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Quarterly Progress Report

For Period

July 1 to September 30, 1968

FUNDAMENTAL STUDIES OF THE METALLURGICAL,
ELECTRICAL, AND OPTICAL PROPERTIES OF
GALLIUM PHOSPHIDE

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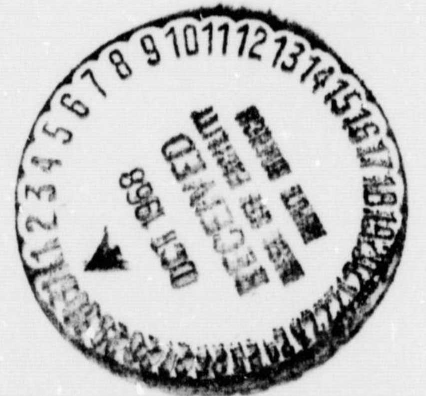
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
CLEVELAND, OHIO



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PROJECT 5115: SEMICONDUCTOR DEVICES FOR HIGH TEMPERATURE USE

National Aeronautics and Space Administration
Grant NsG-555
Principal Investigator: G. L. Pearson
Staff: Y. Nannichi, A. J. Domenico

The purpose of this project is to prepare power rectifiers and solar batteries which will operate at temperatures up to 500°C. During this quarter, extensive testing at elevated temperatures has been conducted on a Schottky barrier diode fabricated from the previously grown material. The results have been sufficiently encouraging that by extension of the present technique, operation at 500°C appears feasible.

A. Test Results

The Schottky barrier diode which was used consisted of a GaP undoped active region grown by vapor epitaxy of carrier concentration $n \approx 3 \times 10^{15}$ cm^{-3}, a Sn-doped GaP substrate grown by liquid epitaxy from a 50 percent by weight Sn solution in Ga of carrier concentration $n \approx 1 \times 10^{18}$ cm^{-3}, a vaporized chromium layer for the Schottky barrier material approximately 1 micron in thickness, and a vaporized nickel-germanium layer alloyed at 650°C for the ohmic contact.

The dynami· I-V characteristics of this diode were measured at various temperatures in a vacuum and are given in Fig. 1. The reverse breakdown at room temperature is off-scale and is in excess of 200 volts. At 500°C, the reverse leakage current at 50 v is less than 2 milliamperes.

More detailed static measurements were also taken and are given in Figs. 2 and 3. As can be seen from Fig. 2, the forward characteristics, after aging in a vacuum for 3 hours at 500°C, contains a current leakage component which must be further evaluated. The series bulk resistance is also seen to be between 20 and 40 ohms, which is too large for a good rectifier. However, the overall results, as exemplified by the reverse breakdown voltages, are very promising.

B. Revised Research Plan

The basic approach of a highly doped substrate to provide both mechanical support and a region suitable for a reliable ohmic contact has been shown to be desirable. Presently, however, the substrate has been grown by liquid epitaxy with the active region formed by vapor epitaxy. It would appear more advantageous to reverse these methods. Undoped liquid epitaxial gallium phosphide should contain a smaller number of crystal imperfections, have fewer deep level traps, and could be grown as a consistently thin layer to reduce the series resistance, while the vapor epitaxial gallium phosphide should provide a suitable thick substrate when properly doped. Therefore we now plan to attempt this reversal of construction techniques.

Several problems must be overcome in order to carry out this plan. Sulfur doping will be used for the n^+ vapor epitaxial substrate. However, since the substrate will then become the seed for the liquid epitaxial growth, the crystalline quality must be as good as possible. Previous efforts have sometimes resulted in large hexagonal pits being formed at high doping levels. We shall try to minimize this problem through the control of the concentration by the introduction of the sulfur vapor in a secondary stream beyond the gallium source, after the method of Hara and Akasaki.[1] The necessary modifications to our system are currently being made for the implementation of this method.

For the undoped region, a thin controlled layer must be grown with liquid epitaxy. One possible way in which this might be accomplished would be through the use of a vertical system, where the seed may be removed from the melt by raising after some desired time. Another possibility would be to achieve the same end in a horizontal system by the mechanical repositioning of the seed, e.g., the method of Panish and Sumski.[2] These and other alternatives will be explored.

C. Crystal Growth

In accordance with the revised research plan, the vapor

epitaxial system has been reactivated. To establish the proper growth conditions, three undoped crystals have been grown. After the system modifications mentioned above, additional undoped vapor epitaxial crystals will be grown, and subsequently, sulfur doped crystals at various levels as well.

D. Plans for the Next Quarter

The revised research plan will be continued. Hopefully, new samples of sulfur doped vapor epitaxial substrates with undoped liquid epitaxial active regions can be produced during the next three months.

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PROJECT 5112: THE PROPERTIES OF RECTIFYING JUNCTIONS IN $GaAs_xP_{1-x}$

National Aeronautics and Space Administration
Grant NsG-555
Principal Investigator: G. L. Pearson
Staff: S. F. Nygren

The purpose of this project is to study the preparation and characterization of rectifying junctions in GaP and $GaAs_xP_{1-x}$. In particular, we wish to relate the structure of the crystals to the electrical properties of the junctions. During this quarter we have completed our study of Be as a dopant in liquid epitaxial GaP. It has been concluded that Be is not a very suitable dopant, primarily because it is a fast diffusant in GaP.

To the best of our knowledge, the use of beryllium in GaP has not been previously explored. In analogy with the work of Poltoratskii and Stuchebnikov[1] in GaAs, Be in GaP might be expected to have shallow acceptor levels and to have a diffusion coefficient at 950°C of about 10^{-13} cm^2/sec. (The diffusion coefficient is estimated by using the rule of thumb that compares Zn diffusions in GaAs and GaP: for a given diffusion time and temperature in the range between 800 and 1000°C, the junction depth in GaP is the same as the junction depth that would occur in GaAs if the temperature were 150°C lower.) In addition, Be has a lower vapor pressure than that of gallium[2]. The above features suggest that Be would be a suitable acceptor for use in GaP liquid epitaxy. It would provide a shallow level; it would not diffuse beyond the interface between the seed and the layer; and the concentration of Be in the Ga solution would remain constant during growth since the Be would not evaporate preferentially.

As it turns out, however, there are major difficulties associated with using Be as a dopant in GaP liquid epitaxy. In the first place, it is difficult to get the Be to dissolve in the Ga solution. Elemental Be does not melt until 1284°C, so that when the growth solution is saturated at 965°C, the Be must be dissolved from a solid. This difficulty is further aggravated by the low solubility of Be in Ga

(3.5 a/o at $965^{o}C$[3]), and the rather high stability of the oxide that is generally found on the surface of the Be source.

In the studies described here, Be doped layers were grown in the vertical liquid epitaxial system. The Be source was either an evaporated layer of Be on a chip of source GaP or a small chip of pure Be that was laid against the Ga source before the source was saturated. In seven cases where the source Be was calculated to be present in the solution in amounts between 5×10^{-6} and 2.5×10^{-3} a/o, the grown layers were n-type, having background carrier concentrations between 8×10^{16} and 2.6×10^{17} cm^{-3}. When the Be source was increased to 2.2×10^{-2} a/o, a degenerate p-type layer was grown. It had a room temperature carrier concentration of 1×10^{19} cm^{-3} and a Hall mobility of 40 cm^2/v-sec. Thermodynamic calculations suggest that if a singly ionized acceptor is incorporated into GaP in an equilibrium, extrinsic fashion, the concentration of the acceptor in the grown layer should be proportional to the square root of the concentration of the dopant in the liquid.[4] Since the solubility in GaP of Be, which is expected to be a single acceptor, apparently does not fit this relationship, the amount of Be in liquid epitaxial GaP seems to be controlled either by incomplete dissolution of the Be source or by some non-equilibrium process.

The second, and crucial, difficulty with Be in GaP liquid epitaxy is that Be is a fast diffusant, at least when the Be concentration is about 10^{19} cm^{-3}. A preliminary experiment had indicated that Be would be a slow diffusant. Layers of Be, about 2000Å thick, were evaporated onto GaP samples. The samples were then diffused at 950 and $1000^{o}C$, and diffusion coefficients were estimated from the resulting p-n junction depths by assuming that the concentration profiles were complementary error functions. The estimates were $D \cong 1.5 \times 10^{-13}$ cm^2/sec at $950^{o}C$ and $D \cong 1.5 \times 10^{-12}$ cm^2/sec at $1000^{o}C$, in agreement with the estimate given above. On the other hand, the diffusion coefficient estimated from the degenerate p-type liquid epitaxial layer described above is considerably higher. That layer was grown by cooling the

growth solution at 0.32°C/min from 950°C for 4.5 hours. The resulting layer was 40 μ thick, and the Be had diffused 30 μ into the seed in addition. Assuming a complementary error function profile, and taking the surface concentration to be 1×10^{19} cm^{-3}, this is an average diffusion coefficient of 2×10^{-11} cm^{2}/sec. It is felt that the latter diffusion coefficient is more accurate and that the smaller values given above reflect experimental difficulties involved in the diffusion experiment; it is possible, for example, that the Be on the surfaces of the diffusion samples oxidized before the diffusion took place. At any rate, the deep diffusion during crystal growth cancels all of the advantages of liquid epitaxy. When liquid epitaxy is attempted with Be as a dopant, the result is simply a diffusion that was done in a complicated fashion.

This project has been completed, and a final report is in preparation.

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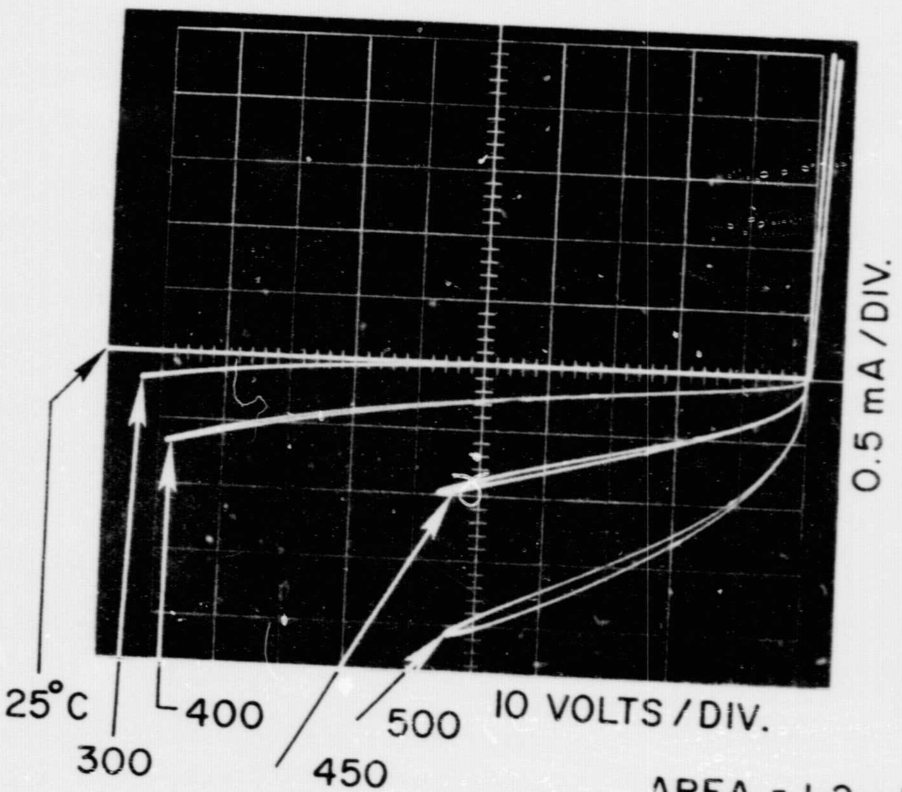

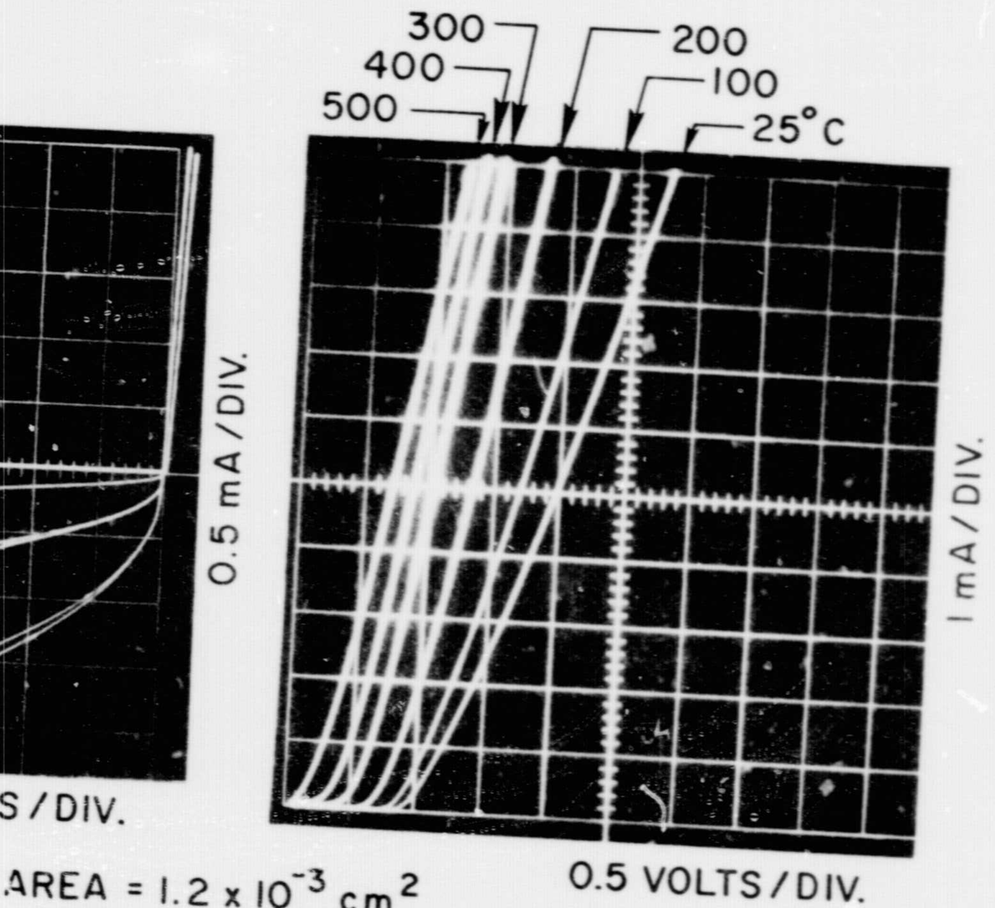

AREA = 1.2×10^{-3} cm^2

n = 6×10^{15} cm^{-3} AT 25°C

$V_B > 200$ volts

FIG. 1 - Current versus voltage traces of Schottky barrier on n-type GaP at temperatures between 25 and 500°C.

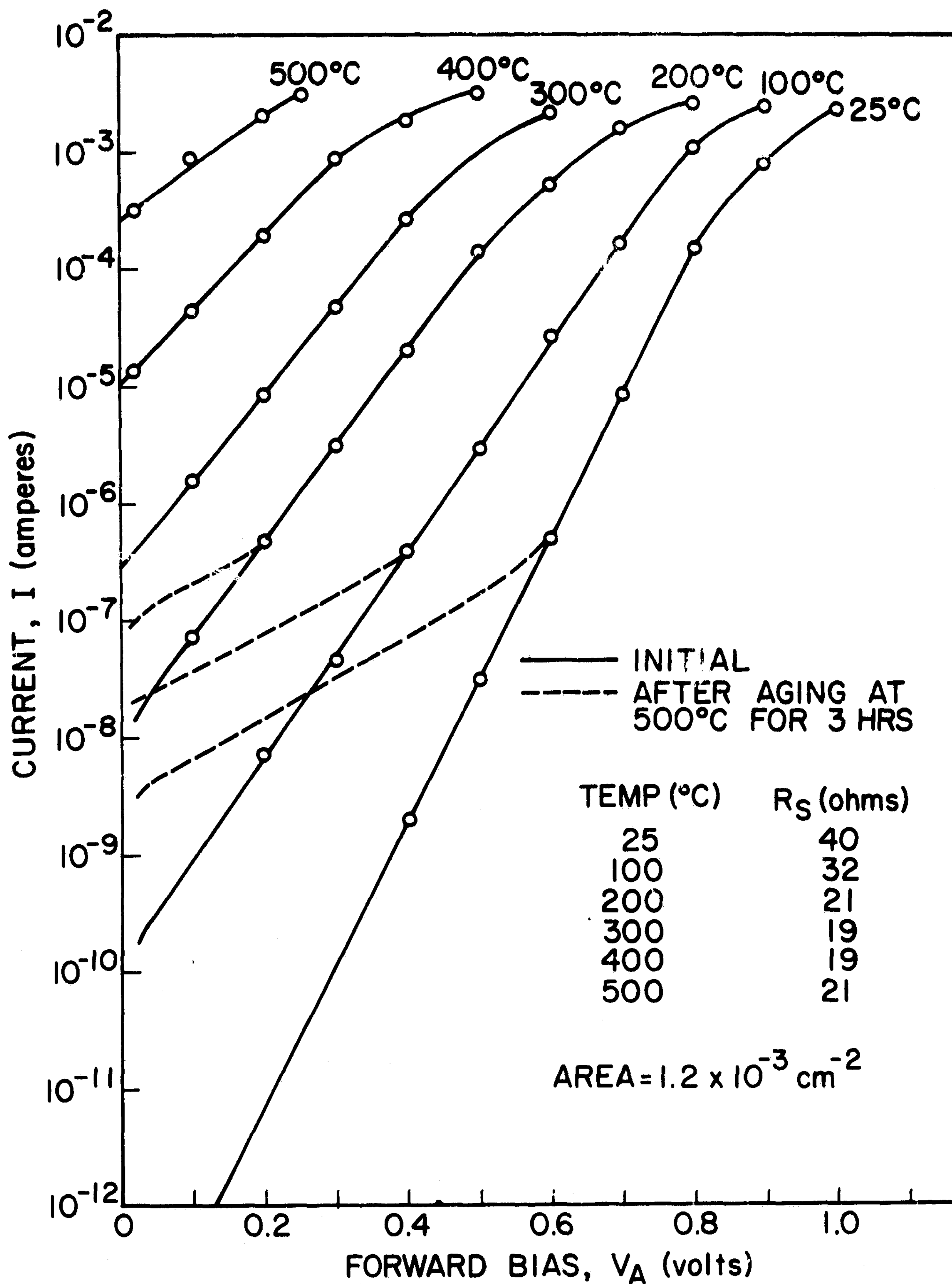

Fig. 2 - Forward bias current versus voltage characteristics of Schottky barrier on n-type GaP at temperatures between 25 and 500°C. Series resistance values and aging effects are indicated.

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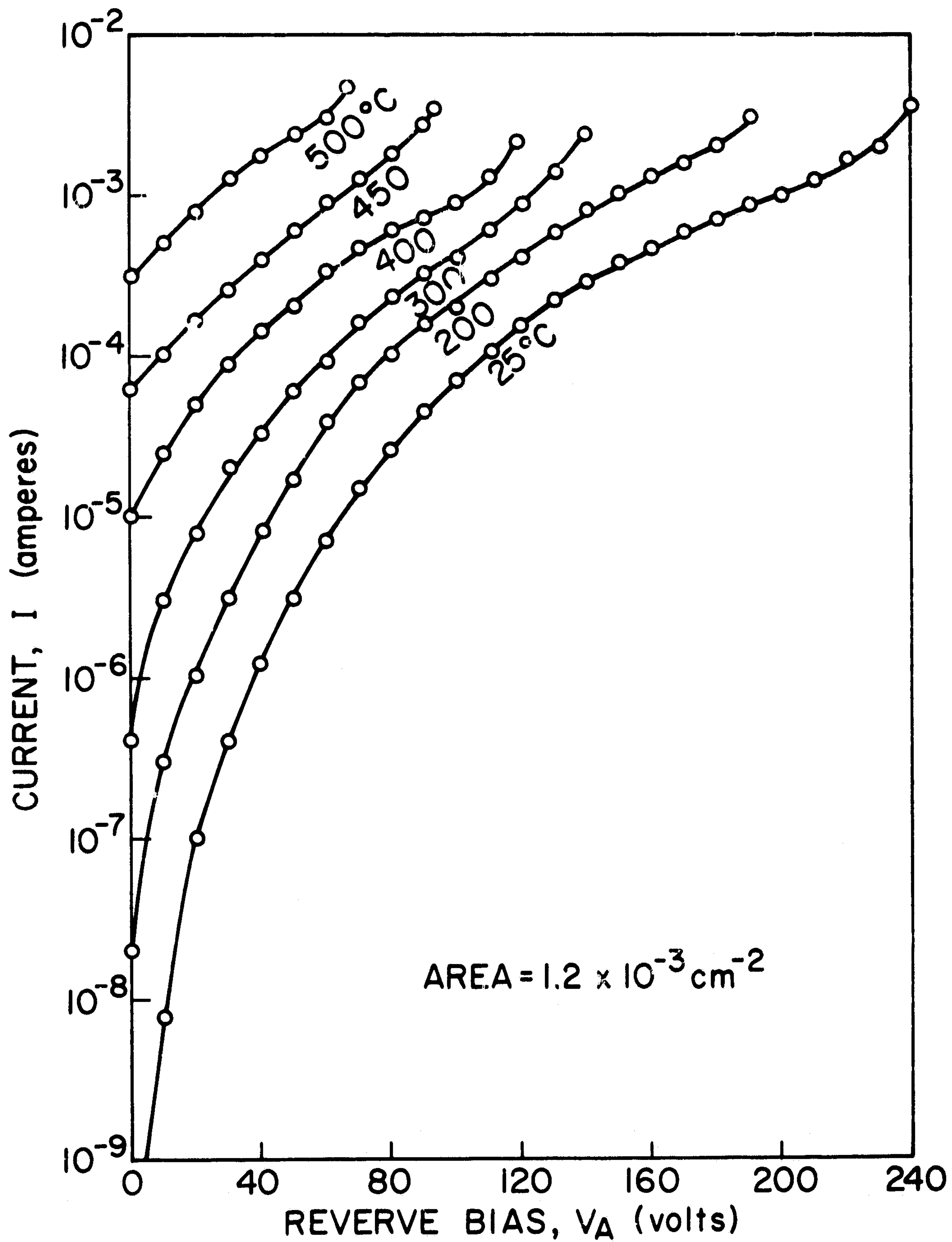

FIG. 3 - Reverse bias current versus voltage characteristics of Schottky barrier on n-type GaP at temperatures between 25 and 500°C.

A45114

PROJECT 5116: DONOR IMPURITIES IN GaP

National Aeronautics and Space Administration
Grant NsG-555
Principal Investigator: G. L. Pearson
Staff: A. Young*

The purpose of this project is to study the behavior of shallow donors in gallium phosphide. In particular, S, Se, and Te will be diffused into GaP to determine solubility and diffusion parameters. This information will be useful in delineating the properties of GaP doped with these shallow donor impurities.

Determination of Electron Concentration in Diffused Layers of Sulfur in GaAs

A plasma reflection technique was used to determine the electron concentration profiles of sulfur diffused layers in GaAs. Calibration of electron concentration and minimum wavelength was obtained from the results of Phillips and Schumann.[1] A typical result is shown in Fig. 1 for a diffusion at 900°C. The electron concentration is constant over a large part of the profile. At lower concentrations, the electron and total sulfur profiles (the sulfur profile is determined by radio-tracer techniques) appear to merge. One or two points near the surface indicate a somewhat lower electron concentration than the bulk, but this appears to be a surface effect which appears after quenching of the sample, and not a concentration effect. This conclusion is based on experiments at lower surface concentrations.

The comparison between the electron and total sulfur profiles indicates that a very large fraction of the diffused impurity is inactive, due either to precipitation or to the presence of a neutral species. This effect has been observed for homogeneously doped melt-grown GaAs[2,3] and for phosphorus-diffused layers in silicon.[4] It is possible that the diffusion process itself could result in the formation of induced dislocations and subsequent precipitation as in the case of zinc

*NSF Fellow

diffusion in GaAs.[5,13] However the use of a dislocation etch[6] ($1HF:3HNO_3:4H_2O$ + 1/4% Ag NO_3) after diffusion did not reveal additional dislocations beyond those present inthe starting material ($1\text{-}2000/cm^{+2}$).

Electron Concentration Versus Total Sulfur Concentration

The results from Fig. 1 can be replotted to show the electron concentration, n, versus the total sulfur concentration, N. This is shown in Fig. 2 for a number of temperatures. As the temperature increases, the maximum electron concentration increases from 1.6×10^{18} cm^{-3} at 900°C to 5-6 $\times 10^{18}$ cm^{-3} at 1130-1200°C. The point at 900°C agrees well with the data of Kendall.[7] The result in Fig. 2 differs somewhat from previous results obtained for melt-grown crystals of GaAs doped with S, Se, and Te,[8] and solution-grown GaP doped with Se and Te.[9] In these cases, a slight increase of n with N was seen above the knee. In the case of solution-grown GaP doped with sulfur, the electron concentration appears to be relatively independent of concentration above the knee.[9]

Maximum Electron Concentration Versus Temperature

In Fig. 3 the results of Fig. 2 are replotted to show the maximum electron concentration versus reciprocal temperature. Also shown on this figure are the results for Se and Te doped GaAs obtained by Fuller and Wolfstirn[10] from annealing experiments. It appears that Se and Te are more efficient dopants than sulfur at any given temperature. Also of interest are the two points for 1130°C. One was obtained with no excess arsenic, the other for an arsenic pressure of several atmospheres. The results indicate that the maximum electron concentration is relatively independent of arsenic pressure.

Annealing Experiments

A sample diffused at 1130°C with sulfur and known to have a constant electron concentration of 4-5 $\times 10^{18}$ cm^{-3} for 20 microns from the surface of the crystal was annealed at 800°C for 15 minutes with

no excess arsenic, and then for 1 hour and 15 minutes with an arsenic pressure of several atmospheres. Except for a 2-3 micron region near the surface, the electron concentration remained unchanged. This is in contrast to the results of Fuller and Wolfstirn for Te and Se doped GaAs[10] and the results of Mil'vidskii for sulfur doped GaAs.[8] In order to determine whether any difference exists between diffused and melt-grown crystals doped with sulfur, annealing experiments will be performed on boat grown GaAs heavily doped with sulfur.

Diffusion of Sulfur into Heavily Doped (Te, $N = 5\text{-}6 \times 10^{18}$ cm^{-3}) GaAs

Figure 4 shows the results of diffusing sulfur into heavily doped ($n = 5\text{-}6 \times 10^{18}$ cm^{-3}) GaAs samples at 1003°C. The profiles are identical within experimental error. The same result was found for a 5-day diffusion at 900°C. This result implies that the diffusion of sulfur is not affected by a change in the Fermi level. Quantitative conclusions depend on a more accurate knowledge of the intrinsic carrier concentration at high temperatures.

Preliminary results of diffusion in heavily zinc-doped material ($p = 2 \times 10^{19}$ cm^{-3}) indicate an order of magnitude increase in the sulfur surface concentration (due either to ion-pairing or to a simple solubility enhancement) but again no change in the diffusion coefficient was seen. This result confirms the conclusions based on diffusion in heavily doped N-type material. The result on surface concentration is somewhat surprising since the zinc might have been expected to out-diffuse considerably before the sulfur diffused in.

Pressure Dependent of Te Out-Diffusion From Homogeneous Crystal of GaAs

It is possible that the results of diffusing into undoped and heavily doped N-type material were identical because of out-diffusion of the Te near the surface. To check this possibility homogeneous crystals of GaAs ($n = 5\text{-}6 \times 10^{18}$ cm^{-3}) were annealed, both with no excess arsenic, and with an arsenic pressure of several atmospheres at 1005°C for 11-1/4 hours. The results after the anneal as determined

by incremental plasma reflection measurements are shown in Fig. 5. The results indicate

(a) although there is significant out-diffusion, the electron concentration is still 4 - 5 times the intrinsic carrier concentration at 1000°C and even more for the n_i at 900°C (the temperatures of our two experiments comparing diffusion in undoped and heavily doped crystals). This should be large enough so that any effect due to the change in Fermi level should be seen if the assumed n_i extrapolated from lower temperature Hall measurements, is correct.[11,12]

(b) Out-diffusion and presumably in-diffusion of the Te is more rapid under the higher arsenic pressure. This would be expected from our previous results for sulfur diffusion in GaAs but has not been measured previously for Te.

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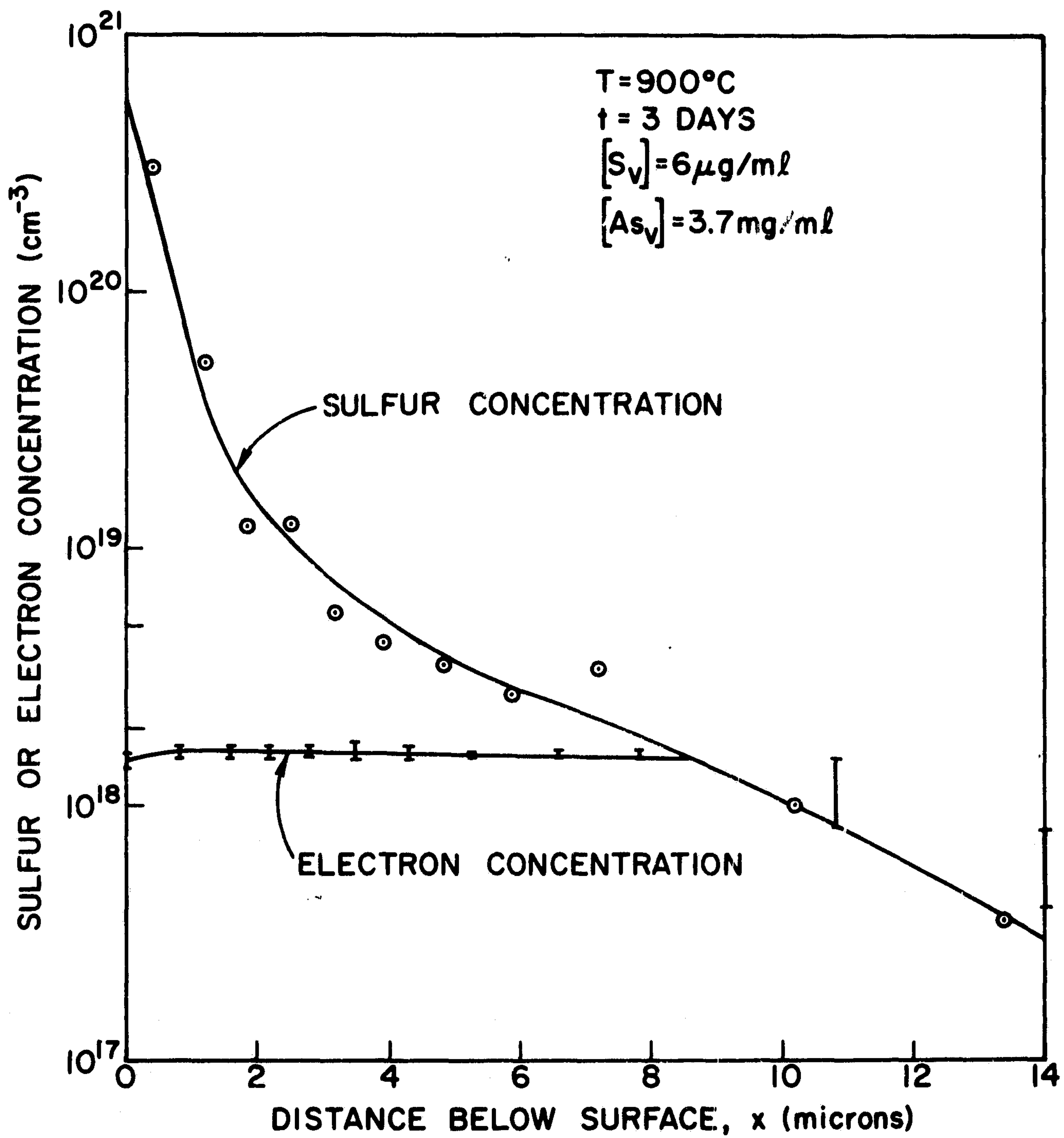

FIG. 1 - Typical plot showing simultaneous determination of sulfur and electron concentration profiles in GaAs.

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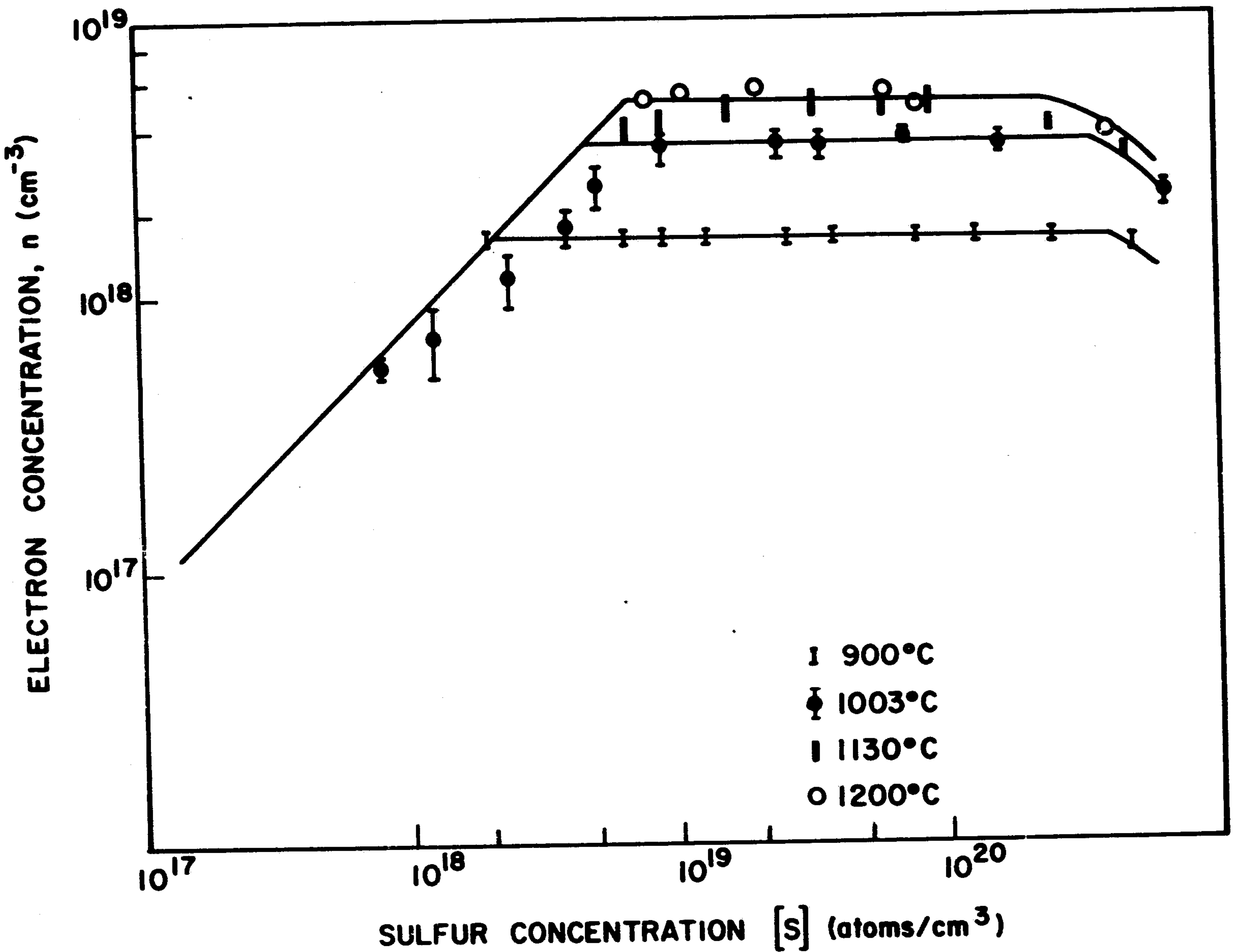

FIG. 2 - Electron concentration, n, versus total sulfur concentration, N, for various temperatures.

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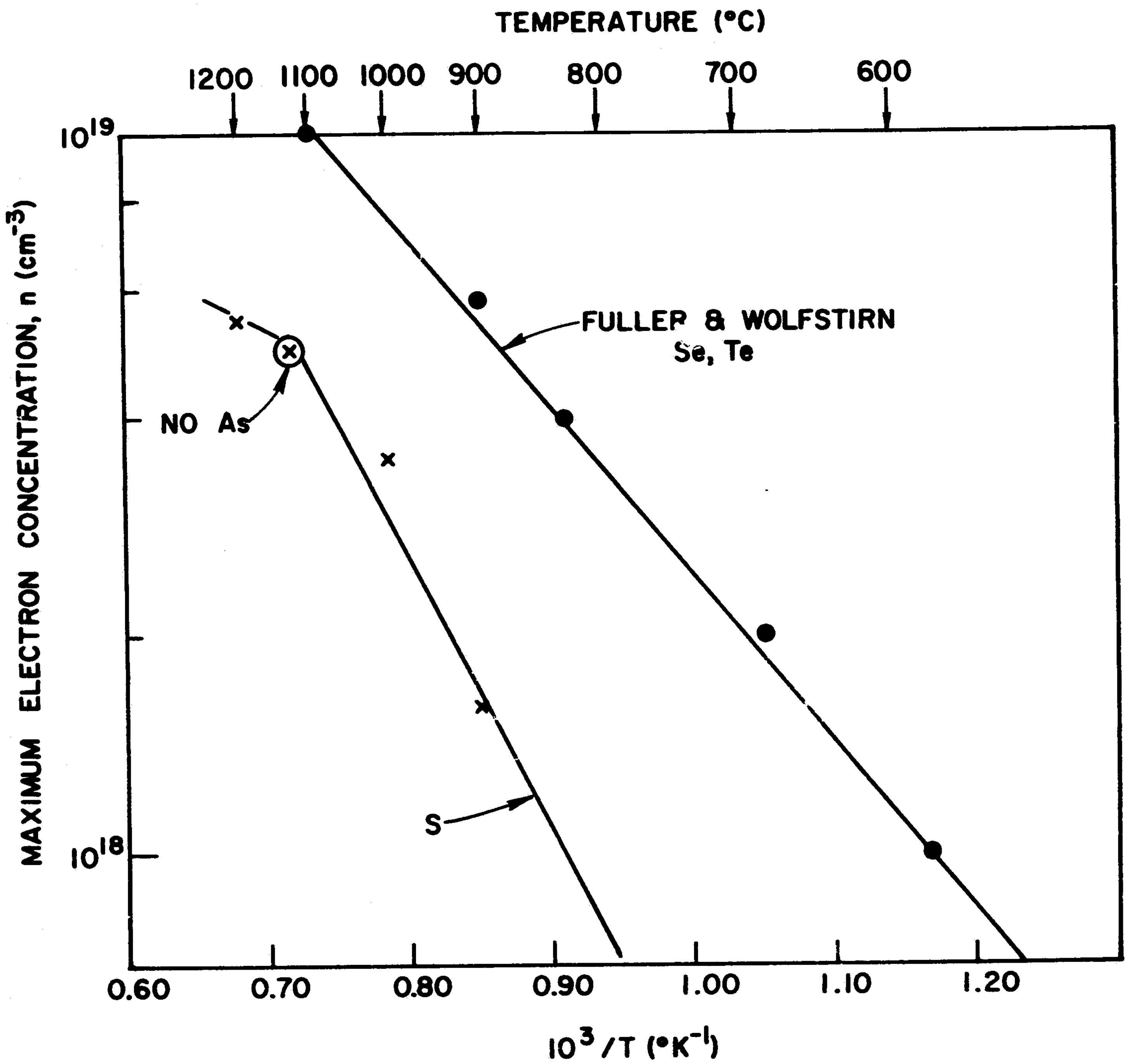

FIG. 3 - Maximum electron concentration versus reciprocal temperature for various dopants.

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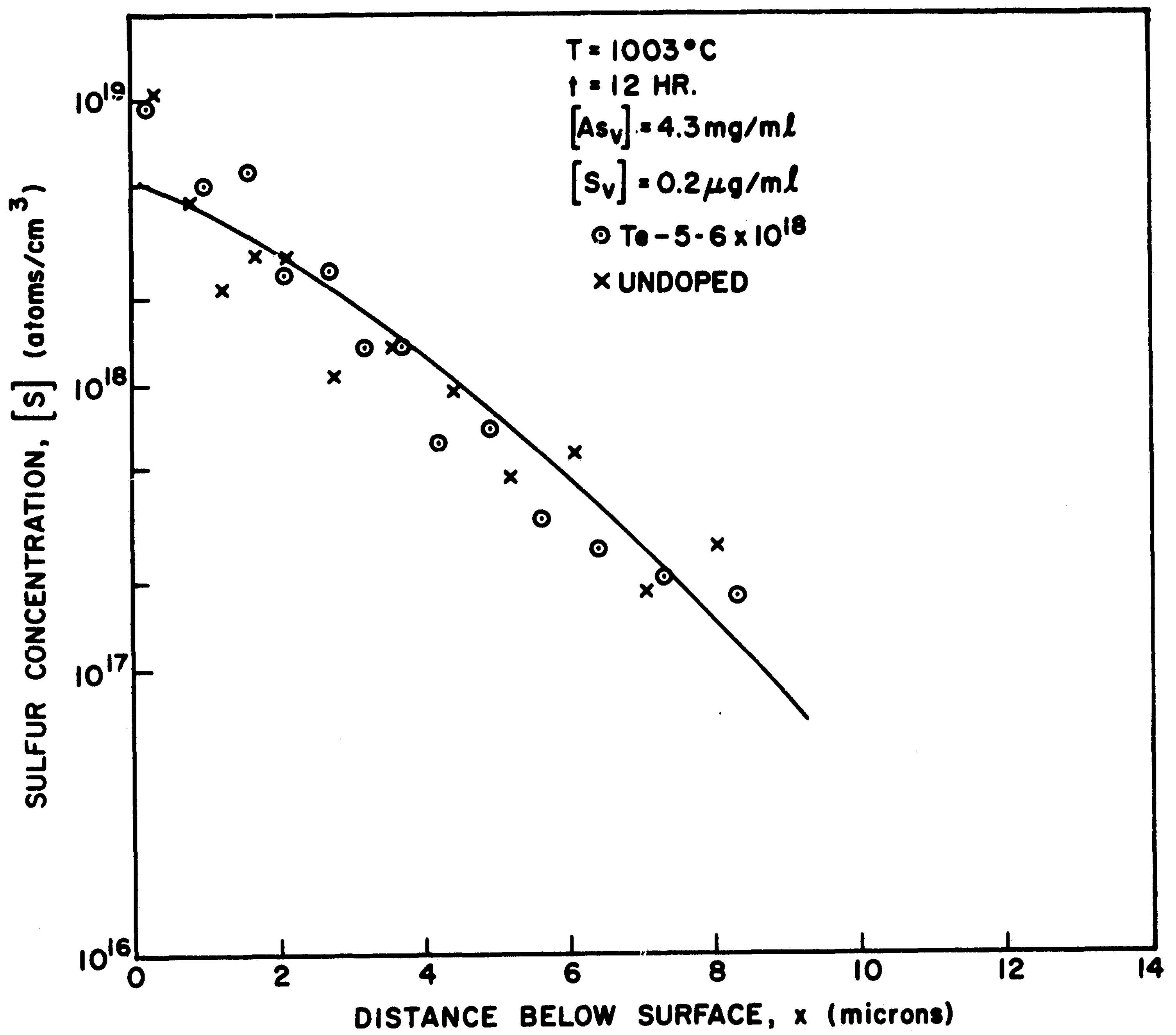

FIG. 4 - Comparison of diffusion into undoped and heavily doped N-type GaAs.

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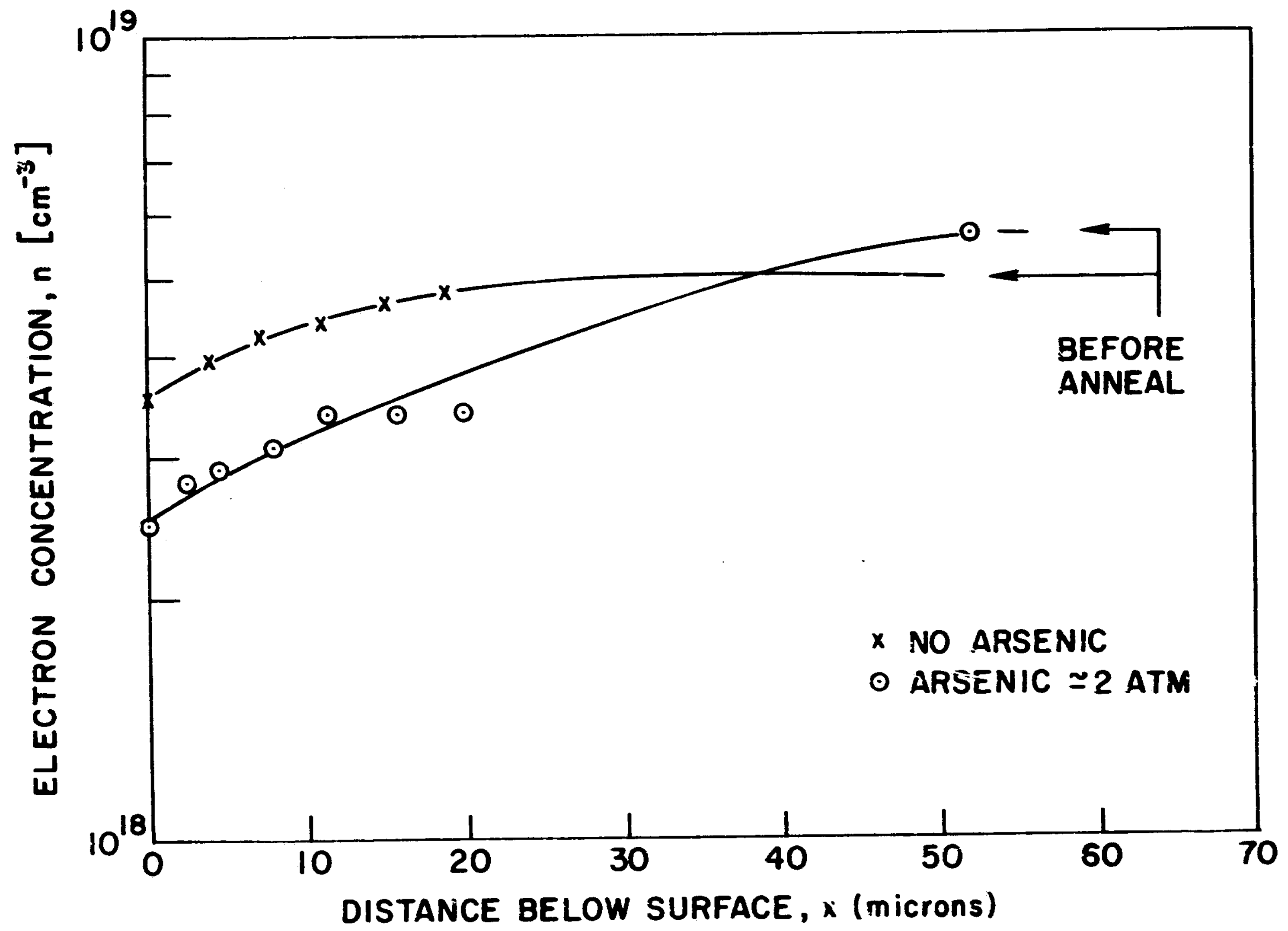

FIG. 5 - Out-diffusion of Te from heavily doped GaAs.

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