

## Electron Irradiation of Indium Arsenide\*†

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(Received March 16, 1959)

The carrier concentration of  $n$ -type InAs increases during irradiation with 4.5-Mev electrons. The increase is followed to a carrier concentration of  $10^{17}/\text{cm}^3$ . The carrier concentration of  $p$ -type samples decreases with irradiation. The increase in the electron concentration suggests that bombardment-produced donors are at least doubly ionized, even when the Fermi level is in the conduction band. Initially  $p$ -type samples exhibited anomalies which may result from  $n$ -type conduction in the vicinity of dislocations.

### I. INTRODUCTION

IN a previous paper<sup>1</sup> the effects of electron irradiation on the electrical properties of indium antimonide were discussed. Similar experiments were performed on indium arsenide, another intermetallic compound quite similar to InSb. These experiments must be considered preliminary because material of sufficient quality to justify a detailed study was not available. Nevertheless, even the gross behavior of InAs upon bombardment is remarkably different from that of InSb and other semiconductors, and is thus of considerable interest.

All samples were polycrystalline and contained impurities in concentrations of  $10^{16}/\text{cm}^3$  or greater. The  $p$ -type material was probably heavily compensated. Good discussions of the electrical properties of InAs are available in the literature.<sup>2-4</sup>

The experimental procedure was the same as described in the above reference,<sup>1</sup> except that in the present case only bombardments at liquid nitrogen temperature were carried out. The energy of the bombarding electrons was 4.5 Mev. The specimens were approximately 0.15 to 0.30 mm thick, considerably less than the range of the bombarding electrons.

### II. EFFECT OF BOMBARDMENT ON $n$ -TYPE InAs

Bombardment increases the carrier concentration of  $n$ -type samples, even though it is initially quite large. Figure 1 illustrates the changes in carrier concentration and the reciprocal of Hall mobility *versus* bombardment flux. The carrier concentration was calculated by the equation  $n=1/Re$ , where  $R$  is the Hall coefficient in  $\text{cm}^2/\text{coul}$ . The sample of Fig. 1 is very nearly degenerate initially, and becomes more degenerate as bombardment proceeds. This behavior indicates that donors are intro-

duced which are ionized even though the Fermi level is in the conduction band. The increase in the reciprocal of mobility is apparently the result of additional scattering by the introduced ionized defects. The initial rate at which the concentration of electrons increases is  $dn/d\phi=6.1/\text{cm}$ . This behavior is quite different from that of other semiconductors such as InSb, Ge, and Si. These materials always exhibit a decrease in carrier concentration if degenerate, or nearly degenerate, specimens are bombarded. Such behavior is attributed to the introduction of donor and acceptor states in the forbidden band.

An annealing experiment indicated that very little annealing occurs until a temperature of approximately 150–175°K is reached. The changes in Hall coefficient and resistivity during annealing occur in the direction of restoring the initial conditions.

### III. EFFECT OF BOMBARDMENT ON DEGENERATE $p$ -TYPE InAs

A  $p$ -type sample with Hall coefficient of  $8.1 \text{ cm}^2/\text{coul}$  was bombarded for the purpose of determining the re-

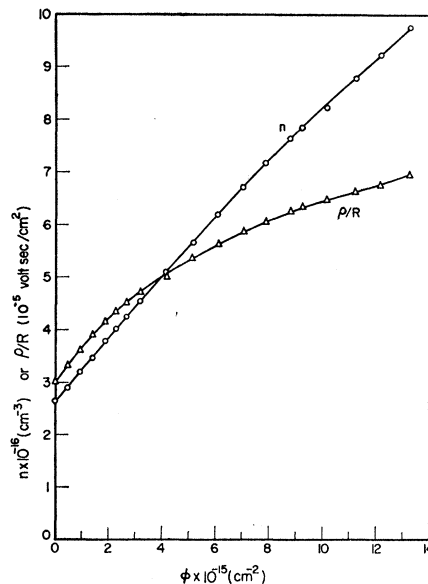


Fig. 1. Effect of bombardment on the carrier concentration and mobility of  $n$ -type InAs.

\* Supported by the U. S. Atomic Energy Commission.

† Submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy at Purdue University, Lafayette, Indiana, 1958.

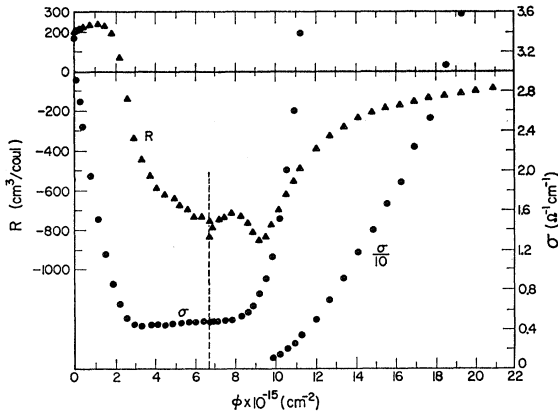
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<sup>1</sup> L. W. Aukerman, preceding paper [Phys. Rev. **115**, 1125 (1959)].

<sup>2</sup> Folberth, Madelung, and Weiss, Z. Naturforsch. **9a**, 954 (1954).

<sup>3</sup> F. A. Cunnell and E. W. Saker, in *Progress in Semiconductors*, edited by Alan F. Gibson (John Wiley & Sons, Inc., New York, 1957), Vol. 2, p. 58.

<sup>4</sup> H. Welker and H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 3.

FIG. 2. Bombardment of *p*-type InAs.

removal rate. The carrier concentration of this sample was so large that only a few percent change could be effected by a rather long bombardment. The carrier removal rate for this sample, calculated by the equation  $p = 1/Re$ , was  $-dp/d\phi = 10.2 \pm 0.5/\text{cm}$ .

The rate at which holes are removed from the degenerate *p*-type sample is nearly twice the rate at which electrons are introduced into a nearly degenerate *n*-type sample. The fact that these two rates are not equal indicates that some levels are introduced in the forbidden band.

#### IV. ANOMALOUS BEHAVIOR OF *p*-TYPE SAMPLES

Bombardment of a *p*-type sample considerably more pure than the degenerate sample described above might be expected to produce a negative Hall coefficient after a reasonable amount of flux. Since the major effect of bombardment is to introduce donors, the Hall coefficient of an initially *p*-type sample should increase,<sup>5</sup> go through a very large maximum, become negative, and after passing through a very large negative maximum should approach zero or a small negative value. The theoretical value of the maxima in *R* for InAs bombarded at liquid nitrogen temperature is of the order of  $10^{30}\text{cm}^3/\text{coul}$ . Obviously such a large Hall coefficient is not measurable. In the region of the conversion from *p*- to *n*-type the sample should behave as an insulator. In a practical case, where there may be considerable inhomogeneity present, the maxima in Hall coefficient and resistivity will be considerably lower than the theoretically predicted values. Nevertheless, the general shape of the bombardment curves just described should be observed. Analogous behavior has been observed in the case of electron bombardment of InSb,<sup>1</sup> for example.

Samples of InAs having an initial Hall coefficient of the order of  $100\text{cm}^3/\text{coul}$  do not behave in the manner described above. The variation of Hall coefficient and conductivity as a function of the bombardment flux is shown in Fig. 2 for an initially *p*-type sample which was

<sup>5</sup> K. Lark-Horovitz, *Semiconducting Materials* (Academic Press, Inc., New York, 1951).

etched before bombardment. The deviations from the expected behavior are even greater for unetched samples; these become *n*-type without showing any positive maximum.

In Fig. 2 the fluctuation in *R* at a flux of  $6.7 \times 10^{15}\text{cm}^{-2}$  is the result of slight annealing after the sample had remained overnight at liquid nitrogen temperature. The changes in Hall coefficient and conductivity both for small bombardments and for the latter stages of bombardment behave as one would predict from the behavior of the degenerate *n*- and *p*-type samples; that is, the concentration of holes appears to decrease at first, and later when the sample is *n*-type the concentration of electrons appears to increase. These changes in carrier concentration agree reasonably well with the values determined for the degenerate *n*- and *p*-type samples above. The initial change in hole concentration for the sample of Fig. 2 is  $-dp/d\phi = 9/\text{cm}$ . The change in electron concentration near the end of the bombardment is  $dn/d\phi = 6.15/\text{cm}$ . However, for intermediate values of flux where the conductivity should become very small the behavior is anomalous. The appearance of the curves of Fig. 2 suggests that in the flux region of  $(2 \text{ to } 10) \times 10^{15}$  electrons/ $\text{cm}^2$  some other conduction mechanism is present which is *n*-type in character. It seems not unreasonable to suggest that this spurious conductivity be the result of some sort of inhomogeneity such as grain boundaries, surfaces, or dislocations.

Folberth and Weiss<sup>6</sup> have found that the Hall coefficient of samples of InAs whose donors have been partially compensated by the introduction of acceptors changes sign twice as the temperature is varied over a suitable range. This fact suggests that such a double reversal of Hall effect might also be observed if a *p*-type sample were compensated by the proper amount of

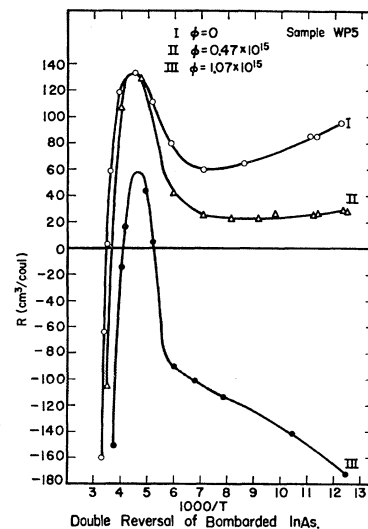


FIG. 3. Temperature curves showing the double reversal of Hall coefficient in bombarded InAs.

<sup>6</sup> O. G. Folberth and H. Weiss, *Z. Naturforsch.* **11a**, 510 (1956).

bombardment. In order to observe this effect a *p*-type sample was bombarded at liquid nitrogen temperature, but before each temperature run was made, the sample was warmed to 290°K for 25 minutes. After this period of time the amount of annealing at this temperature was small, and at lower temperatures negligible. In Fig. 3 three temperature curves for this sample are plotted. The Hall coefficient is plotted linearly in order better to illustrate the changes in sign of *R*. The first curve corresponds to zero bombardment, curve II to a flux of  $0.47 \times 10^{15} \text{cm}^{-2}$ , and curve III to a flux of  $1.07 \times 10^{15} \text{cm}^{-2}$ . This sample, before bombardment, showed a very pronounced dip in the Hall coefficient which is not well understood. It is possible, however, that this dip is the result of the polycrystallinity of the sample. Curves II and III illustrate the transition from a single reversal to a double reversal. Whether or not this double reversal and the behavior observed by Folberth and Weiss are caused by the same mechanism is a question yet to be answered. It appears at least plausible that electronic conduction along grain boundaries, surfaces, or dislocations might explain the double reversal behavior as well as the apparent spurious conductivity observed during bombardment.

#### V. DISCUSSION AND CONCLUSIONS

The effects of radiation damage on the electrical properties of semiconductors may frequently be interpreted in terms of a model suggested by James and Lark-Horovitz<sup>7</sup> which postulates that interstitials are donors and vacancies are acceptors. In the present experiments on InAs it was found that the electrical behavior of bombarded *n*-type samples could be explained by the introduction of donor levels of very low activation energy. No necessity of assuming the existence of acceptors was encountered; nor was this assumption ruled out, since acceptors might be introduced at a slower rate, or might be less highly ionized than the donors. In view of experiments performed on other semiconductors (see reference 1 for a discussion of these experiments), which demonstrate that both donors and acceptors are introduced by bombardment, the latter assumption seems more reasonable. Nor is it unlikely that the donors be so easily ionized. For example the Bohr model<sup>7</sup> applied to a doubly ionized donor site predicts an electronic orbit of 106 angstroms, and the second ionization potential to be approximately 0.0113 ev. The same calculation for the first ionization potential of the acceptors gives 0.028 ev. These calculations were made under the assumption that the dielectric constant<sup>8</sup> of InAs is 12,

<sup>7</sup> H. M. James and K. Lark-Horovitz, *Z. Physik Chem.* **198**, 107 (1952).

<sup>8</sup> F. Oswald and R. Schade, *Z. Naturforsch.* **9a**, 611 (1954).

the effective mass<sup>3,9</sup> of electrons  $0.03m_0$ , and the effective mass of holes  $0.3m_0$ . The very low ionization energies of the donors is obviously the result of the small effective mass of the electrons.

A calculation of the rate at which primary vacancy-interstitial pairs are introduced, utilizing the cross section for differential Coulomb scattering,<sup>10</sup> and an assumed 30 ev for the threshold displacement energy, yields the value 2.96/cm. Consideration of the secondary displacements should not increase the calculated number of displacements by more than 30 or 40%. Threshold experiments performed<sup>11-13</sup> on other semiconductors suggest that the threshold displacement energy may lie in the range 15 to 30 ev for most materials. Thus the rate of introducing Frenkel pairs is expected to lie between approximately 4/cm and 8/cm. Or the net amount of bound charge introduced per Frenkel pair is expected to be approximately  $6/8 = 0.75$  to  $6/4 = 1.5$  for *n*-type samples. If the donors are doubly ionized and the acceptors singly ionized, the net bound charge introduced per Frenkel pair would be 1.0 for *n*-type samples (assuming that vacancies are acceptors and interstitials are donors).

The anomalous behavior of *p*-type samples during bombardment has been attributed to a spurious conductivity which has negligible effect when the concentration of either holes or electrons is very large, but which obscures the changes in hole and electron concentration when both are small. This spurious conductivity might consist of conduction along grain boundaries, since these samples were polycrystalline; however, in view of heat treatment studies reported by Dixon<sup>14,15</sup> one is tempted to ascribe this behavior to conduction in the vicinity of dislocation lines. Dixon has shown that the double reversal of InAs can be attributed to inhomogeneity produced as a result of the segregation of *n*-type impurities near dislocations.

#### ACKNOWLEDGMENTS

The author is indebted to the late Dr. K. Lark-Horovitz who suggested the problem and to Dr. J. R. Dixon who made preprints of his studies available. The specimens were very generously provided by Dr. A. C. Beer of Battelle Memorial Institute, Columbus, Ohio, and Dr. H. Welker of Siemens-Schuckertwerke, Erlangen, Germany.

<sup>9</sup> W. G. Spitzer and H. Y. Fan, *Phys. Rev.* **106**, 882 (1957).

<sup>10</sup> W. A. McKinley and H. Feshbach, *Phys. Rev.* **74**, 1759 (1948).

<sup>11</sup> E. E. Klontz and K. Lark-Horovitz, *Phys. Rev.* **82**, 763 (1951).

<sup>12</sup> J. J. Loferski and P. Rappaport, *Phys. Rev.* **98**, 1861 (1955).

<sup>13</sup> W. L. Brown and W. M. Augustyniak, *Bull. Am. Phys. Soc. Ser. II*, **2**, 156 (1957).

<sup>14</sup> Jack R. Dixon, *Bull. Am. Phys. Soc. Ser. II*, **3**, 120 (1958).

<sup>15</sup> Jack R. Dixon (to be published).