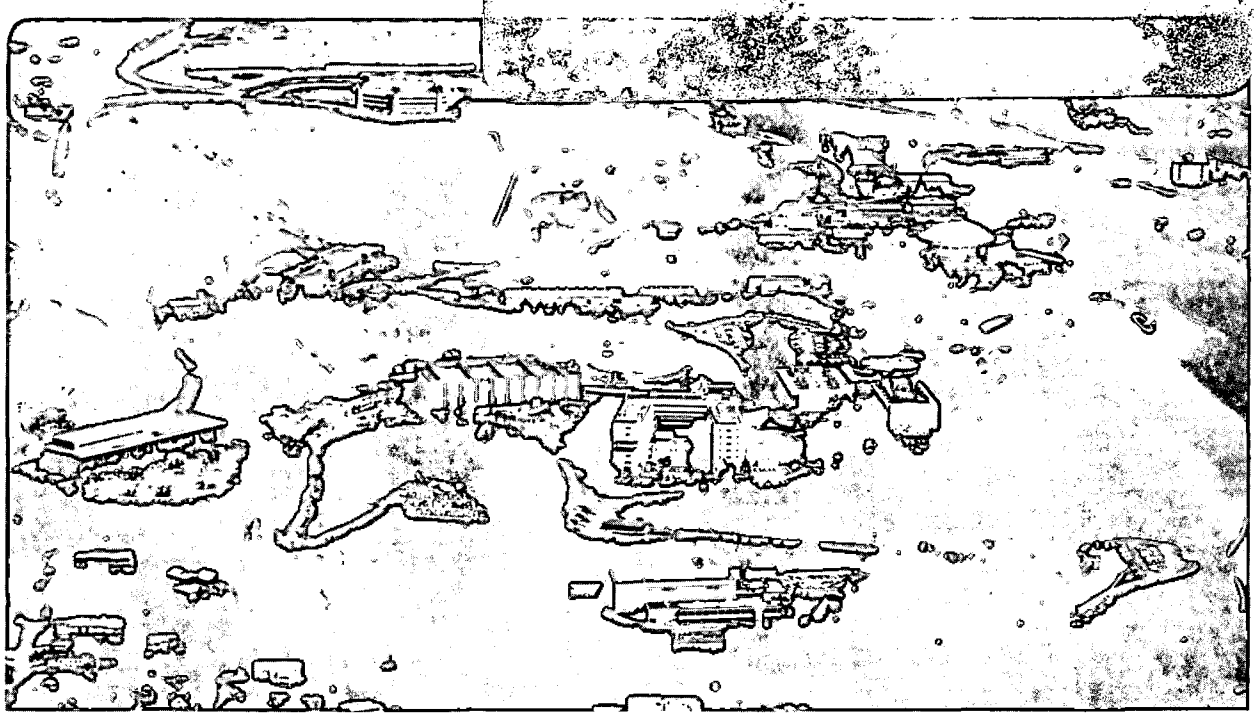

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Photo Hall effect characterization of closely compensated Ge:Be

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The temperature dependence of the free carrier lifetime in germanium doped with the double acceptor Be has been investigated using the photo Hall effect technique and found to be strongly temperature dependent when the residual shallow impurities are closely compensated. Close compensation ($N_A \simeq N_D$) of shallow levels was achieved by controlling the concentration of a beryllium-hydrogen acceptor complex A(Be,H) which is present in crystals grown under a H_2 atmosphere. This complex can be removed with high temperature annealing. An increase of up to two orders of magnitude in free carrier lifetime as a function of temperature is found to occur between 5 and 11 K in closely compensated material due to the population inversion of ionized centers created by optical pumping.

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I. INTRODUCTION

Germanium doped with the helium-like double acceptor beryllium (Ge:Be) has been the subject of several recent piezospectroscopy and photoluminescence experiments.[1,2] Beryllium is a semi-deep double acceptor with ionization energies of 24.5 and 58 meV. Large single crystals of beryllium-doped germanium, with excellent crystallographic perfection and very small residual shallow impurity concentrations, have been developed for use as far-infrared extrinsic photoconductor material for optimized detectors in the 30-50 μm wavelength range.[3]

The performance of Ge:Be photoconductors is strongly affected by the presence of residual concentrations of shallow acceptors (primarily boron and aluminum) which are unavoidably present in the starting material for crystal growth. A model has been proposed[4] which predicts a strongly temperature-dependent majority carrier lifetime in multilevel systems in which the residual impurities are closely compensated, i.e., $N_A(\text{shallow}) \simeq N_D$. "Multilevel system" is a term used to refer to any material with a deep or semi-deep primary dopant and residual shallow dopants. Ge:Be is one example. Other p-type materials which could be characterized as multilevel would include Ge:Zn, Ge:Hg, Si:Ga, and Si:In. In the limit of close compensation of the shallow acceptors, the free hole lifetime in these materials can increase rapidly with increasing temperature, leading to very high values of the photoconductive gain. Evidence of this behavior has been reported in Si:In and Si:Ga.[5,6] Strongly temperature-dependent values of the photoconductive gain have also been observed in Ge:Be photoconductors.[3]

The model proposed by Alexander, et al[4] is based on the calculation of the generation-recombination equilibrium in a space charge neutral detector under a constant photon flux Q. It predicts a step-like increase in free

carrier lifetime as a function of temperature in materials where the shallow levels are closely compensated. At a low enough temperature, the residual shallow acceptors are neutral. In the absence of a photon flux, these centers would be ionized due to compensation, but the ionized centers capture free holes when the sample is illuminated. The probability of photoionization of a shallow acceptor is small compared to that of the semi-deep acceptor (Be) because the latter is present at much larger concentration. As a result, this dynamic equilibrium state in the presence of a photon flux is different from the equilibrium state in the dark. Under illumination, the semi-deep level, rather than the shallow acceptor level, will be partially ionized.

As the temperature of the material is increased (assuming a constant photon flux Q), thermal generation from the shallow acceptors becomes significant, and the number of ionized shallow levels increases. Because the total concentration of ionized sites is approximately constant for low background flux [i.e., $N(Be)^- + N(\text{shallow acceptor})^- = N_D + p \simeq N_D$ for $p \ll N_D$], the population of ionized centers shifts from the Be level to the shallow acceptor level. This causes an increase in carrier lifetime because the free holes have a greater probability of thermal reemission if they are captured by an ionized shallow level. The average time then for which any single hole is in the valence band will be increased in comparison to the low temperature condition.

Alexander <u>et al.</u> show that the free hole concentration under constant flux rate Q will increase from

$$p = (N\sigma Q)/(N_D gC) = \dot{p}\,\tau_1$$

to

$$p = (N\sigma Q)/((N_D - N_A)gC) = \dot{p}\,\tau_2$$

as the temperature is increased through the range where the population shift of ionized centers occurs [p is the free hole concentration, N is the

concentration of neutral Be centers, g is the degeneracy factor, C is the recombination coefficient, N_A is the shallow acceptor concentration, τ is the hole lifetime, σ is the optical cross section, Q is the photon flux rate and $\dot{p}$ is the hole generation rate]. One sees that for very close compensation of shallow levels, the hole concentration can increase rapidly with temperature as a result of the increase in free carrier lifetime.

The photo Hall technique can be used to measure the free carrier lifetime as a function of temperature in an illuminated sample. For cases where the optical generation rate is larger than the thermal generation rate $[\dot{p}\tau >> N_V e^{(\varepsilon - \varepsilon_F)/kT}]$, the free carrier concentration is given by the expression $p = \dot{p}\tau$, as previously described. For a constant hole generation rate $\dot{p}$, the temperature dependence of the free carrier lifetime is obtained by measuring the temperature dependence of the free carrier concentration in the material.

In this paper, we present photo Hall effect results showing the influence of close compensation of the residual shallow acceptors on the free carrier lifetime in Ge:Be. A method for achieving close compensation of the residual shallow levels in this material is described.

II. EXPERIMENTAL

A. Growth of closely compensated Ge:Be

Ge:Be single crystals were grown using the Czochralski technique. Beryllium is added to a high purity polycrystalline Ge charge in the form of a heavily doped "master alloy" with the [Be] = $3.0 \times 10^{18} cm^{-3}$. The optimum concentration of Be for photoconductors is approximately 10^{14} to 10^{15} cm^{-3}. This allows for maximum absorption without excessive noise due to impurity conduction. Although high-purity Ge[7] can be grown with net residual concentrations

of electrically active impurities of ~ 10^{10} cm^{-3}, net residual acceptor concentrations in our as-grown Ge:Be ranged typically from 10^{11} to 10^{12} cm^{-3}. Because Be forms a very stable oxide, the SiO_2 crucible generally used in the growth of ultra-pure Ge is removed during Ge:Be crystal growth since Be in the melt could reduce the SiO_2 crucible to form stable BeO. This eliminates one of the major sources of oxygen in the melt environment. In the absence of the crucible, the melt is in direct contact with the graphite susceptor. The graphite is a source of boron and increases the residual concentration of boron in the melt. Also, limiting the availability of oxygen in the melt increases the concentration of electrically active Al. Oxygen is known to react with the Al to form electrically inactive oxide compounds. As a result, the final concentration of residual acceptors in the Ge:Be crystals generally is one to two orders of magnitude larger than the ultra-pure crystals. The residual acceptor concentration exceeds the residual donor concentration.

Normally one would compensate these shallow acceptors by counterdoping in the melt with an n-type master alloy such as Ge:P. Although this can be done, it is difficult to counterdope accurately enough to obtain the high degree of compensation required to observe the lifetime enhancement which theory predicts. In silicon, neutron transmutation doping (NTD) has been successfully used to closely compensate, in a controlled and reproducible manner, material which initially has N_A(shallow) > N_D.[5] NTD of Ge cannot be used for compensating residual shallow acceptors, however, because different isotopes of Ge transmute into both acceptors (Ga) and donors (As, Se).[8] Because more acceptors are created than donors, the net result of this process is to increase the net shallow acceptor concentration.

Closely compensated samples for the photo Hall effect measurements reported here were obtained by varying the concentration of a hydrogen-related shallow

acceptor complex [A(Be,H)] which has been discovered in Ge:Be crystals grown under a hydrogen atmosphere.[9] A(Be,H) has a split ground state with ionization energies of 10.8 and 11.3 meV and has an effective-mass-like series of excited states. The concentration of these shallow acceptor complexes, initially present at ~ 10^{13} cm^{-3} in as-grown crystals with [Be] = 10^{15} cm^{-3}, can be reduced with thermal annealing through dissociation of the complex followed by out-diffusion of atomic hydrogen.

Beginning with a counterdoped charge, in which $N_D > N_A$ for elemental residual impurities, a range of compensation from N_A(complex + elemental)$>N_D$ to N_A(complex + elemental)$<N_D$ was obtained by varying annealing times and temperatures. Samples were annealed at temperatures of 500 - 660°C. The samples were rinsed with potassium cyanide solution prior to annealing to limit Cu contamination during the high temperature process.[10]

B. Material Characterization

The doping levels and compensation of the materials were determined by variable temperature Hall effect. Free carrier concentration and resistivity were measured as a function of temperature using the van der Pauw technique[11] with samples of dimension 6x6x1 mm^3. A variable temperature cryostat with two light shields was used. The samples were in thermal contact with a copper cold finger. Indium alloyed contacts (p++) were used and exhibited good ohmic behavior down to 4.2 K. The dark Hall and photo Hall effect measurements were performed at a magnetic field of 0.1 Tesla. The Hall factor, r_H, was assumed to be equal to unity. The error resulting from this assumption is small in the low temperature freeze-out range which is of interest to this experiment.

Photo Hall effect measurements were made using the same samples and cryostat. The samples were illuminated through a small (d ≈ 0.2 mm) aperture in

the inner radiation shield by the 300 K blackbody radiation of the outer wall of the cryostat. Radiation from the inner shield ($T = T_{sample}$) is negligible compared to the external illumination at temperatures where free carrier generation in the sample is photon dominated. The hole generation rate was $\simeq 5 \times 10^{15}$ $cm^{-3}s^{-1}$, calculated using geometric optics and a reflectivity of 0.36 for Ge.

C. Results

The equilibrium Hall effect data without external illumination are given in Figure 1 for a series of annealed samples. The data for the as-grown material are also included, showing the initial state with $N_A(shallow) >> N_D$. The data are presented as an Arrhenius plot, log(p) versus inverse temperature. For cases where $N_D > N_A(shallow)$, the net donor concentration $[N_D - N_A(shallow)]$ is given by the point where the slope of the freeze-out curve changes from $E_{Be}/2k$ to E_{Be}/k, where E_{Be} is the ionization energy of the neutral Be center and k is Boltzmann's constant (Fig. 2).

In Fig. 1, one sees that, as the concentration of A(Be,H) is reduced with annealing, the material becomes more closely compensated. Case C in Fig. 1 is the most closely compensated case. The net donor concentration (i.e., the concentration of donors compensating Be acceptors) is $\simeq 10^{10}$ cm^{-3}. Since the as-grown material has a donor concentration of $\simeq 10^{12}$ cm^{-3}, this indicates a compensation of shallow levels to approximately one percent. After annealing for two hours at 660°C, the final state where $N_A(complex) << N_A(elemental)$ is reached. Additional annealing beyond this point will not change the Hall effect result.

The photo Hall effect results for several annealed samples are plotted in Fig. 3. The increase in free carrier lifetime as a function of temperature

and compensation is shown more clearly in Fig. 4 where four sets of data are plotted as log (p) versus log (T) over the region of interest to show the temperature dependence of the lifetime. In the closely compensated cases, the free carrier lifetime increases much more rapidly with temperature than the T^1 to T^3 increase predicted on the basis of the temperature dependence of the capture cross section and the mean thermal velocity. The dopant concentrations and magnitude of the lifetime increase are summarized in Table 1.

In the limit of exact compensation, the model of Alexander, et al.[4] predicts a temperature dependence of the carrier lifetime given by:

$$\tau \propto e^{-E_A/kT}$$

where T is the device temperature (K), and E_A is the ionization energy of the shallow acceptor (eV). The slope obtained from the data in Fig. 2 for case C is 10.7 meV. Photothermal ionization spectroscopy of this material shows that both B (E_i = 10.8 meV) and Al (E_i = 11.3 meV) are present as residual shallow acceptors. This indicates good agreement with the theory. The energy resolution of our Hall effect measurement is not sufficient to differentiate between the group III shallow acceptors in Ge.

The temperature at which the increase in free carrier lifetime due to thermal generation from the shallow acceptors will occur is given approximately by the temperature at which the ionized shallow acceptor concentration is equal to the neutral shallow acceptor concentration. Assuming no photoionization of shallow acceptors, this is given by:

$$T = \frac{E_A}{k \ln\left(\frac{N_v}{gp}\right)}$$

where g is the degeneracy factor for the acceptor level, and N_v is the valence band effective density of states. Extrapolating the low temperature

dependence of the free hole concentration, we calculate a transition temperature of T = 6.5 K for the parameter values given below:

$E_A = E_{boron} = 10.8$ meV

$N_v = 1.2 \times 10^{15} T^{3/2}$ cm^{-3}

$g = 4$

$p = \dot{p}\tau = 2 \times 10^5 \times T^{2.5}$ cm^{-3}

This is in good agreement with the data of Fig. 4 which shows that the closely compensated samples begin to deviate from a power law dependence between 6 and 7 K.

The temperature dependence of the recombination cross section ($c = \sigma < v > \propto \tau^{-1}$) which is measured for the fully annealed sample varies from T^{-1} to T^{-3} over the temperature range from 10 to 5 K. This may be due to the transition from a T^{-1} to T^{-3} dependence, as predicted by theory[12] for the capture cross section. Carrier heating, due to broad band illumination and field effects, may also be causing a deviation from the $T^{-2.5}$ dependence which has previously been reported[12].

III. SUMMARY

Compensation of shallow residual impurities to within 1% of the net doping has been achieved in Ge:Be by controlling the concentration of a hydrogen-related acceptor complex. This shallow acceptor complex, A(Be,H), is present in the as-grown crystals. Its concentration can be reduced with annealing until the residual shallow donor concentration is closely compensated.

Photo Hall effect measurements of free carrier lifetime as a function of temperature and compensation under broad band illumination show a strong temperature dependence of the lifetime as the degree of compensation is increased.

Results obtained are in good agreement with the theoretical model suggested by Alexander, et al.[4] for closely compensated multilevel extrinsic photoconductors.

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Table I. Summary of data obtained from different annealing treatements of Ge:Be grown under a hydrogen atmosphere. * indicates experimentally determined values: (1) $N_D-N_A(s)$ measured from dark Hall effect measurements. (2) N_D measured from dark Hall effect on as-grown material and assumed constant. $N_D/N_D-N_A(s)$ was determined from the size of the lifetime step in the Photo Hall effect data.

Crystal Slice	Annealing Time	Temp.	$N_D-N_A(s)$ (cm^{-3})	N_D (cm^{-3})	$N_A(s)$ (cm^{-3})	$\frac{N_D}{N_D-N_A(s)}$
728-4.6	As grown	-	$>10^{13}$*	10^{12}*	$>10^{13}$	-
728-4.6	120 min	660°C	$2\text{-}6\times10^{11}$*	10^{12}	$4\text{-}8\times10^{11}$	1.2-2*
728-4.3	90 min	600°C	5×10^{11}	10^{12}	5×10^{12}	≃ 2*
728-4.3	30 min	660°C	$\simeq10^{11}$*	10^{12}	10^{12}	> 30*
728-4.3	75 min	600°C	$\simeq10^{10}$*	10^{12}	10^{12}	>100*

FIGURE CAPTIONS

FIG. 1. Hall effect data plotted as carrier concentration as a function of inverse temperature for the following cases:

A. Ge:Be 728-4.6 As grown

B. Ge:Be 728-4.6 annealed 30 min. at 600°C

C. Ge:Be 728-4.3 annealed 75 min. at 600°C

D. Ge:Be 728-4.6 annealed 120 min. at 660°C

FIG. 2. Schematic of freeze-out behavior for Ge:Be for cases with $N_A(\text{shallow}) > N_D$ and $N_A(\text{shallow}) < N_D$.

FIG. 3. Photo Hall effect results plotted as carrier concentration as a function of inverse temperature for the following cases:

C. Ge:Be 728-4.6 annealed 75 min. at 600°C

D. Ge:Be 728-4.6 annealed 120 min. at 660°C

E. Ge:Be 728-4.3 annealed 90 min. at 600°C

FIG. 4. Photo Hall effect results plotted as log (carrier concentration) versus log (temperature) for the following cases:

C. Ge:Be 728-4.3 annealed 75 min. at 600°C

D. Ge:Be 728-4.6 annealed 120 min. at 660°C

E. Ge:Be 728-4.3 annealed 90 min. at 600°C

F. Ge:Be 728-4.3 annealed 30 min. at 660°C

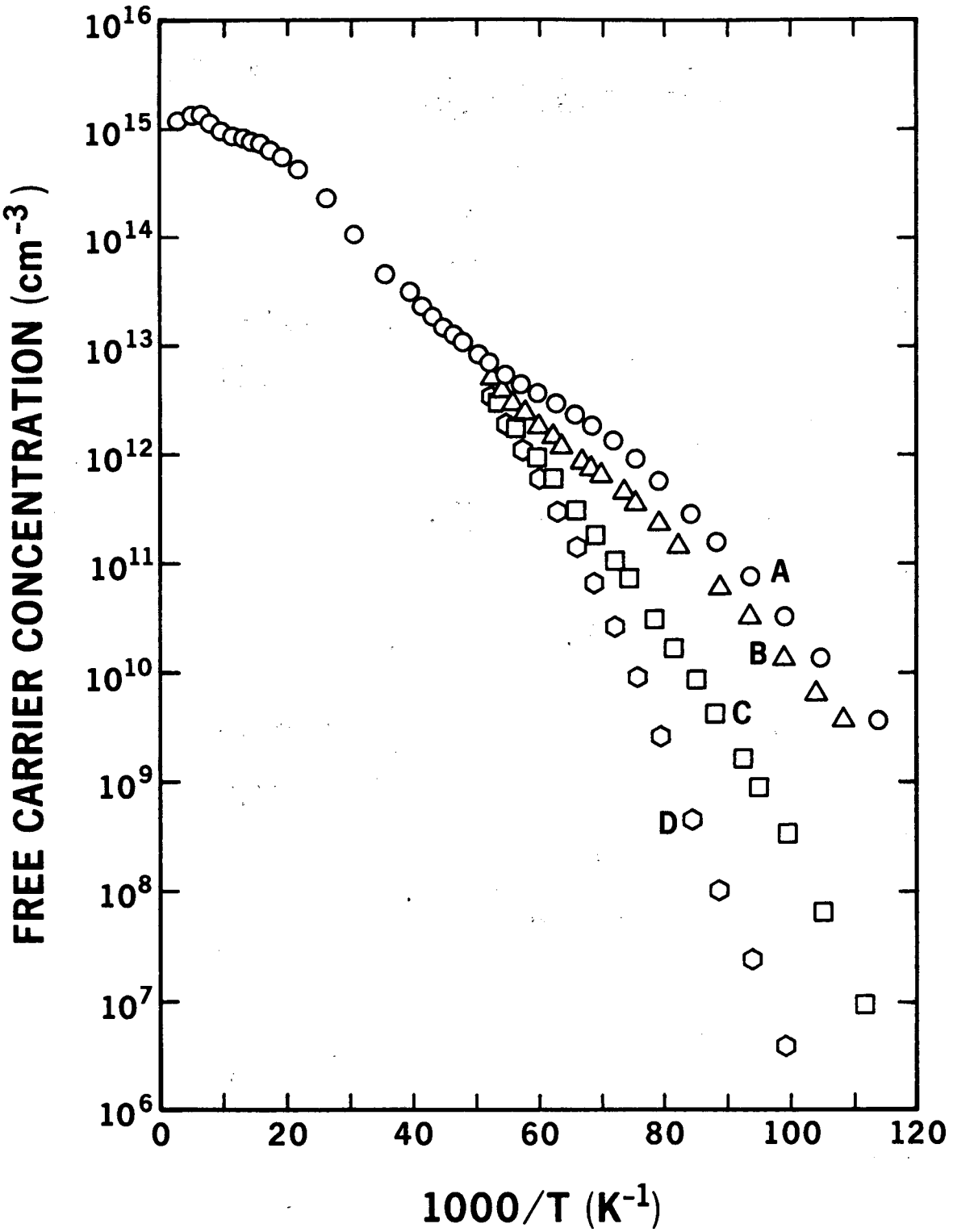

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Fig. 1.

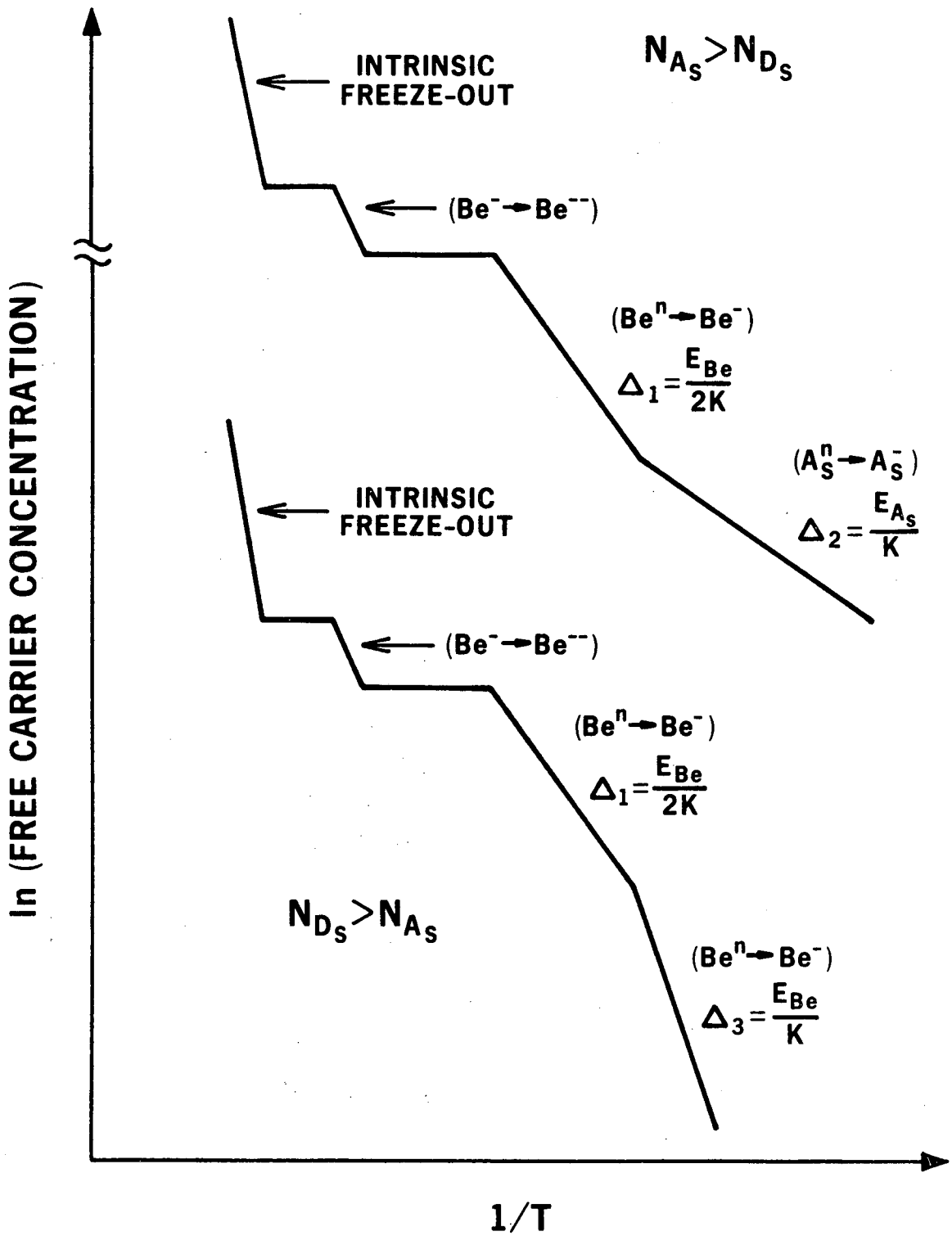

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Fig. 2.

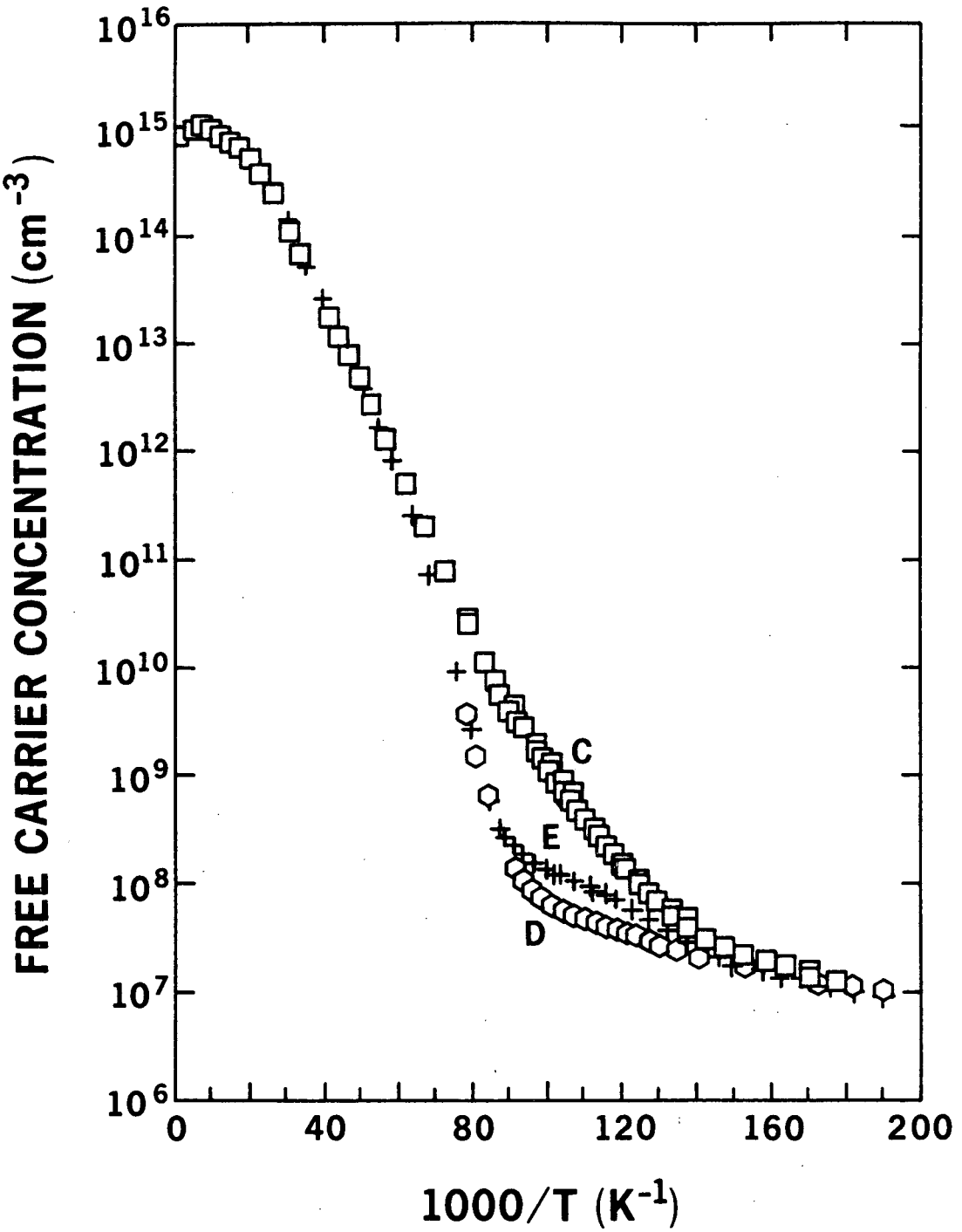

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Fig. 3.

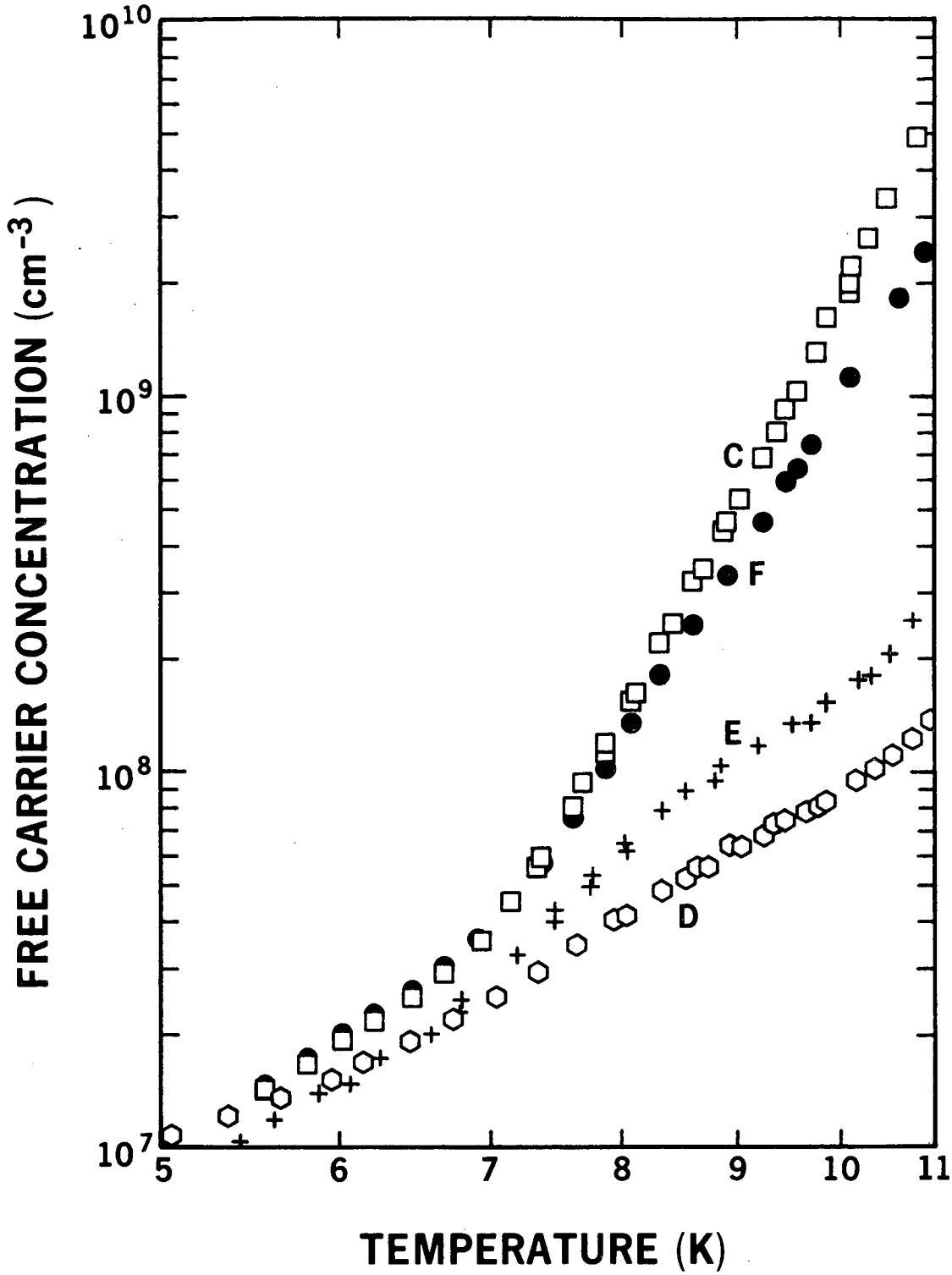

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Fig. 4.

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