PHYSICAL REVIEW VOLUME 99, NUMBER 2 JULY 15, 1955

Optical Properties of Indium-Doped Silicon

R. Newman
General Electric Research Laboratory, Schenectady, New York

(Received February 21, 1955; revised manuscript received March 31, 1955)

Absorption and photoconduction have been studied in indium-doped silicon at low temperatures. The optical properties indicate a level at about that obtained from thermal-resistivity measurements, i.e., 0.16 ev. Sharp absorption lines are observed at 20°K which broaden and essentially disappear by 77°K.

INTRODUCTION

The ionization energies of Groups III and V elements, as impurities in silicon, were recently obtained by Morin *et al.*[1] from resistivity measurements. The ionization energies were all approximately 0.05 ev with the exception of that of indium, which was measured as 0.16 ev.

The case of indium, with its large ionization energy, was of especial interest because it afforded an opportunity to study impurity optical phenomena over a convenient range of temperature (e.g., $T\leqslant 77^\circ$K) with the important condition satisfied that the carrier population in the impurity centers remained essentially constant over this range. In addition a possibility existed of preparing a material which would be a useful infrared detector out to 7 or 8μ and which could be operated at the readily accessible temperature of liquid air.

The work reported here paralled that of another group.[2] Where the results of the two efforts overlap they are essentially identical. The present paper may in part, therefore, be considered as corroboration of the work of Burstein's group.

EXPERIMENTAL

Six single crystals of indium-doped silicon were prepared by conventional doping and crystal-pulling techniques. The original starting material was zone-melted DuPont silicon of approximately 40 ohm cm, *p*-type. It was, therefore, necessary to compensate the starting material with *n*-type impurity and back dope with indium to get a crystal with the desired property, i.e., all uncompensated acceptors derived from the indium. In practice the starting material was doped with enough Sb-Si alloy so that the initial portions of the pulled crystal prior to indium doping were 1 to 10 ohm cm *n*-type. Indium was added in different runs to give initial concentrations in the melt which ranged from 0.01 percent to 1 percent by weight. In all cases, because of the segregation, the minimum room temperature resistivity that could be obtained was 1 ohm cm, which corresponded to 5×10^{16} carriers/cm^3. In all the ingots grown, polycrystalline growth would develop at a concentration of about 2 percent indium by weight in the melt.

Samples were mounted in a cryostat equipped with NaCl windows. For photoconductive measurements the cryostat was at the exit port of a Perkin Elmer spectrometer. For absorption measurements the crystat was placed in the sample section of the spectrometer. CaF_2 and NaCl optics were employed. The photoconductive spectra were taken in 13-cps chopped light by using a constant-voltage-input circuit and the Perkin Elmer 13-cps amplifier system. Equivalent data were obtained in 450 cps chopped light by using a Baird phase-sensitive amplifier. Indium soldered contacts were used. The energy output of the globar source was monitored with a thermocouple.

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of indium-doped silicon at 77°K and 21°K for a sample having 5×10^{16} holes/cm^3 at room temperature. Figure 2 shows a detail of these spectra in the region from about 0.14 to 0.16 ev with this sample at several temperatures in the 77°–20°K range. The region of lattice absorption is not shown in the latter figure.

Figure 3 shows a plot of the photoconductive spectrum at 77°K of a sample again having a room temperature carrier density of 5×10^{16}/cm^3. Figure 4 shows the same for a sample having a room temperature carrier density of $\sim 1\times 10^{16}$/cm^3.

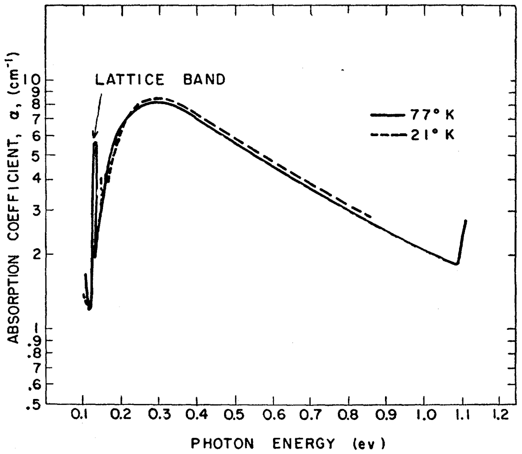

FIG. 1. Absorption spectrum of indium-doped silicon at 77°K and 21°K. Sample had 5×10^{16} holes/cm^3 at 300°K.

---

[1] Morin, Martin, Shulman, and Hannay, Phys. Rev. 96, 833 (1954).

[2] Burstein, Picus, Henvis, Schulman, and Lax (to be published), quoted in Burstein *et al.*, Atlantic City Photoconductivity Conference, November, 1954 (unpublished).

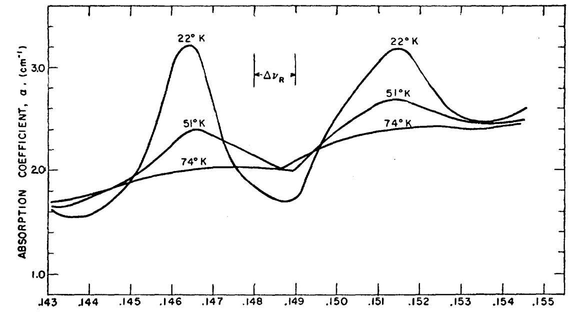

FIG. 2. A detail of the absorption spectrum of indium-doped silicon showing the effect of temperature on the absorption lines.

Conductivity-temperature measurements on one of our samples were made by W. W. Tyler. They showed a 0.16_4 ev ionization energy in agreement with Morin's results and indicated a room temperature mobility of 180 cm^2/volt sec and a mobility maximum at about 80°K.

The model employed to describe the optical properties of a hydrogen-like atom has been carried over to explain the optical properties of the so-called hydrogen-type impurities in semiconductors, notably silicon.[3] The model has met with success in predicting the existence of discrete excited impurity levels and in explaining the form of the continuous absorption corresponding to photoionization. Since the application of the model to the case of indium-doped silicon has already been described,[2] only brief comment will be made here.

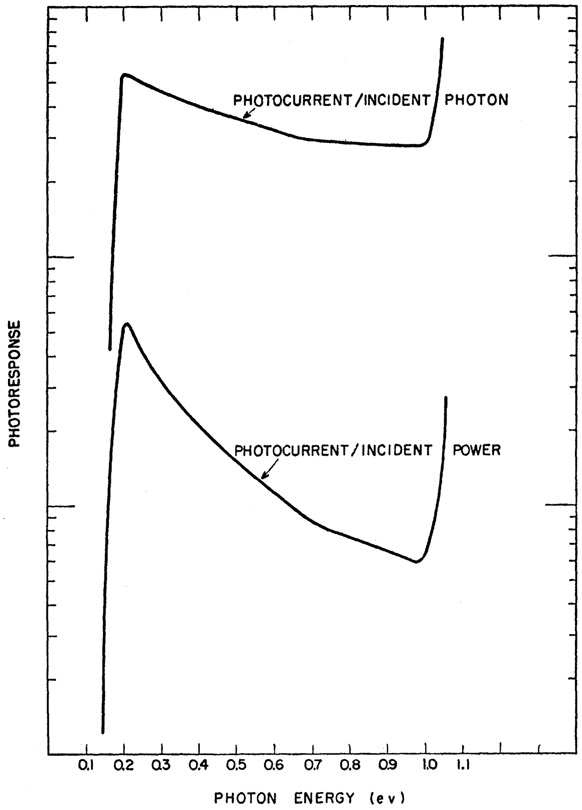

FIG. 3. Photoconductive spectrum (arbitrary log scale) of an indium-doped sample at 77°K having a carrier density of 5×10^{16} holes/cm^3 at 300°K. Sample thickness 0.65 cm.

Referring to Fig. 1, the continuous absorption extending toward higher energy from about 0.15 ev is identified with the photoionization of holes from the indium centers. The low-energy threshold of absorption at about 0.15 ev is in agreement with the ionization energy that has been determined by resistivity measurement (0.16 ev). The photoionization can also be studied through a measurement of the impurity photoconduction. For a sample in which the product of absorption constant (α) and sample thickness (d)$\ll1$ (case 1), it would be expected that the photocurrent/incident quantum would be proportional to α. On the other hand, for the case where $\alpha d\gg1$ (case 2), the sample should show a flat response in photocurrent/incident quantum over the range where this condition is satisfied. Under the conditions for which the data of Fig. 3 were obtained, $\alpha d>1$ should be satisfied out to about 0.15 ev. Conversely, for the data of Fig. 4, the condition $\alpha d<1$ should be satisfied over the entire impurity range.[4] Thus the photocurrent/incident quantum curve of Fig. 4 should be superposable with the absorption curve of

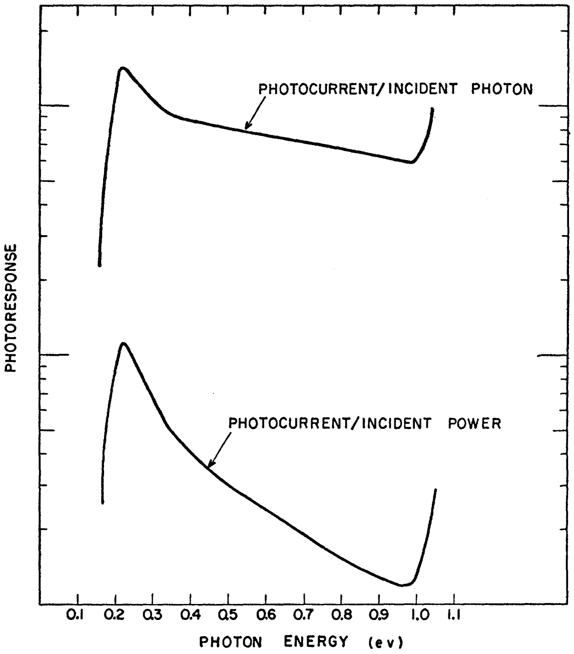

FIG. 4. Photoconductive spectrum (arbitrary log scale) of an indium-doped sample at 77°K having a carrier density of $\sim1\times10^{16}$ holes/cm^3 at 300°K. Sample thickness 0.30 cm.

---

[3] Burstein, Bell, Davisson, and Lax, J. Phys. Chem. **57**, 849 (1913).

[4] Absorption coefficient was not measured for this sample. It is assumed from the room temperature carrier density (1×10^{16}) that α would be $\frac{1}{5}$ of that shown in Fig. 1.

Fig. 1. This is only roughly so. The reason for the discrepancy between them is not understood.

As remarked previously, one of the predictions of the hydrogen-like model of impurities is the existence of discrete excited levels. Such levels may be evidenced by the existence of relatively sharp absorption lines in the spectra of doped materials at low temperatures. Two such lines are found in indium-doped silicon (see Figs. 1 and 2). We have located them at 0.147 ev and 0.152 ev. Burstein has identified these lines respectively, with the $1s \rightarrow 3p$ and $1s \rightarrow 4p$ transitions.[2]

An interesting feature of these lines is their temperature dependence as illustrated in Fig. 2. Unfortunately our measurement of this dependence was hindered by an inferior resolving power ($\Delta\nu_R \sim 10^{-3}$ ev). It is, however, obvious from the figure that at about 74°K the line width is greater than 10^{-3} ev (i.e., resolving power), at about 50°K it is comparable to 10^{-3} ev and at about 20°K it is less than or equal to 10^{-3} ev. This type of temperature dependence has been previously observed in boron-doped silicon.[3] It has been treated theoretically by Lax and Burstein.[5] They indicate that the line broadening is due to a broadening of the ground state of the impurity due to an interaction with lattice vibrations. The temperature range over which the line width transition is observed in the present case is essentially that predicted by their theory.

ACKNOWLEDGMENTS

I should like to express my appreciation to W. W. Tyler for resistivity and Hall measurements and to J. H. McTaggart for his assistance.

---

[5] M. Lax and E. Burstein, Phys. Rev. 91, 208 (1953).

PHYSICAL REVIEW VOLUME 99, NUMBER 2 JULY 15, 1955

Electrical Conductivity and Seebeck Effect in $Ni_{0.80}Fe_{2.20}O_4$

F. J. Morin and T. H. Geballe
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received March 25, 1955)

Electrical conductivity and Seebeck effect have been measured as functions of temperature on single-crystal samples of $Ni_{0.80}Fe_{2.20}O_4$. A thermal hysteresis has been observed in the conductivity but not in the Seebeck effect. This suggests that the hysteresis involves the charge carrier transfer process but not the production of carriers. The activation energy associated with the transfer process is estimated to be 0.10 ev in the high-temperature state and 0.06 ev in the low-temperature state.

1. INTRODUCTION

MAGNETIC losses in ferrites have been interpreted[1,2] as being due to an electron transfer of the type

$$Fe^{2+} + Fe^{3+} = Fe^{3+} + Fe^{2+},$$

with an activation energy required for the transfer process. It is generally believed that the process of electrical conduction in ferrites also involves such a transfer. We have therefore made measurements of electrical conductivity and Seebeck effect as functions of temperature in order to determine an independent value of the energy required for the electron transfer. This result is presented below. In the course of measurements, an unexpected thermal hysteresis was encountered for which we offer no explanation at the present time.

2. EXPERIMENT

The two crystals of nickel ferrite used were obtained from Linde Air Products Company. Chemical analysis indicated the composition to be $Ni_{0.80}Fe_{2.20}O_4$. The growth direction was within a few degrees of [111].

A rectangular bar 0.608 in. long (in the growth direction), 0.206 in. wide, and 0.0600 in. thick was cut from the crystal. Electrical contacts were fired on in air at about 660°C for 5 minutes using a silver paste. The contacts were arranged so that 4-point electrical conductivity, Hall effect, and Seebeck effect measurements could be made. The contacts were nonrectifying. The Hall voltage was found to be too small to detect. The Seebeck voltage per degree, or thermoelectric power proved to be a smoothly varying function of temperature. The results are shown in Fig. 1 and interpreted in

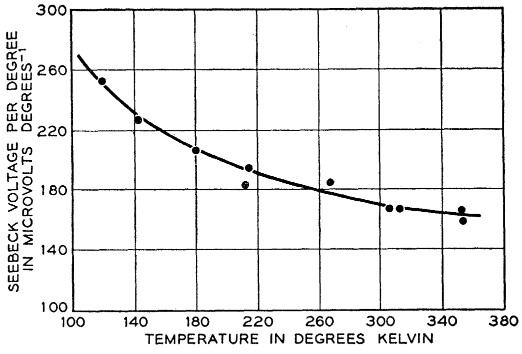

FIG. 1. Seebeck effect as a function of temperature.

---

[1] J. K. Galt, Bell System Tech. J. 33, 1023 (1954).

[2] H. P. J. Wijn and H. van der Heide, Revs. Modern Phys. 25, 99 (1953).