nnealing of Fast Neutron Damage in Impurity-Conducting N-Type Germanium*

E. L. Wolf, W. Dale Compton, and S. W. Depp

Department of Physics, University of Illinois

The nature of the damaged regions produced by irradiation of germanium by fast neutrons,[1,2] and the resultant changes in the electrical properties[3] of the material have been previously studied. In addition, the annealing of electrical changes produced by x-ray and fast electron damage in lightly doped samples[4-6] has been carefully studied and has been explained in terms of the formation and subsequent dissociation of vacancy-impurity complexes.

The present work is concerned with the thermal annealing of fast neutron induced changes in the electrical properties of highly doped (but non-degenerate) n-type germanium. Two samples containing 2.2×10^{17} cm^{-3} antimony donors were studied and gave identical results. At temperatures below 10°K the resistivity in these samples is temperature-independent. This behavior shown in the lowest curve in Fig. 1, results from conduction in an antimony impurity-conduction band[7] that arises from such a strong overlap of the donor electron wavefunctions that these electrons become delocalized. The concentration

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is sufficiently high in these samples that hopping-conduction processes are unimportant.

Irradiation of such a sample with fast neutrons has been shown[7] to break up such an impurity band giving rise to a temperature dependence of the low temperature resistivity and an increase in this resistivity by more than an order of magnitude over its value prior to irradiation. At the low temperatures the resistivity may then be described by the equation $\rho = \rho(\infty) \exp(\epsilon_2/kT)$ where $\rho(\infty)$ is the intercept of the low temperature curve as $1/T \rightarrow 0$. Irradiation of germanium introduces acceptors (of density N_A) with levels deep in the forbidden gap and thus reduces the concentration of electrons free to conduct to $n = N_D(1-K)$ where $K = N_A/N_D$ is the compensation. Below 10°K the $N_D(1-K)$ electrons are condensed (but not necessarily "frozen") on the concentration-broadened donor ground state levels. Prior to irradiation conduction occurs in a ground state band; after irradiation conduction is believed to occur by excitation of carriers to a split-off impurity-conduction band lying higher in energy by the amount ϵ_2. It is believed that the dominant effect of irradiation on the impurity conduction parameters arises from the resulting change in occupation of the broadened donor ground state, and that the influence of the detailed nature of the compensating defects or their distribution is relatively minor. A set of anneals offered the possibility of changing the distribution of compensating defects without changing their total number, and therefore a possibility of observing the possible influence of the distribution of the compensating defects on the impurity conduction parameters.

The samples were irradiated for six hours at ambient in the Triga Mark II Experimental reactor, corresponding to an integrated neutron flux of $\sim 4 \times 10^{16}/cm^2$ having an energy exceeding 10 KeV. The samples were shielded from thermal neutrons by a cadmium foil shield and were placed in the "Lazy Susan" position at a depth of 6" in the graphite reflector, rather than at the core. This is expected to give an energy spectrum somewhat degraded from a fission spectrum, and to reduce the importance of large damage clusters[1,2] which have been shown to electrically resemble insulating voids. The high doping and consequent large carrier concentration n furthermore lead to a short Debye screening length[1] $L_D = \sqrt{\frac{\epsilon kT}{4\pi ne^2}}$ (about 150 Å at 300°K) and to correspondingly narrow space charge regions surrounding damage clusters. The carrier concentration at 0°C was reduced to about 56% of its value prior to irradiation, corresponding to a value of K = 0.44 for the compensation. The mobility at 0°C was reduced by the irradiation from 1700 cm^2/volt sec to 1250 cm^2/volt sec, a result consistent with an increase in charged center scattering, as given by the Brooks-Herring formula,[8] of $N_A = 0.44\ N_D$ additional charged centers. Such agreement does not necessarily imply the absence of radiation induced scattering other than that from charged centers. It is likely, however, in view of the probable unimportance of large insulating voids that charged center scattering accounts for the major part of the mobility change.

Following irradiation the samples were annealed at 10°C intervals from 100°C to 380°C, 45 minutes at each temperature. The samples were wrapped in platinum foil, placed in a metal container sealed in air,

and immersed in an oil bath. Electrical contacts were made with Cerroseal 35 solder which was removed with aqua regia before each anneal. The Hall constant R_H and the resistivity ρ at 0°C and 78°K were measured after each anneal. After selected anneals the complete resistivity vs 1/T data were taken as shown in Fig. 1. The annealing data are presented in terms of the fraction unannealed f:

$$f = \frac{\text{value after irradiation - value after anneal}}{\text{value after irradiation - value before irradiation}}$$

of the carrier concentration ($\propto 1/R_H$) and the reciprocal of the mobility at 0°C and 78°K. It is presumed that changes in the latter quantity, $1/\mu = \rho/R_H$, are proportional to changes in the concentration of charged centers. The annealing of the impurity conduction (resistivity from 2°K to 10°K) is represented by the fraction f of the activation energy ϵ_2 and the resistivity intercept $\rho(\infty)$ remaining. These data are shown in Fig. 2 and Fig. 3. The 0°C data, not shown, are very similar to the 78°K data.

The major features of these data are the lack of major annealing below 300°C of all quantities except the scattering center concentration, the gradual annealing and then distinct anneal stage of $1/\mu$ at 275°C, and the failure of the carrier concentration to completely anneal. These observations are to be contrasted with the results obtained on the annealing of n-type germanium that has been irradiated with Co^{60} gamma rays.[6,9,10] Annealing of the damage introduced by room temperature gamma ray irradiation of antimony doped germanium indicates a substantial anneal of the

carrier concentration at about 157°C with a nearly complete anneal by 277°C.[9] An inverse relationship exists between the recovery of damage and the concentration of antimony following gamma irradiations at 77°K.[10] That is, the recovery occurred at a lower temperature and with a more unique activation energy for crystals with 1.445×10^{14} than for crystals with 1.074×10^{15} Sb atoms/cm^3. These comparisons suggest that two factors may be responsible for the differences between the present results and the previous results on gamma-ray irradiated crystals. First, the nature of the damage is certainly different for the neutron irradiation than for the gamma irradiation. Second, the very high antimony content in the crystals of this experiment would tend to result in a more complete complexing of the interstitials with the impurities forming interstitial antimony or a substitutional antimony-interstitial germanium or vacancy-antimony pairs. This assumption is consistent with the absence of low temperature annealing that has been interpreted as resulting from motion of individual vacancies or the break-up of impurity interstitial-vacancy complexes. The lack of a complete anneal of the carrier concentration appears consistent with the observation of Bertolotti et al[11] that remnants of neutron-induced damage regions remain in germanium after an anneal of 12 hours at 460°C.

It is clear that the anneal of the impurity conduction parameters more nearly resembles that of the 78° carrier concentration than of the scattering center concentration. In particular, the impurity conduction parameters do not reflect the gradual anneal of $1/\mu$ which occurs between

110° and 250° nor the initial drop in the 275° $1/\mu$ annealing stage. It seems likely that this anneal of $1/\mu$ results from a redistribution of charged defects resulting in pairing of oppositely charged species, without reducing the number of deep acceptor states available.

A detailed interpretation of the annealing has not been possible. We suggest, however, that the sharp annealing stage at 310°C is more likely the breakup of some complex of simple defects with the abundant antimony than the breakup of disordered regions. The damage regions presumably have a broad distribution of sizes and breakup temperatures, which should lead to a relatively featureless anneal. Gradual breakup of the damage regions, we speculate, may occur in the range 110° to 250°, with charged decay products complexing with the antimony and reducing the charged scattering center concentration. That such complexing with some fraction of the K N_D ionized donors in the range 110° to 250°C should not affect ϵ_2 and $\rho(\infty)$ is consistent with the view that the ϵ_2 conduction process does not depend on the presence of unoccupied donor ground state levels, and supports the contention that the impurity conduction parameters, at least for concentrations near the metallic transition, are only slightly affected by the distribution of compensating defects. Thus, the complexing of the acceptors does not measurably affect the overlap of the occupied donors. The observation that ϵ_2 completely recovers suggests that the irradiation and anneal have not altered the average distribution of the antimony in any substantial fashion. It should be noted that this is not inconsistent with the

observation that the carrier concentration has not completely recovered, since brief initial irradiations were found to decrease n without changing ϵ_2 from zero. Only when the average overlap of electrons on the occupied donors fell below some minimum did ϵ_2 become non-zero.

The complex which decays at 310° could possibly be the strongly bound antimony-divacancy. The remaining deep states which do not anneal by 380°C are most probably associated with the more severely damaged regions.

It is clearly seen that the nature of the annealing process in highly doped materials that have been irradiated with neutrons is substantially different from the processes observed for more pure material that has been gamma ray irradiated.

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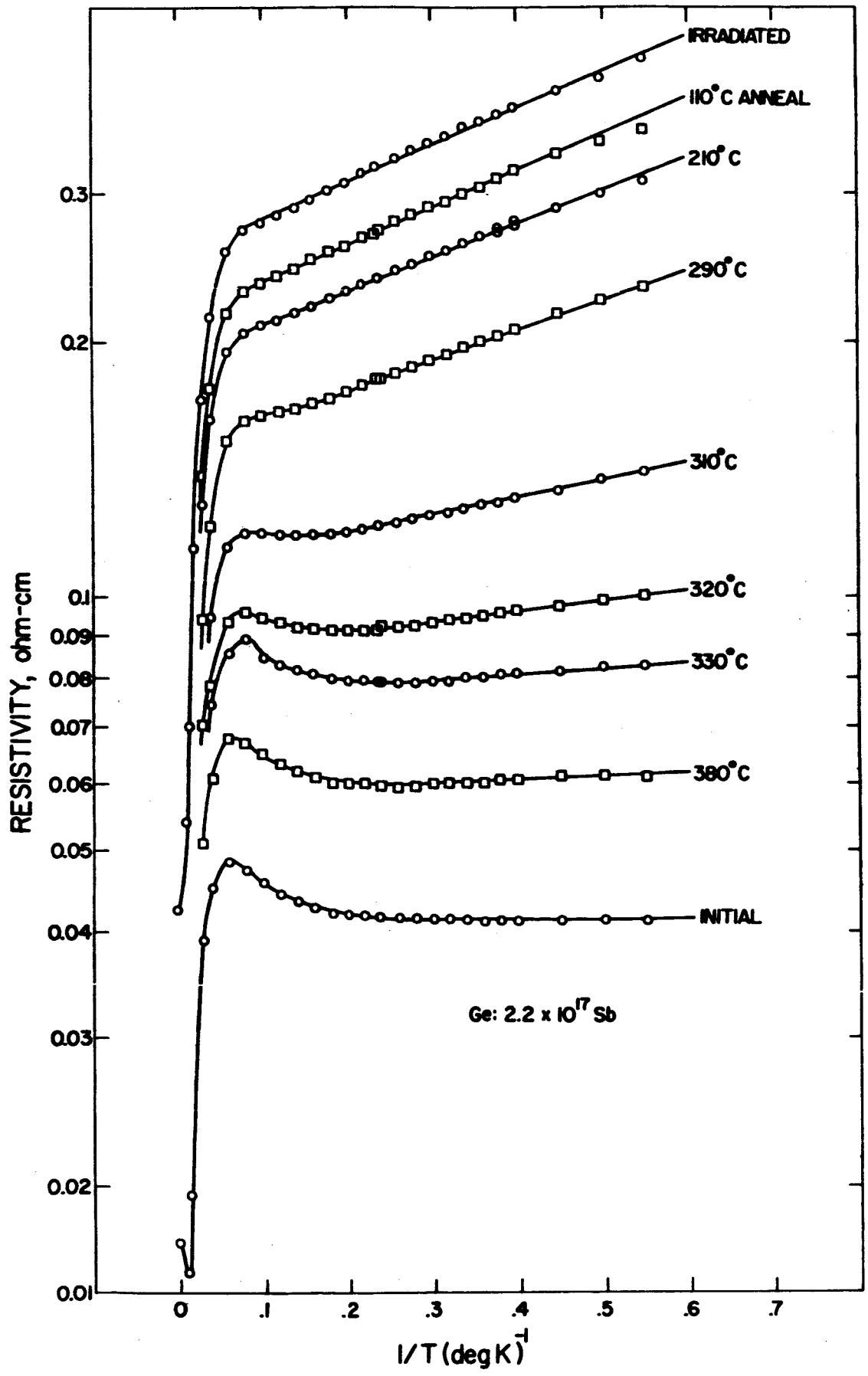
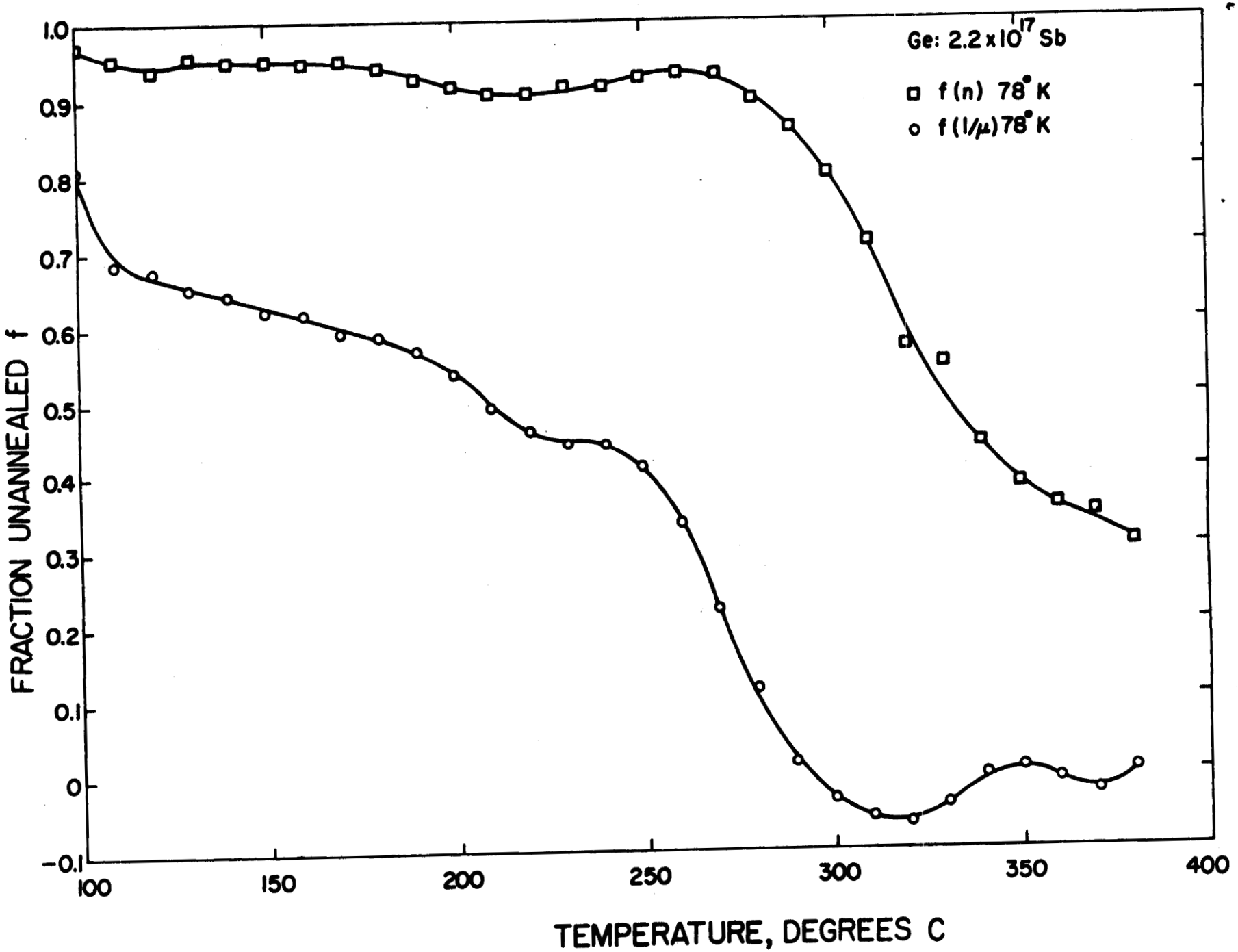
FIGURE CAPTIONS

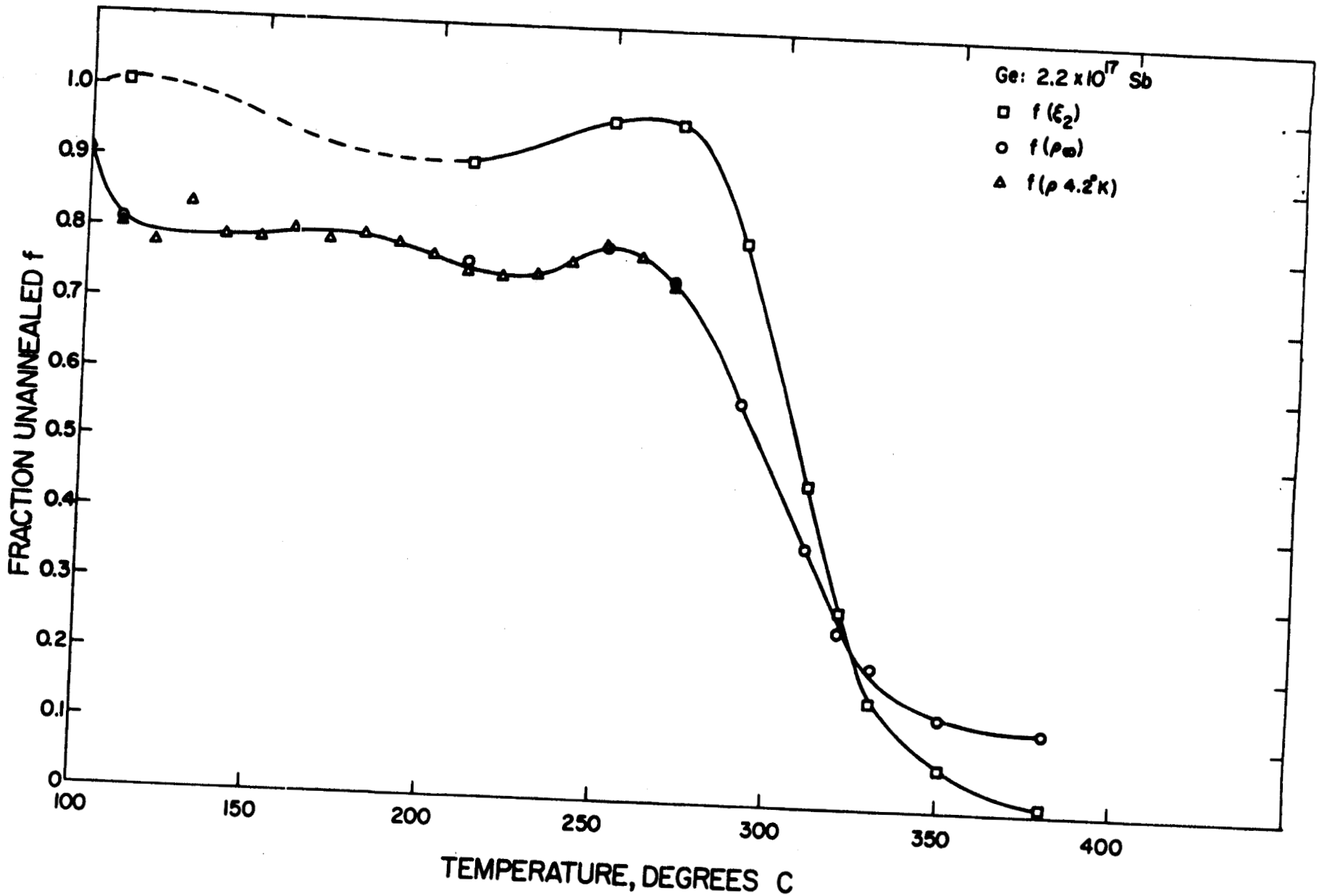
Fig. 1 Resistivity on log scale versus reciprocal temperature for germanium containing 2.2×10^{17} antimony, including data after a fast neutron flux of $4 \times 10^{16}/cm^2$ and a sequence of 45 minute anneals.

Fig. 2 Isochronal annealing of the 78°K carrier concentration (the squares) and the reciprocal mobility, presumed proportional to the charged scattering center concentration (the circles).

Fig. 3 Isochronal annealing of the impurity conduction parameters; the activation energy ϵ_2 (the squares) and the high temperature intercept $\rho(\infty)$ (the circles). The triangles are the fraction unannealed of the resistivity at 4.2°K, which, by virtue of the constancy of ϵ_2 is similar to the anneal of $\rho(\infty)$.


IRRADIATED
110°C ANNEAL
210°C
290°C
310°C
320°C
330°C
380°C
INITIAL
Ge: 2.2 x 10^17 Sb
RESISTIVITY, ohm-cm
0.3
0.2
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
.1
.2
.3
.4
.5
.6
.7
1/T (deg K)^-1


Ge: 2.2 x 10^17 Sb
□ f(n) 78°K
○ f(1/μ) 78°K
FRACTION UNANNEALED f
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
100
150
200
250
300
350
400
TEMPERATURE, DEGREES C


Ge: 2.2 x 10^17 Sb
□ f(ξ2)
○ f(ρ∞)
△ f(ρ 4.2°K)
FRACTION UNANNEALED f
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
100
150
200
250
300
350
400
TEMPERATURE, DEGREES C