

## Properties of Silicon Doped with Manganese

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Manganese acts as a donor impurity in silicon, introducing a level  $0.53 \pm 0.03$  eV from the conduction band. The distribution coefficient of manganese in silicon is  $\sim 10^{-5}$  as determined by radioactive tracer techniques and checked by electrical measurements. Precipitation limits the electrically active manganese to  $5 \times 10^{14}$   $\text{cm}^{-3}$  in crystals grown from a melt by the Czochralski technique. Higher concentrations can be obtained by diffusing in manganese at  $1200^\circ\text{C}$  and quenching. Manganese introduces recombination centers into a crystal with observable effects at the  $10^{12}$   $\text{cm}^{-3}$  concentration in the crystals. Studies of Hall mobility under external radiation and lifetime studies by the photoconductive decay method show the presence of electron traps. Heating to only  $200\text{--}300^\circ\text{C}$  causes the precipitation of the manganese and loss of electrical activity.

### INTRODUCTION

THE addition of metallic element impurities other than the Column III and Column V elements to a germanium crystal has produced interesting electrical and optical effects. Among these effects are the high resistivity of *n*- and *p*-type crystals below room temperature as compared to undoped crystals, high infrared photosensitivity, quenching, and trapping of charge carriers.<sup>1</sup> Germanium is available with residual electrically active impurity concentrations of less than  $10^{13}$  atoms per  $\text{cm}^3$ . Even relatively insoluble impurities can be studied in germanium because of its high purity. Studies have been made of the energy levels introduced in the germanium forbidden energy band by more than twenty elements.<sup>2</sup>

Silicon has not been generally available with residual concentrations below  $10^{14}$  atoms per  $\text{cm}^3$ . It has, therefore, been more difficult to observe the effects of added impurities in silicon than in germanium. Outside of the Column III and Column V elements and lithium, energy levels in silicon have been reported thus far only for zinc,<sup>2</sup> iron,<sup>3</sup> and gold.<sup>4</sup> In this paper the effect of the presence of manganese in silicon is discussed.

### CRYSTAL PREPARATION

The crystals used in this study were grown from DuPont Hyperpure silicon that had been zone-refined. It was generally *p* type with resistivity between 50 and 100 ohm-cm, i.e., with uncompensated acceptor concentration of 2 to  $4 \times 10^{14}$   $\text{cm}^{-3}$ . Crystals with a (111) orientation were pulled from a melt in a quartz crucible by the Czochralski technique at speeds of one to five inches per hour with rotation rates ranging from 3 to 60 rpm.

The manganese used in this study came from three

sources: Johnson-Matthey Company, Electro-Manganese Corporation, and Johnson-Matthey material which had been zone-refined in an alumina boat in this Laboratory. All three sources of manganese gave substantially the same results in doped silicon crystals. Woodbury and Tyler<sup>1</sup> similarly had found that all three sources of manganese gave the same results in doped germanium crystals.

In order to correlate the electrical properties with the presence of manganese, it is necessary to know the concentration of manganese in the silicon. To this end, two crystals were grown under an average growth condition (2 in. per hour) from a melt containing initially some radioactive manganese as well as normal manganese. Manganese 54 has a half-life of 310 days emitting beta and gamma radiation. After the crystal was grown, it was sliced transversely to the growth axis and gamma radiation measured for slices along the crystal. The concentration of manganese in the crystal calculated from the radioactivity pattern could be fitted by a distribution coefficient of  $10^{-5}$  over the range of manganese in the melt of  $7 \times 10^{18}$  to  $3 \times 10^{20}$   $\text{cm}^{-3}$ . Considerable scatter in the data was due largely to statistical errors in counting the gamma radiation. For melt concentrations above  $\sim 3 \times 10^{20}$   $\text{cm}^{-3}$  ( $\frac{1}{2}$  atomic percent manganese in silicon), the crystal was no longer single, the normal segregation process broke down, and a sharp increase in the concentration of manganese in the crystal was noted. Probably there were inclusions of manganese trapped in the crystal at the growth interface which precipitated on cooling from the melt.

Evidence for the precipitation of manganese in silicon is found by infrared image tube studies of transmission and birefringence.<sup>5</sup> Figure 1 shows transmission and birefringence of the bottom end of a longitudinal slab 1.8 mm thick from a silicon crystal doped with 26 milligrams of manganese. The grid lines are part of the infrared image tube. The grid spacing corresponds to 1.1 mm on the crystal. The transmission pattern in the lower picture indicates that precipitates have formed in the region in which there is visible lineage on the crystal

<sup>1</sup> H. H. Woodbury and W. W. Tyler, *Phys. Rev.* **100**, 659 (1955); Newman, Woodbury, and Tyler, *Phys. Rev.* **102**, 613 (1956).

<sup>2</sup> H. Brooks in *Advances in Electronics and Electron Physics* (Academic Press, Inc., New York, 1955), Vol. VII, p. 110.

<sup>3</sup> C. B. Collins, *Bull. Am. Phys. Soc. Ser. II*, **1**, 49 (1956).

<sup>4</sup> C. B. Collins and R. O. Carlson, *Bull. Am. Phys. Soc. Ser. II*, **1**, 127 (1956); E. A. Taft and F. H. Horn, *Phys. Rev.* **93**, 64 (1954).

<sup>5</sup> W. C. Dash, *Phys. Rev.* **98**, 1536(A) (1955).

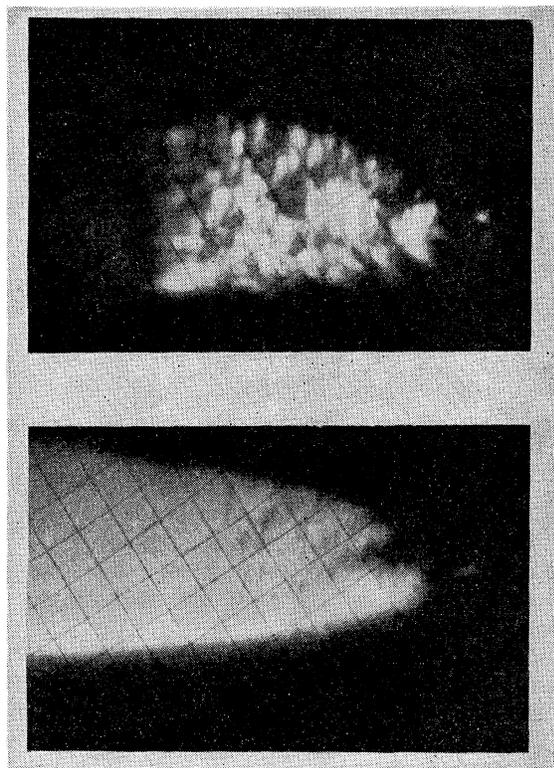


FIG. 1. Infrared image tube study of longitudinal slab from the sprout end of a manganese-doped crystal. Lower picture is taken by transmitted light and specks are probably precipitated manganese. Upper picture shows the birefringence pattern and illustrates the strain introduced into the crystal by the precipitation process. The grid spacing is 1.1 mm.

surface. Birefringence, being considerably more sensitive than transmission for detecting inhomogeneities, indicates a sudden onset of strain closer to the seed end of the crystal than in the transmission picture. The concentration of manganese where the birefringence indicates precipitation is  $4 \times 10^{20} \text{ cm}^{-3}$  in the melt and therefore about  $4 \times 10^{15} \text{ cm}^{-3}$  in the crystal. Two other doped crystals, grown under similar conditions, show these patterns by transmission and birefringence starting at concentrations of 2 to  $4 \times 10^{20} \text{ cm}^{-3}$  in the melt.

#### DIFFUSION SAMPLES

To provide samples suitable for diffusion studies, several *n*- and *p*-type crystals were grown with no rotation of the seed holder. These samples showed no appreciable change in resistivity after many hours at  $1200^\circ\text{C}$  whereas samples from rotated crystals did show marked changes in resistivity.

One sample was coated with radioactive manganese from a  $\text{MnCl}_2$  solution and placed in a quartz tube which was then evacuated and sealed off. After 24 hours at  $1200^\circ\text{C}$  to allow the manganese to diffuse into the interior of the  $0.3 \times 0.3 \times 1.0 \text{ cm}^3$  sample, the sample was removed, ground, and etched to remove any surface

layer of manganese. Gamma counts on the manganese 54 revealed a total manganese concentration of  $1.5 \times 10^{16} \text{ cm}^{-3}$  in this sample. Further grindings and etchings showed the sample to be homogeneous. This concentration of greater than  $10^{16} \text{ cm}^{-3}$  is a reasonable solubility limit<sup>6</sup> at  $1200^\circ\text{C}$  for an impurity whose distribution coefficient is  $10^{-5}$ . The diffusion coefficient for manganese in silicon must be greater than  $2 \times 10^{-7}$  at  $1200^\circ\text{C}$ .

#### APPARATUS

A cryostat was constructed to carry out measurements of various electrical and optical properties of doped silicon samples over a wide temperature range. For *p*-type or high-resistivity samples of  $0.3 \times 0.3 \times 1.0 \text{ cm}^3$  size, gold or rhodium was plated on the ground ends and at four points cut into the sides of the sample by a diamond saw. Contact was then made to the end plated areas by copper blocks under spring tension for the current leads and to the four side points by phosphor bronze springs for the potential leads. For low-resistivity *n*-type samples, five-mil gold wire containing one percent antimony was attached by sparking through the gold plated area. All potentials, including that across a standard resistor in series with the sample to obtain the current, were measured on an Applied Physics Corporation "vibrating reed electrometer." The volt-

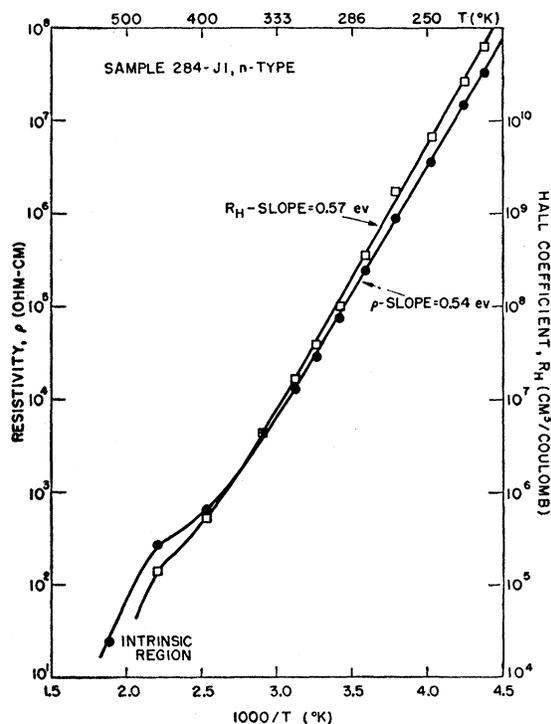


FIG. 2. Resistivity and Hall coefficient *versus* inverse temperature for an *n*-type manganese-doped silicon sample.

<sup>6</sup> R. N. Hall (private communication); C. D. Thurmond and J. D. Struthers, *J. Phys. Chem.* 57, 831 (1953); R. J. Hodgkinson, *Phil. Mag.* 46, 410 (1955).

age across the sample ends was always less than one volt. The magnetic field used in this study was provided by a Varian electromagnet with 4-in. pole faces and a 2-in. pole gap. Measurements reported here were carried out in a field of 6000 gauss. A quartz window in the outer shield of the cryostat permitted study of doped samples under external irradiation.

#### ELECTRICAL MEASUREMENTS

Manganese added to a melt of *p*-type silicon serves to increase the resistivity of a crystal grown from this melt. When the concentration of manganese in the crystal, as determined from the concentration of manganese in the melt and the distribution coefficient of  $10^{-5}$ , is greater than the residual acceptor concentration, the crystal becomes *n* type with near intrinsic resistivity. Figure 2 is a plot of Hall coefficient  $R_H$  and resistivity  $\rho$  versus inverse temperature for such an *n*-type sample in which the concentration of manganese is  $\sim 5 \times 10^{14} \text{ cm}^{-3}$  and the concentration of acceptor is  $\sim 4 \times 10^{14} \text{ cm}^{-3}$ . The slopes of  $R_H$  and  $\rho$  indicate a deep level at 0.55 eV from the conduction band. Hall mobility at room temperature (300°K) for this sample is  $1100 \text{ cm}^2/\text{volt-sec}$  and varied as  $T^{-2.2}$ . Other initially *p*-type crystals show similar behavior to this crystal sample with ionization energies in the range 0.52 to 0.56 eV. Further toward the sprout end, these crystals become *p* type where the concentration of manganese in silicon is between  $5 \times 10^{14}$  and  $10^{15} \text{ cm}^{-3}$ . This is close to the concentration range for which the birefringence studies indicate that precipitation of manganese is occurring.

When manganese is added to a melt of *n*-type silicon, the resistivity of the grown crystal increases but the calculated added acceptor concentration is only about one-twentieth of the manganese concentration of the crystal. These acceptors are probably due to the presence of impurities in the manganese used for doping. Under heavy doping the crystal remains *n* type but the resistivity becomes high and the  $\rho$  vs  $1/T$  curve shows 0.50- to 0.55-eV ionization energy. This may be due to the domination of the original donors by the acceptor impurities in the manganese.<sup>8</sup>

Manganese diffused into *p*-type samples at 1200°C causes the sample to convert to *n* type with  $\sim 0.53$ -eV level. The quench from 1200°C, being more rapid than that in a crystal grown from a melt, stops the precipitation process in a few seconds. More than  $10^{15}$  electrically active manganese donors per  $\text{cm}^3$  have been observed in the diffused samples. No measurable effect was seen on diffusing manganese into *n*-type samples at 1200°C; in

<sup>7</sup> The observed slope for the  $R_H$  vs  $1/T$  curve must be corrected for the  $T^3$  dependence of the density of states near the bottom of the conduction band. The slope for the  $\rho$  vs  $1/T$  curve must be corrected for this  $T^3$  dependence and also for the conductivity mobility temperature dependence of  $T^{-2.6}$ .

<sup>8</sup> Heating at 300°C causes these samples to convert to  $\sim 75 \text{ ohm cm}$  *p* type, whereas the original undoped silicon was *n* type and also  $\sim 75 \text{ ohm cm}$  in resistivity.

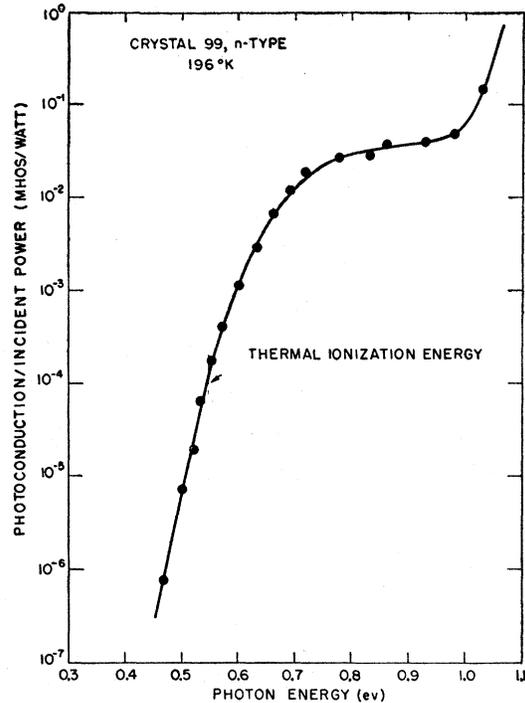


Fig. 3. Photoconductive spectrum of an *n*-type, high resistivity, manganese-doped silicon sample.

this case, any of the Column III acceptor impurities present in manganese would not have time to diffuse more than a few tens of microns into silicon in the time periods of 24 to 64 hours<sup>9</sup> so no increase in resistivity might be expected. In this connection, the doping and diffusing techniques provide good checks on one another. It is the Column III and Column V elements which are the troublesome impurities in doping because of their relatively large distribution coefficients while other metallic impurities such as the transitional elements are rejected because their distribution coefficients are less than  $10^{-3}$ . On the other hand, in the diffusion technique the fast diffusing elements such as copper and iron would be the troublesome impurities in the doping material.

The electrical behavior of manganese can be accounted for by a donor level at  $0.53 \pm 0.03 \text{ eV}$  from the conduction band with each soluble manganese atom capable of giving up an electron. No other levels have been found either by doping with manganese or by diffusing it into a sample.

#### OPTICAL MEASUREMENTS

Infrared photoconduction was studied in several high-resistivity *n*-type samples by R. Newman of this Laboratory and Fig. 3 is typical of his results. The threshold for optical excitation in the impurity photo-

<sup>9</sup> C. S. Fuller and J. A. Ditzenberger, J. Appl. Phys. 27, 544 (1956).

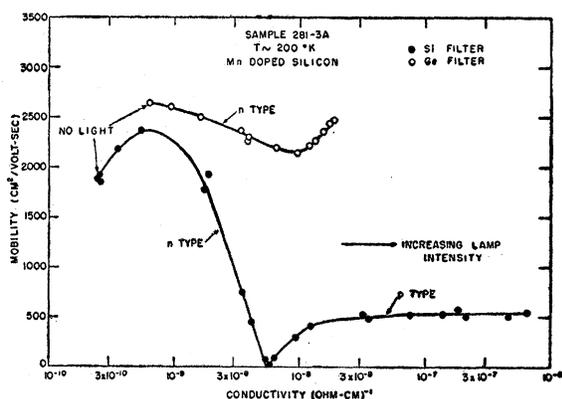


FIG. 4. Effective Hall mobility ( $R_H/\rho$ ) vs conductivity for an  $n$ -type, high-resistivity, manganese-doped silicon sample. The conductivity is changed by varying the intensity of tungsten lamp radiation incident on the samples through either a germanium or silicon filter.

conduction range ( $<1.1$  eV) is in reasonable agreement with the ionization energy found from temperature dependence of  $\rho$  and  $R_H$ .

Electrical measurements of several high-resistivity  $n$ -type samples were carried out at fixed low temperatures under excitation by light. The source was a tungsten lamp whose intensity was varied by changing the current through it. The light was filtered by a thin slice of germanium or silicon maintained at the temperature of liquid nitrogen. With the germanium filter, only impurity photoconduction can be excited. With the silicon filter, however, some intrinsic radiation will reach the doped sample since the absorption cutoff for silicon in the neighborhood of the intrinsic edge ( $\sim 1.1$  eV) is not sharp.<sup>10</sup> Thus with the silicon filter one will have both intrinsic and impurity photoconduction. Figure 4 shows representative results on a sample with effective Hall mobility ( $R_H/\rho$ ) plotted against the conductivity ( $1/\rho$ ) of the sample. The upper curve, obtained with use of the germanium filter, is characteristic of impurity photoconduction. The lower curve, obtained with use of the silicon filter, indicates that when hole-electron pairs are produced by the intrinsic radiation, the electrons are trapped leaving the holes as the charge carriers and converting the sample from  $n$  type to  $p$  type. The mobility after conversion is about  $\frac{1}{4}$  of the initial mobility, in agreement with the usual ratio of hole to electron Hall mobility for silicon.<sup>11</sup> The initial rise in mobility for low light levels may be due to a decrease in charged impurity scattering or to greater homogeneity of the sample when irradiated. The fixed sample temperature was slightly lower for the silicon filter data than for the germanium filter data.

These results can be interpreted as due to a larger cross section for capture of electrons than for holes. This electron trapping effect in silicon doped with

<sup>10</sup> W. C. Dash and R. Newman, Phys. Rev. **99**, 1151 (1955).

<sup>11</sup> F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

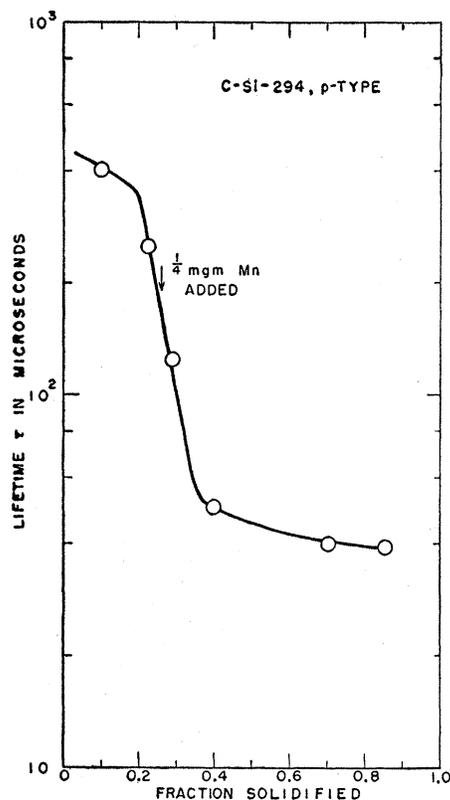


FIG. 5. Lifetime along a  $p$ -type silicon crystal doped with manganese as measured by a photoconductive decay experiment.

manganese is in interesting contrast to the hole trapping effect in germanium doped with manganese.<sup>1</sup>  $P$ -type germanium doped with manganese to high resistivity converts to  $n$  type under intrinsic radiation.

#### LIFETIME MEASUREMENTS

One of the phenomena noted when doping silicon with manganese was its effect on recombination lifetime. Figure 5 is a plot of recombination lifetime along a  $p$ -type crystal lightly doped with manganese. Lifetime was measured by the photoconductive decay method. At the doping point, the concentration of manganese in the melt is  $4 \times 10^{17} \text{ cm}^{-3}$ ; assuming a distribution coefficient is  $10^{-5}$ , then the concentration of manganese in the crystal at the doping point is only  $4 \times 10^{12} \text{ cm}^{-3}$ . Back diffusion of manganese could account for the reduction in lifetime before the doping point.

The lifetime values given in Fig. 5 are taken from the first parts of the photoconductive decay curves, which are approximately exponential. A long tail is found on the decay curves for the doped portion of the crystal, indicating trapping of the electrons, the minority carriers. The amplitude of this tail can be decreased, but not altogether eliminated, by increasing the intensity of the ambient light.

In more heavily doped crystals, the recombination

lifetime is so short that only the traps are observed by photoconductive decay measurements. Measurements taken over a range of temperatures, however, will distinguish between recombination lifetime and the trap time constant. In one particular *p*-type crystal, Watters and Ludwig<sup>12</sup> indicate a recombination lifetime for electrons of 100 microseconds at 300°K in the undoped portion of the crystal, increasing with increasing temperature, while in the manganese-doped portion of the crystal, the photoconductive decay time<sup>13</sup> was 400 microseconds at 300°K, decreasing with increasing temperature. Pulse drift techniques,<sup>12</sup> which can distinguish recombination lifetime from trapping effects, give 100 microseconds in the undoped portion of this same crystal and less than 10 microseconds in the doped portion, at 300°K.<sup>12</sup> Deep traps, with a time constant at room temperature of about 100 seconds, were also observed in manganese-doped silicon by Watters and Taft of this Laboratory.

#### HEAT TREATMENT EFFECTS

Samples were taken from the doped region of an initially *p*-type silicon crystal which was converted to high-resistivity *n* type by the addition of manganese. After being in a 300°C oven for 30 to 40 minutes, the samples were found to be strongly *p* type with a resistivity comparable to that in the undoped portion of the crystal. This conversion was presumably due to the precipitation of  $\sim 5 \times 10^{14}$  manganese atoms/cm<sup>3</sup>. Attempts to observe electrically the precipitated manganese put back into solution by heating at 1200°C and fast quenching have been unsuccessful. One reason for this was interfering resistivity changes associated with

<sup>12</sup> R. L. Watters and G. W. Ludwig, J. Appl. Phys. 27, 489 (1956).

<sup>13</sup> It is not clear from these experiments whether this photoconductive decay time is representative of a single or a multiple trapping process. See J. A. Hornbeck and J. R. Haynes, Phys. Rev. 97, 311 (1955); J. R. Haynes and J. A. Hornbeck, Phys. Rev. 100, 606 (1955).

unknown impurities or defects introduced into the silicon by the high-temperature quench.<sup>14</sup>

#### SUMMARY

The addition of manganese to a silicon melt results in the introduction of donors to the crystal grown from the melt. The donor concentration is equal to the concentration of manganese in the crystal as determined by radioactive tracer techniques up to a limit of  $\sim 5 \times 10^{14}$  cm<sup>-3</sup> in grown crystals. Evidence that this limit is due to the precipitation of manganese, and hence removal from electrical activity, is given by infrared birefringence and transmission studies. The solubility of manganese is  $\sim 10^{16}$  cm<sup>-3</sup> when diffused into silicon at high temperatures, but only about one tenth of this remains soluble and is observed electrically on cooling to room temperature. Manganese reduces recombination lifetime and under certain conditions acts as an electron trap. Heating at only 200–300°C causes the precipitation of manganese in silicon. Only one donor level at  $0.53 \pm 0.03$  eV from the conduction band has been detected in either doped or diffused silicon samples containing manganese.

It is interesting to speculate as to whether manganese in silicon is an interstitial impurity in view of its relatively fast diffusion coefficient and its donor behavior. In germanium it is more likely that manganese is a substitutional impurity in view of the two acceptor levels that it introduces into the germanium forbidden band.

#### ACKNOWLEDGMENTS

I am indebted to G. D. Brower and R. F. Riehl for assistance in all phases of this work. Most of the lifetime data were taken by R. L. Watters, G. W. Ludwig, and E. A. Taft. W. C. Dash carried out the infrared image tube studies. The initial work on manganese-doped silicon was carried out by F. H. Horn and E. A. Taft. Part of this work was carried out jointly with C. B. Collins.

<sup>14</sup> C. J. Gallagher, Phys. Rev. 100, 1259 (1955).

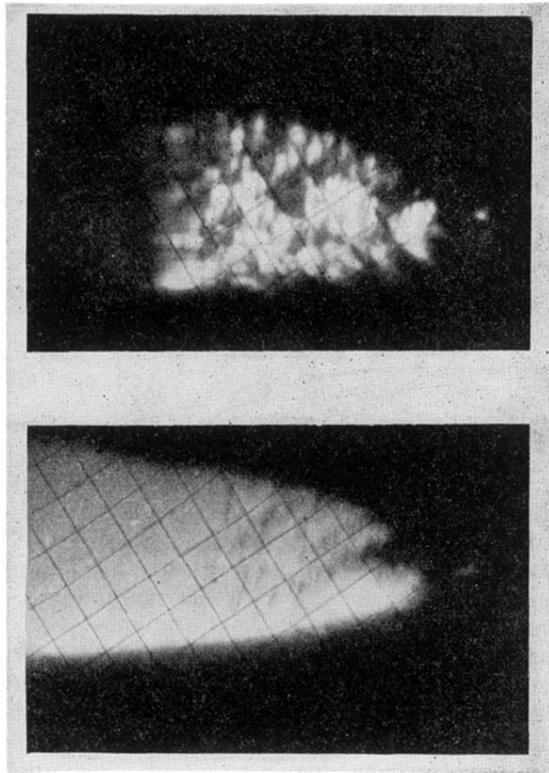


FIG. 1. Infrared image tube study of longitudinal slab from the sprout end of a manganese-doped crystal. Lower picture is taken by transmitted light and specks are probably precipitated manganese. Upper picture shows the birefringence pattern and illustrates the strain introduced into the crystal by the precipitation process. The grid spacing is 1.1 mm.