already produces maximum splitting. In addition, the spin must be integral because of Kramers' doublet rule. Unfortunately a ground state integral nuclear spin of two or larger is rare.

III. ACKNOWLEDGMENT

The author is greatly indebted to Dr. Jan Korringa who introduced him to the study of groups and supervised the progress of the present work.

PHYSICAL REVIEW VOLUME 105, NUMBER 6 MARCH 15, 1957

Recombination Radiation from Deformed and Alloyed Germanium *p-n* Junctions at 80°K

R. NEWMAN
General Electric Research Laboratory, Schenectady, New York
(Received December 10, 1956)

The recombination radiation from germanium *p-n* junctions ($T\sim 80$°K) which have been plastically deformed shows two bands of radiation. One band, which peaks at 0.7 ev, is an intrinsic property. The second, which peaks at about 0.5 ev, appears to be characteristic of deformed material or material in which slip has occurred. A slight change in the position of the 0.5-ev peak occurs upon annealing. The band at 0.5 ev is also found in the radiation from alloyed *p-n* junctions. Junctions containing copper show a radiation band at 0.59 ev.

INTRODUCTION

THIS work was initiated in the hope of finding evidence for a radiative recombination mechanism in germanium involving known recombination active impurities (Au, Mn, Ni, Fe, Cu, etc.). To this end, a number of alloyed junction diode units were prepared. In these, the germanium had been previously doped with the elements of interest. It was found that the recombination radiation which was obtained on forward injection at liquid nitrogen temperatures consisted of two bands. One, the intrinsic band, peaked at about 0.7 ev. In addition, there was a band peaked at about 0.5 ev. This latter feature was the more interesting since it seemed to be the phenomenon we wished to study, namely, the manifestation of a radiative recombination center. However, the spectral characteristics of the 0.5-ev band were independent of the composition of the germanium sample. In particular, its appearance in units made from samples known (from resistivity and lifetime measurements) to be of very high purity, cast doubt on its assignment to the activity of any chemical impurity. Further we were unable to find any evidence for the 0.5-ev band in grown *p-n* junctions, even when these had been doped with the recombination active impurities. This suggested the possibility that mechanical strain or deformation produced in the alloying process might be the origin of the 0.5-ev band. To test this hypothesis samples containing grown junctions were deformed by twisting at 550°C by varying amounts. Subsequent optical measurements clearly indicated a correlation of the extra 0.5-ev band to the mechanical deformation of the crystals. In large part, the work reported here relates to the grown junctions, as these afforded a more tractable experimental system.

After the mechanical effect had been identified, it was subsequently found that grown junctions into which Cu was diffused showed the presence of a band on the low-energy side of the intrinsic radiation peak. This presumably is the effect we were first seeking, *viz.*, a recombination center showing radiative effects.

EXPERIMENTAL

The experimental arrangement for measurement was straightforward. The *p-n* junction under study was mounted in a cryostat with good thermal contact to the refrigerant. In some cases the contact was made through a soldered connection to the refrigerant container, in others through the use of a calorimeter adhesive. In neither case did the average temperature of the unit rise more than about 10°K for the maximum electrical power input employed in obtaining the data of this report. Temperatures were measured by a Cu-constantan thermocouple soldered to the sample itself. All the data presented in this report were obtained at temperatures near 80°K.

The diodes were operated in the forward direction using 13 cps on-off modulation. The actual modulator was a Western Electric 275A relay. This was actuated by a rotating switch operated in conjunction with the synchronous rectifier of the detector amplifier. The junction radiation was detected by a dry-ice-cooled PbS cell. The detector signal was fed through a high-impedance preamplifier into a Perkin-Elmer thermocouple amplifier and was displayed on a chart recorder. A Perkin-Elmer spectrometer with a CaF_2 prism was used for monochromatization.

The junctions studied were of several types. The details of their fabrication and processing have been included in Appendix A.

The possibility that the effects that have been observed were either spurious (i.e., instrumental) or trivial (i.e., thermal radiation) has been considered in

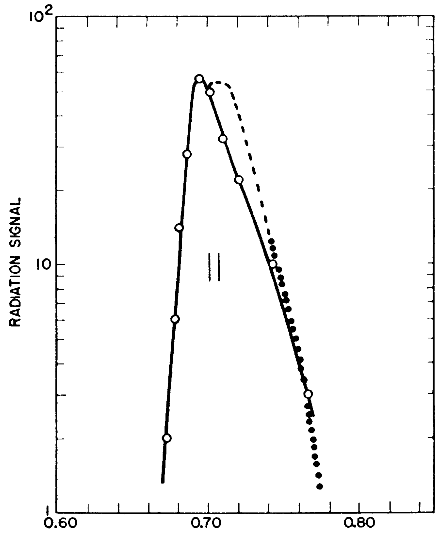

FIG. 1. Spectrum of recombination radiation of a germanium *p-n* junction at 80°K (solid line). The dots and dashes represent a theoretical calculation of the spectral band shape using the data of reference 6 (dots) extended by photovoltaic data (dashes). The resolution is noted.

detail. Several experiments designed to test this possibility have indicated that the effects are neither instrumental nor do they result from temperature modulation of the samples. Further, radiation law calculations have been made for the temperature modulation actually observed (e.g., ~10°K). They indicate that the maximum radiation signal that would be seen by the detector would be a factor of 10^{15} less than the minimum detectable signal (~10^{-12} watt). The same considerations apply to emissivity modulation effects. The possibility of local "hot spots" giving rise to thermal radiation has not been eliminated but is considered very unlikely. It is thus felt that the effects reported here do have veridical significance.

RESULTS

A. Intrinsic Radiation Peak

In Fig. 1 the radiation band peaked at ~0.70 ev is the intrinsic recombination radiation, presumably due to the direct recombination of electrons and holes. Except for absolute magnitude it is identical in all the junctions studied. This band has previously been discussed by several authors.[1–3] The data of Fig. 1 were obtained with sufficiently high resolution to show the pronounced asymmetry of the band. The resolution was insufficient to give the true band shape, particularly on the low-energy side. Existing absorption data[4–6] for germanium do not extend to low enough values (i.e., ≪0.1 cm^{-1}) to permit an accurate theoretical calculation of the radiation band shape.[3] However, by using data previously reported,[4,6] extended through the use of unpublished photovoltaic data, the dotted and dashed curve of Fig. 1 was obtained. The calculated curve was adjusted to give the same peak height as the experimental curve. Some measurements made in the liquid H_2 range (T~40°K) indicated that the entire shape of the observed line was being limited by the resolving power, which was the same as that employed for obtaining the data of Fig. 1.

B. Grown Junctions Deformed by Twist

Figure 2(a) shows a spectrogram of the radiation emitted by a control sample cut from a grown *p-n*

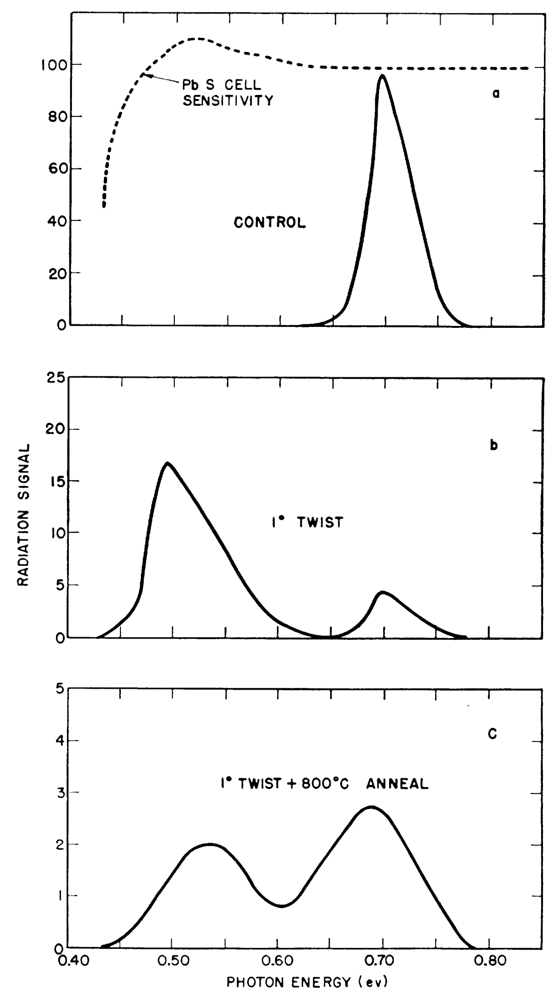

FIG. 2. A series of radiation spectrograms (T~82°K) for a junction unit which has had the treatments indicated in the figure and described more fully in the text. The same current density was used throughout. Figures 2(b) and 2(c) were obtained using a larger spectrometer slit than for Fig. 2(a). The different curves were adjusted to give the correct relative magnitudes. The 300°K junction characteristics prior to bending were p~0.01 ohm-cm, n~1 ohm-cm, τ_h~50 μsec.

[1] J. R. Haynes and H. B. Briggs, Phys. Rev. **86**, 647 (1952).
[2] R. Newman, Phys. Rev. **91**, 1313 (1953).
[3] W. van Roosbroeck and W. Shockley, Phys. Rev. **94**, 1558 (1954).
[4] Fan, Sheppard, and Spitzer, *Proceedings of the Conference on Photoconductivity, Atlanta* (John Wiley and Sons, Inc., New York, 1956).
[5] G. G. Macfarlane and V. Roberts, Phys. Rev. **97**, 1714 (1955).
[6] W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

junction of the characteristics noted. Figure 2(b) is a spectrogram of another sample cut from the same grown junction after it has been twisted by an angle of $\sim 1°$ and restraightened at 550°C. Figure 2(c) shows the spectrogram of the same sample after it has been twisted and restraightened at 550°C and then annealed at 800°C for 15 hours. Prior both to twisting and to annealing, the sample was gold-plated to minimize the introduction of copper. Another control sample, processed in the same way as the twisted sample except for the actual bending, gave a spectrogram identical to that shown for the control sample except for a small decrease in absolute magnitude.

As may be seen from Fig. 2, the process of mechanical deformation at 550°C causes the appearance of a radiation band peaked at 0.50 ev. Upon annealing the sample for 15 hours at 800°C, this peak apparently shifts to 0.53 ev. If, after bending, the sample was annealed for only an hour at 800°C, the only change from Fig. 2(b) was a change in the relative heights of the 0.50 and 0.70 ev peaks at the current level employed. This short annealing treatment is sufficient to remove essentially all the 0.1-ev acceptors seen by Tweet.[7]

As will be noted in more detail below, the ratio of heights of the intrinsic peak and the appropriate extrinsic (e.g., 0.50 ev) peak depends on the current passing through the junction. For this reason, specification of the ratio, without regard to the current, for a given junction unit is meaningless. Further, even at the same current density, different samples from the same ingot which have been treated differently cannot be compared in quantitative detail with regard to the ratio of peak heights or to the absolute magnitude of the peaks.[8] However, if it is assumed that the measurements for a group of samples taken at the same current level do provide at least a basis for a qualitative comparison, then certain conclusions may be drawn.

For a series of samples from the same ingot twisted by different amounts, a correspondence existed between the ratio of the extrinsic peak to the intrinsic peak and the amount of the twist. A series of related curves like that of Fig. 2(b) would show ratios ranging from about 3/1 for a 1° torsion to $\sim$100/1 for a 20° torsion for this particular ingot. However, the reproducibility of data from samples prepared similarly from the same ingot or from similar ingots was not good enough to justify any quantitative discussion.

An interesting difference showed up between junctions in which the injection current consisted of holes going into n-type material and junctions in which the injection current was electrons into p-type material. Namely, the extrinsic/intrinsic ratio was much greater in the latter case than in the former for the same torsion angle. In fact, it was found that the minimum deformation ($\sim 1°$) that could be applied reduced the intrinsic peak to below a detectable level for the p-type material.

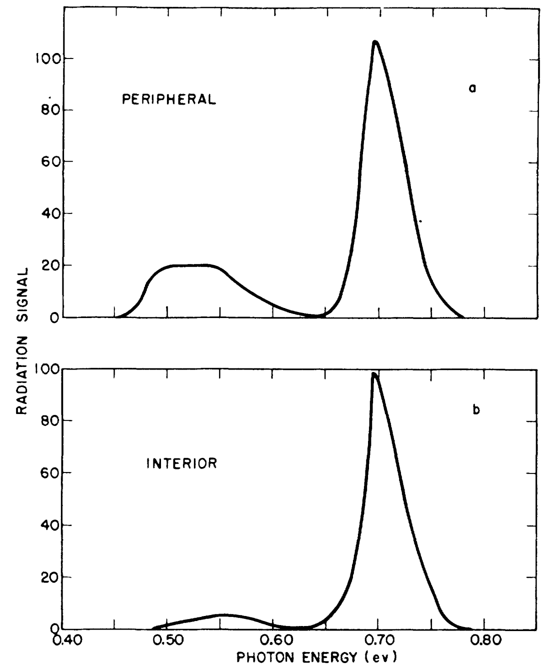

FIG. 3. Radiation spectrograms ($T\sim 82°$K) of a junction occurring in a crystal which had been slipped in growth. The terms "peripheral" and "interior" refer to the position of the samples relative to the cylindric axis of the crystal.

C. Grown Junctions Slipped during Growth

As described in Appendix A, crystals could be grown in such a way as to produce a large amount of "built in" slip. The density of slip lines is greatest at the outside of such crystals and diminishes toward the center. Figure 3 shows two radiation spectrograms from samples of such a crystal. One sample was cut from an interior section, the other from a peripheral section. Both spectrograms show the presence of an extra peak at 0.50–0.53 ev. For the peripheral sample, the extrinsic band would appear to be a composite of the 0.50- and 0.53-ev bands. This could perhaps indicate some sort of partial annealing. Again comparing magnitudes at a fixed current density, the sample from the interior of the crystal shows a smaller extrinsic peak than does the sample from the periphery. This is what might be expected from the distribution of slip lines.

It is of interest to note that crystals which have been subjected to a mild heat cycle during growth, in order to produce multiple junctions,[9] the so-called rate-grown

[7] A. G. Tweet, Phys. Rev. **99**, 1245 (1955).

[8] Consider the case of a junction where the injection current is entirely a diffusion current and the minority carrier density is small compared to the majority carrier density. Here one can readily show that the radiation output is jointly proportional to the current density and the minority carrier lifetime either for the direct recombination process or any other radiative process involving a single recombination center. In the present case, analysis is limited by (1) ignorance of lifetime values in samples of interest ($\tau<1$ μsec), which leads to (2) ignorance of detailed nature of injection current, and (3) nonlinear current dependence of radiation.

[9] R. N. Hall, Phys. Rev. **88**, 139 (1952).

junctions, also show an extrinsic peak but of a considerably smaller magnitude than is shown in either curve of Fig. 3.

D. Alloyed Junctions

As was mentioned in the introduction, the extrinsic peak at 0.50 ev was first found in alloyed p-n junctions. The junctions were of two kinds, indium alloyed to n-type germanium and an In-As alloy alloyed to p-type germanium. In both cases the 0.50-ev extrinsic peak is found to be indistinguishable from that for the twisted samples to the resolution of the measurements. This prompts the conclusion that in the alloying process, some sort of deformation or slip takes place.

It is of interest to note that in general for a group of identically sized alloyed junctions fabricated from the same ingot, the magnitude of the 0.50-ev peak increased with the temperature at which the alloyed junction was made. In this experiment a constant heating period was employed. For diodes fabricated at ~300°C the ratio of extrinsic to intrinsic peak was of order 1/30; for units made at 600°C the ratio was often as high as 1/1. Again the comparisons are made at an *arbitrary* fixed diode current level.

It was also of interest to note that in several cases where a given alloyed junction unit could be mounted so as to present different aspects to the detector slightly different ratios of extrinsic and intrinsic radiation obtained. This is consistent with the idea that the extrinsic radiation was being generated in a localized region of strong deformation, (i.e., immediately below the indium dot) whereas the intrinsic radiation would be largely developed in another region of undeformed material, further removed from the dot. Possibly, because of the problems of internal reflection and irregular surface scattering, the observed orientation dependence of the light was not as large as might be expected from this interpretation.

E. Current Dependence of Radiation in Deformed and Alloyed Junctions

In units for which the radiation signal was large enough, it was possible to study the current dependence of both the extrinsic and intrinsic components. In Fig. 4 a plot of the magnitude of each component is shown as a function of current, in this case for an alloyed junction unit. The data points marked as an "Extrinsic (with Ge filter)" were obtained with the detector looking directly at the junction with a thick Ge filter between the two to completely eliminate the intrinsic component. These points were normalized to fit the points obtained using the monochromator, the latter data representing the peak heights. Curves of this form appear typical for both kinds of alloyed junctions and for the grown junctions as well. For the latter the data were not obtainable over as wide a range.

Of special interest is the fact that the extrinsic component appears to vary with a high power (~5) of the current at the lowest levels, and with a steadily decreasing power as the current level increases.

In this particular unit the intrinsic component varied as the square of the current, in others a power between 1 and 2 was observed. In cases where the minority carrier density is equal to or greater than the equilibrium majority carrier density, and the drift contribution is small, a square law would be expected. A lower power could merely indicate that either or both of these conditions was not satisfied.

F. Temperature Dependence

The temperature dependence of the extrinsic radiation was not studied in any detail. However, for a representative unit, operated at a fixed current density the following was observed: the magnitude of the extrinsic component was independent of temperature in the range from about 40°K to 120°K, it decreased about a factor of 20 from its value in this range in going to 200°K, and it was unobservable at 300°K.

G. Junctions Containing Copper

In Fig. 5 is shown the radiation spectrum of a grown junction into which copper has been diffused. It is of interest to note the presence of a band peaked at 0.59 ev which is presumably due to the action of the copper. The position of this peak is independent of whether the injection is into n or p material. At the temperature of the diffusion (700°C) the equilibrium solubility of

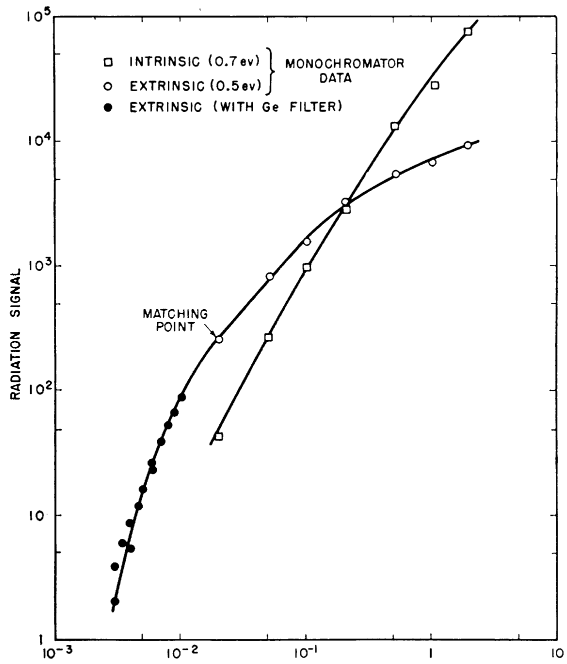

FIG. 4. Radiation signal (T~82°K) as a function of p-n junction current. 300°K junction characteristics: In dot, n~20 ohm-cm, τ_h=400 μsec.

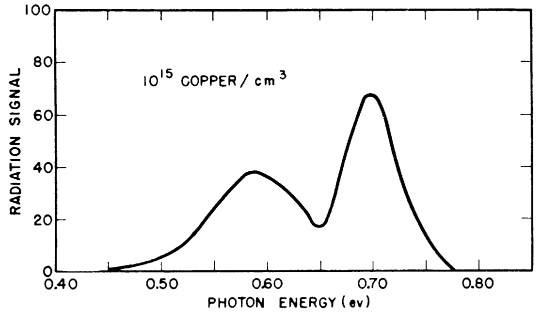

FIG. 5. Radiation spectrogram ($T \sim 82°K$) of a junction into which copper had been diffused at 700°C.

electrically active copper is $\sim 10^{15}/cm^3$.[10] As was remarked above, copper is the only chemical impurity center that has been found to show a radiation effect. Since even at the $10^{15}/cm^3$ level its effect is small, conceivably more careful work would be required to detect the presence of the impurity centers (e.g., Ni, Fe) which can be introduced only in lower concentrations.

Copper introduces three acceptor levels in germanium, one 0.26 ev below the conduction band, and two which are 0.33 ev and 0.04 ev above the valence band.[11] One would like to be able to correlate, say, the energy difference between the positions of the maxima of the extrinsic copper band and the intrinsic band to one of these energy levels. However, such a correlation is not necessary. The shapes of the radiation bands may depend sensitively on the form of the appropriate absorption cross sections.

The current dependence of extrinsic radiation is linear in this case. This is consistent with recombination at a simple center.

DISCUSSION

The empirical correlation between mechanical deformation of the germanium and the existence of the extrinsic radiation peaks at ~ 0.5 ev seems established from the work described above. However, the interpretation of the results in terms of a specific model must be regarded as a speculative exercise at the present time. One essential difficulty resides in the lack of appropriate ancillary information about the nature of electrically active centers in deformed germanium.

As a working hypothesis it is proposed that the extrinsic band results from a radiative capture of a carrier at some defect center associated with dislocations approximately 0.5 ev from a band edge. The radiative recombinations are a small fraction of the total recombination (i.e., $< 10^{-5}$).

It is felt that the group of bands at ~ 0.5 ev do manifest true dislocation phenomena. The reasons for this assertion are the following:

1. The relative insensitivity of the magnitude of the 0.50-ev band in twisted material to an annealing treatment sufficient to remove the annealable acceptors (800°C for one hour).
2. The presence of an extrinsic band in crystals which have severely slipped during growth but which were probably annealed at temperatures close to the melting point.
3. The distinction between the spectrum for the deformed material and that containing diffused copper.

As a consequence of this view one would propose that the difference between the spectra of samples which were twisted, twisted and annealed, or slipped during growth, were due either to different states of aggregation of the dislocations (e.g., polygonization) or to different degrees of cleanliness of the dislocations (i.e., freedom from impurity atoms).

The current dependence of the extrinsic radiation is not understood. In particular the fact that the extrinsic radiation over a certain range depends on a high power (e.g., ~ 5) of the injection current is surprising. Consideration of several alternative mechanisms which involve the trapping of one carrier and its subsequent recombination with another of opposite sign at a single center fail to suggest a method whereby the observed results could be explained. However, in work with some conventional luminescent materials a phenomenon is found similar to that observed here. Namely, that over a certain range of excitation intensity the luminescent output increases as some power of the excitation intensity which is greater than unity.[12,13] Typically this power may be of order 3.5. This behavior has been explained using the idea of two competing recombination centers, one responsible for the luminescence, the other producing nonradiative recombination.[14,15] Conceivably in the present case a similar situation prevails.

Before concluding, a few comments about alloyed junctions seem appropriate. As mentioned above, in general all the alloyed junction units studied show to a greater or lesser degree the 0.50-ev band. This has been interpreted as a dislocation phenomenon. That is, it is proposed that in the neighborhood of the alloyed region there is a region where the germanium has been deformed, the magnitude of the deformation depending on some inverse function of the distance from the alloyed region. In general, measurements of lifetime by the junction recovery method[16,17] in alloyed junction units have indicated a gradient of local lifetime.[18] The interpretation has been that the short lifetimes at the beginning of the recovery curve are characteristic of material close to the junction. The longer lifetimes, to which the recovery curves asymptotically conform, are

[10] Fuller, Struthers, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).
[11] H. H. Woodbury and W. W. Tyler (to be published).

[12] N. Riehl, Z. tech. Phys. **20**, 152 (1939).
[13] Nail, Urbach, and Pearlman, J. Opt. Soc. Am. **39**, 690 (1949).
[14] S. Roberts and F. E. Williams, J. Opt. Soc. Am. **40**, 516 (1950).
[15] C. A. Duboc, Brit. J. Appl. Phys. Suppl. **4**, S-107 (1955).
[16] E. M. Pell, Phys. Rev. **90**, 27 (1953).
[17] B. Lax and S. F. Neustadter, J. Appl. Phys. **25**, 1148 (1954).
[18] E. M. Pell, J. Appl. Phys. **26**, 658 (1955).

then believed to be characteristic of regions further removed from the junction. This is consistent with the picture of the junction structure that has been drawn. However, because of the uncertainties attending any quantitative analysis of the radiation magnitudes it is difficult to make any precise statement relating to the dimensions of the deformed regions in the alloyed junctions. Suffice it to note that if the strongly deformed region had a local lifetime of order 1 μsec and had a thickness of order 10^{-3} cm, then about 10% of the total recombination would occur in such regions. As a very rough estimate, this situation could probably account for the observed radiation effects. Such small regions of deformed material lying close to the junction should contribute to the determination of the reverse characteristics of alloyed *p-n* junctions.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the help of A. G. Tweet, who furnished the twisting apparatus and many fruitful suggestions during the course of this work. The assistance of J. H. McTaggart especially during several discouraging periods is appreciated.

APPENDIX A

The alloyed junctions consisted of an indium (or indium arsenic) dot alloyed to the top of a germanium wafer, the bottom of which was alloyed to tin, which in turn was soldered to a Fernico plate. Units with wafers of different sizes were studied. Several commercial power rectifiers of this type were also studied. In all, thirty alloyed junctions prepared from the material of fifteen ingots were studied.

The grown junction units were cut from crystals containing a *p-n* junction put in by conventional doping techniques. For a series of related operations a group of units were cut from the same ingot to an essentially identical size. One unit of this group was set aside as a control sample. Contacts were soldered onto the samples at least 0.5 cm from the junction region. All the junctions were chemically etched (1 HF$-$3 HNO_3) before use. Twenty-seven grown junction units were prepared from ten different ingots and studied.

Several crystals were grown under conditions believed to produce a large amount of slip. Namely, shortly after doping to give the junction, the still growing ingot was withdrawn to a cooler section of the furnace for a few seconds and then returned to the melt and the crystal growth continued. This technique was originally developed in our laboratory by C. J. Gallagher.

While most of the samples were obtained from one furnace and were grown by one operator, some of the samples were obtained from a different source. No difference between the two types was apparent. It is thus felt that the results presented are representative of germanium crystals at least at the present state of the art.

The units which were intentionally deformed were cut from crystals into rectangular parallelopipeds 750$\times$40 $\times$100 mils on a side. The *p-n* junction was perpendicular to the long dimension and approximately at its midpoint. The units were twisted by known angles about an axis parallel to the long dimension and then twisted back to the original configuration. In most cases the twist axis was [100].

The deformation was carried out at 550°C. The samples were kept at this temperature for a total elapsed time of about 5 minutes. As there is some slight possibility of copper contamination, the following procedures were employed. Prior to insertion in the twisting apparatus, the samples were etched and washing in distilled water and then given either (1) no further treatment, (2) a rinse in KCN followed by a rinse in distilled water obtained from an all-quartz still, or (3) a gold plate followed by a rinse in distilled water. After twisting, the samples were again etched and contacts affixed for measurement. Control samples were prepared and heated under the same conditions as the bent samples. These control samples were, in optical behavior, identical to the so-called "absolute" control samples which had received no treatment other than the affixing of contacts. No differences were found between the behavior of samples treated differently to minimize the copper.