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Trapping of Minority Carriers in Silicon. II. *n*-Type Silicon

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Experimental evidence of temporary trapping of holes in the volume of *n*-type silicon in at least two different traps is presented. The trap parameters of cross section for capture and energy level above the valence band are determined by measuring the unfilled trap density, the hole density, the rate at which holes are trapped, and the rate at which holes are released from traps. Measurement of the temperature dependence of these quantities for the deeper traps gives, in addition, the temperature variation of the cross section for capture, the energy level of the traps below the conduction band and a second determination of the trap level above the valence band. The values obtained are consistent with accepted values of the energy gap. There is evidence for a loss mechanism for holes (recombination) from the deeper traps at a rate which is found to be proportional to the square of the electron concentration.

INTRODUCTION

In Part I of this paper,[1] we discussed the trapping of electrons in *p*-type silicon. It is the purpose of this section to present the results of our studies of the trapping of excess holes in *n*-type silicon.

Like the electron traps, hole traps must be crystal imperfections or impurities which can immobilize minority carriers and hold them in an unrecombined state for relatively long periods of time.[2] Also like the electron traps, hole traps evidence themselves by an increased conductivity that is associated with added majority carriers which exactly neutralize the space charge of the trapped minority carriers. Unlike the traps in *p*-type silicon, however, traps in *n*-type silicon produce a decay in photoconductivity which is very nearly a simple exponential function of time, showing that multiple trapping is not an important mechanism in this case. That is, an excess hole in the valence band is much more likely to be caught in a recombination center—and disappear—than to be caught in a trap. The absence of multiple trapping means that *n*-type silicon is a simpler trapping system to study than is *p*-type. Mainly for this reason we have made more extensive measurements of the temperature dependence of the trap parameters using *n*-type specimens.

n-type silicon differs from *p*-type also in the number density of traps that are found. In single crystals of *n*-type silicon which we have studied, trap densities have varied from less than $2\times10^8/\text{cm}^3$, i.e., an undetectable density, to approximately $10^{15}/\text{cm}^3$. Unlike *p*-type silicon, in *n*-type no correlation is found between resistivity and trap density. There is, however, the same correlation as in *p*-type between trap density and rotation of the crystal relative to the crucible when the crystal is grown. It should be emphasized that the traps discussed here occur "naturally" in the silicon as grown into single crystals at these Laboratories.

The trap densities found in *n*-type crystals can be so large that the resistivity in the dark of the crystal is affected appreciably by the trap's presence. In other words, the β traps behave, as we shall see, as an added set of donor (or acceptor) levels.

Measurements of the resistivity variation with temperature caused by "Fermi level filling" of the traps, together with data on the temperature variations of the capture cross section and mean-time-in-a-trap, fit together into a self-consistent picture of trap energy depth, and further, provide experimental proof that the principle of detailed balance applies to the traps.

KINDS OF TRAPS IN THE VOLUME OF *n*-TYPE SILICON

We have been able to isolate with certainty two kinds of traps in the volume of *n*-type silicon, and there is considerable evidence for the existence of at least two more trapping levels. The two prominent sets of traps occur in nearly all of our samples of *n*-type silicon grown by the crystal pulling technique of Teal and Little.[3] We shall call these centers α traps and β traps.

The α traps in 25 ohm cm material at room temperature are characterized by a time constant of the decay of photoconductivity of 45 milliseconds while the β traps have a decay constant of 300 seconds.

α Traps: Experimental Techniques and Methods of Measurement

Density and Time Constants

The α traps were studied with the aid of the chopped light and dc oscilloscope equipment used to investigate the shallow traps in *p*-type silicon described in Part I. The samples used were cut from single crystals into rectangular rods having dimensions $0.2\times0.2\times2$ cm and subsequently plated on the ends with rhodium followed by copper. A typical oscillogram obtained using an *n*-type silicon sample (42 A) with this apparatus is shown in Fig. 1. This is a reproduction of a photograph of the oscilloscope tube showing a trace of photoconductivity as a function of time. The sample is illuminated from A to C and the remainder of the time is in the dark. The conductivity rise from A to B is caused by the

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[1] J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).

[2] These traps should not be confused with ordinary recombination or "deathnium" centers wherein recombination or re-emission occurs in a time less than the free time in the conduction stream.

[3] G. K. Teal and J. B. Little, Phys. Rev. **78**, 697 (1950).

excess electrons and holes produced by the light in the conduction and valence bands. These added carriers reach an equilibrium concentration in a time which is the order of the lifetime of holes in this material (40μ sec), which is short compared to the resolving time of the apparatus. The finite slope shown by the oscillogram is associated with the rise time of the light pulse.

A further, nearly linear increase in photoconductivity (from B to C) follows the initial rise. This photoconductivity change is evidence of the trapping of holes in α traps. At C, the light is extinguished and the conductivity suddenly drops to D. This drop, which is equal in magnitude to AB, reflects the decrease in carrier density caused by recombination of excess holes and electrons in the valence and conduction bands, i.e., a normal recombination process. A negligible number of traps have emptied in this length of time, however, so that the conductivity at D is higher than that at A by very nearly the difference between C and B. The line GHI was obtained approximately 0.1 sec after the illumination was cut off. It represents the conductivity of the specimen after practically all of the electron-hole pairs in the conduction stream have recombined and essentially all of the α traps have emptied. The sample still has an increased photoconductivity caused by some filling of the β traps, but no measurable decay of the β traps occurs on this time scale. Hence, we use the line GHI as a base line from which to measure the photoconductive decay time associated with the emptying of the α traps. This decay is very closely exponential with a time constant of 45 milliseconds.

If the intensity of illumination is doubled, the conductivity changes AB, CD, and BC increase nearly proportionally. With increasing illumination, however, a point is reached where, although AB and CD increase, BC does not. Under these conditions the trace BC is no longer linear but rises exponentially to a value which cannot be exceeded with further increase in illumination. Evidently this saturation is associated with the filling of all of the normally empty α trapping centers. As in Part I, we compute the density of α traps from the saturated value of the conductivity change DH, since for each trapped hole there is one added mobile majority carrier: $N_\alpha = (\Delta\sigma_{DH})_{\max} q\mu_-$, where q is the electronic charge and μ_- is the drift mobility of electrons. For specimen 42 A, which we are using as an example, we find $N_\alpha = 1.4\times 10^{12}$ cm^{-3}.

Capture Cross Section

The cross section for capture of holes by α traps may be calculated from data such as those shown in Fig. 1. The calculation makes use of an approximate formula which is derived in the Appendix from the general trapping equations (1) of Part I. The essential feature of the approximation is the interpretation already given of Fig. 1, *viz.*, that after a weak light is turned on, the excess hole density p rises quickly to very near its steady state value p_0 (the rise AB), and that subsequently trapping in α traps begins to appear. The initial trapping rate dp_1/dt, given by the initial slope of BC, is closely equal to $(N_\alpha Sv)\,p_0$, where S is the trapping cross section, v is thermal velocity, $(N_\alpha Sv)$ is the trapping rate, and p_0 is the reservoir of holes from which the trapping occurs. Obviously p_0 is obtained from the measured conductivity change σ_{AB} by the relation $p_0 = \sigma_{AB}/q(\mu_+ + \mu_-)$, and $dp_1/dt \simeq (\Delta\sigma/\Delta t)_{BC}(1/q\mu_-)$ where by $(\Delta\sigma/\Delta t)_{BC}$ we mean the initial slope of BC. With weak sources of illumination the change BC can be made linear so that there is little problem in determining this slope. These amplitude and slope measurements together with a knowledge of the mobilities and the trap density N_α yield S. For specimen 42 A we find $S_\alpha = 4\times 10^{-18}$ cm^2.

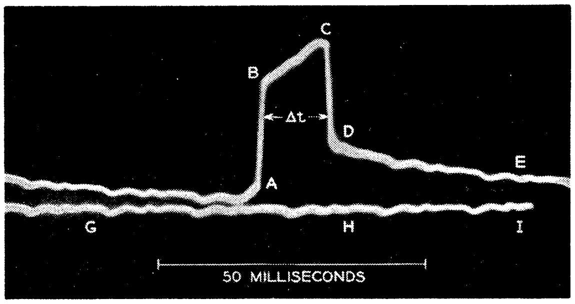

FIG. 1. Photograph of oscilloscope trace showing photoconductivity as a function of time. The sample was illuminated from A to C and the remainder of the time was in the dark. The conductivity difference from H to D was produced as a result of holes caught in α traps.

This value[4] is five orders of magnitude less than the capture cross section for traps in p-type silicon, which accounts for the absence of multiple trapping in the present case. More quantitatively, this may be illustrated as follows. The measured rate of recombination from the valence band of 2.5×10^4 sec^{-1} is about 400 times greater than the trapping rate $(NSv) = 60$ sec^{-1} from the valence band. Thus a hole trapped in an α trap in this specimen has only one chance in 400 of being trapped again, even when all the traps are empty. Thus the time constant associated with the photoconductive decay DE is also the time constant τ associated with the emptying of the α traps. The emptying process could be either thermal ejection back to the valence bond band with subsequent normal recombination, or direct recombination in the trap, or a combination of these. If recombination in the trap is involved, we might expect the time constant of photoconductive decay to be a function of the majority carrier density.[5] The time constant, however, is found to be independent of majority carrier concentration, at least in this conductivity range. We, therefore, believe that the measured time

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[4] This value was erroneously published as 40×10^{-16} cm^2 in J. R. Haynes and J. A. Hornbeck, Phys. Rev. **94**, 1438(A) (1954).

[5] As shown in Part I, the time constant involved in recombination of trapped minority carriers in deep traps for p-type silicon varies as the square of the majority carrier density. This same law will be shown for the β traps in n-type silicon.

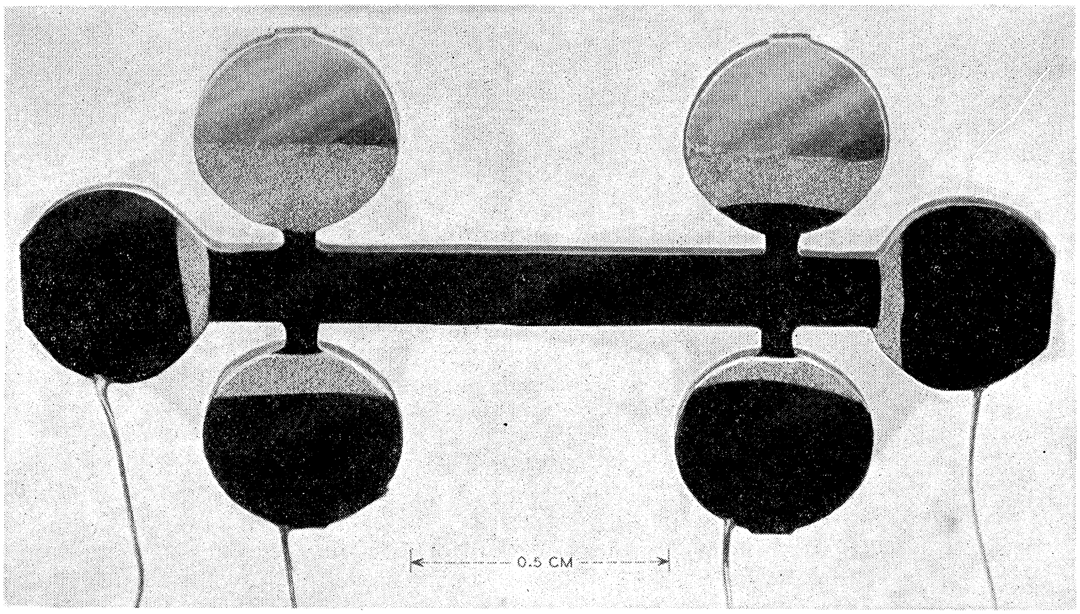

FIG. 2. Photograph of sample 376D-2. The etched surface of the silicon is visible in the central portion of the sample. The upper middle circular sections show the plated areas (top) and the sand blasted regions (bottom). The other four circular sections (with wires attached) are coated with black enamel.

constant τ is the time constant τ_g associated with the rate of generation to the valence band.

Energy Level

The energy level of the α traps with respect to the valence band was calculated from the experimentally determined values of S and τ (assumed equal to τ_g) using the detailed-balance formula, Eq. (1), which is discussed later. The result is that the α traps are located ~0.45 ev from the valence band or ~0.63 ev from the conduction band if the energy gap is 1.08 ev wide. For a resistivity of 25 ohm cm, the Fermi level lies 0.30 ev below the conduction band at room temperature, so that the α trapping centers are normally empty of holes.

β Traps: Experimental Techniques and Methods of Measurement

Experimental Techniques

Because of the long time constant associated with the decay of photoconductivity produced by β traps, it is essential in the study of these centers that the silicon samples be allowed to reach equilibrium in a close approach to absolute darkness.[6] An additional requirement, due to the high-temperature coefficient of resistance of silicon, is that the temperature of the sample remain essentially constant during the decay in photoconductivity. Both of these requirements were met by enclosing the samples in concentric, light tight boxes, with the space between the boxes thermally insulated, and finally placing the assembly in a Cenco-DeKhotinsky constant temperature furnace. Temperatures above room temperature were obtained by heating the furnace. Temperatures below room temperature were achieved by placing predetermined amounts of dry ice in the "furnace."

To produce photoconductivity, the samples were illuminated by the filtered light from a small flash light lamp placed in the inner box. The filter used was an optically polished silicon plate 0.07 cm thick. Light passing through this filter is deeply penetrating and produces electron-hole pairs throughout the volume of the sample. Variation of the intensity of the filtered light by known amounts was achieved by a calibrated resistance in series with the lamp.[7]

The silicon specimens were single crystals nearly all of which were cut into rectangular rods having similar dimensions to sample 42A (described earlier) and plated in the same way on either end. These two-electrode samples were placed in one arm of a Wheatstone Bridge circuit with a dc amplifier and pen recorder substituted for the usual galvanometer. The bridge was balanced with a sample in the dark. On closing a key, the light from the flash light bulb irradiated the sample. A record of the resultant bridge unbalance and subsequent slow decay of photoconductivity was produced by the pen recorder. Time constants longer than 10 seconds were recorded with a Leeds and Northrup stabilized dc amplifier and an Esterline-Angus recorder. Shorter

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[6] The traps integrate the effect of all of the light which illuminates the sample during approximately a time constant. This may be a matter of several hours.

[7] The light was calibrated with a silicon *p-n* junction in terms of relative concentration of electron-hole pairs produced.

time constants were recorded with a Sanborn amplifier and recorder.[8]

With two-electrode samples there always exists the possibility that spurious resistance is produced at the electrodes.[9] In order to test the extent of the errors introduced in this way, a sample (376D-2) was cut as shown in Fig. 2. The circular sections were sand blasted and plated over half their area, first with rhodium and then with copper as shown on the upper two middle electrodes. Copper wires were then soldered to the two end and lower middle electrodes, which were finally given a thick coating of black glyptol.[10]

This four-terminal specimen was used in a circuit shown in Fig. 3. Current flows through the end of electrodes of the sample producing a potential difference between the two middle electrodes. This potential difference is balanced by an equal and opposite voltage produced by current flow through a resistance. The dc amplifier, with an input impedance of 20 megohms, and recorder give a trace of the voltage unbalance produced by a photoconductivity as a function of time.

The measurements obtained with this four-terminal sample were compared with those using a two-terminal sample (376D-1) which was cut from an adjacent region of the same silicon crystal. This comparison shows that the two samples give the same conductivity values except at the lowest temperature used (*ca*$-30°$C) where only minor differences occur. Because of this result, most of the measurements taken at room temperature were made with two-electrode samples while all measurements involving lower temperatures were made with the four-electrode specimen.

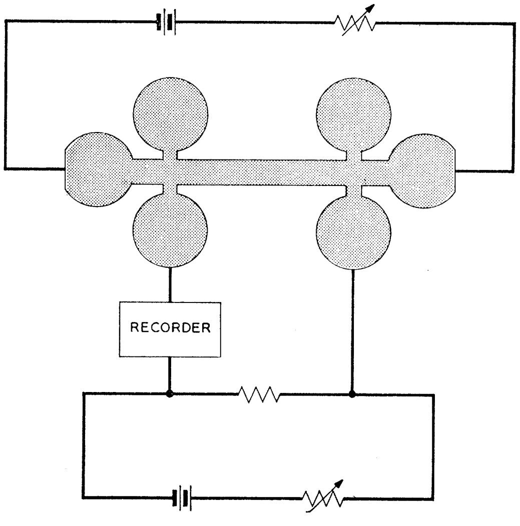

FIG. 3. Schematic diagram of circuit used with sample 376D-2. Current flows through the end electrodes and the resultant potential difference between the middle electrodes is balanced by the lower circuit. A permanent record of conductivity changes is obtained by the pen recorder.

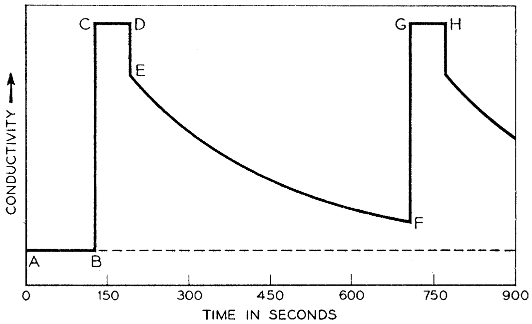

FIG. 4. Schematic of pen recorder chart of sample conductivity as a function of time obtained with relatively strong light. The sample was illuminated from B to D and from F to H, and the remainder of the time was in the dark. Analysis of such charts gives the mean time which holes remain in β traps and their concentration.

Measurement of Density and Time Constants

Both the density of normally unfilled β traps and the time constant of the decay in photoconductivity can be obtained from a pen recorder trace of photoconductivity as a function of time. A typical record made at room temperature is shown in Fig. 4. The trace from A to B is obtained with a sample in the dark and in equilibrium. At B, the sample is illuminated and in consequence its conductivity rises rapidly to a new value CD. At D, the light is extinguished and the conductivity drops to E as the holes in the valence band recombine and the α traps empty. This process is virtually complete in a few tenths of a second, during which time the concentration of holes in β traps remains essentially unchanged. From E to F, the β traps empty and the conductivity drops as the space charge neutralizing electrons in the conduction band disappear. At F, the sample is again illuminated with the same light intensity. The new conductivity represented by GH gives a check on the zero drift of the apparatus, a necessary precaution when long time constants (up to 10 000 sec) are measured. With no apparatus drift, the decay from E to F represents a true decay of the photoconductivity, and the conductivity difference BE results from the filling of some or all, if the light intensity is high enough, of the normally empty β traps, the density of which is given by this conductivity difference divided by $q\mu_-$. Normally only a very weak light is required to fill all of the β traps. In order to assure that this condition was fulfilled, a second recording was made with the light intensity increased by an order of magnitude. In this way, we measured for the β traps both N_β and the decay time τ as a function of temperature.

Measurement of Capture Cross Section

We shall next discuss the experimental measurement of the capture cross section of the β traps. As in the case

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[8] The time constant of the L&N Amplifier and E-A Recorder is ~0.5 sec. The time constant of the Sanborn is less than 0.01 sec.

[9] With silicon at liquid nitrogen temperature, such effects are known to be large.

[10] The purpose of the glyptol, which extends more then a millimeter beyond the plating (approximately 10 diffusion lengths), is to prevent the minority carriers produced by light from diffusing to the electrodes and possibly producing spurious potentials.

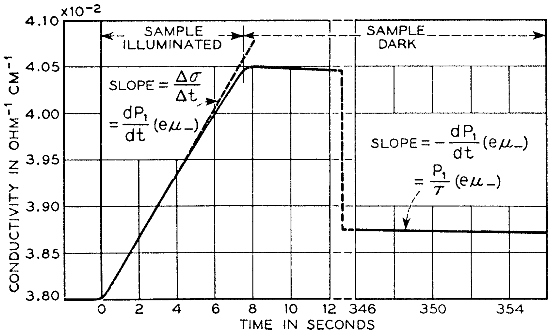

FIG. 5. Sample conductivity as a function of time obtained with relatively weak light and used in the determination of the capture cross section of β traps.

of the α traps, the method involves suddenly illuminating the specimen with weak, penetrating light and measuring the initial rate of trapping. Figure 5 is a typical recorder trace showing the sample conductivity as a function of time. The important difference between Fig. 5 and Fig. 1, which pertains to α traps, is that at $\tau=0$ no abrupt change in conductivity is observed corresponding to $p_0 \simeq l/r$, the rise AB in Fig. 1. This is explained by the fact that in the β trap measurement the light intensity is so weak that p_0 is negligible ($\sim 10^8$ or 10^9 cm^{-3}) compared to the number of holes in β traps after a time corresponding to the time resolution of the apparatus, a few tenths of a second. In this time filling of the α traps reaches a steady state, but a negligible number of holes are caught there.

Lacking the amplitude change corresponding to p_0, we must measure l and r independently. The value of l was determined by using an n-type sample having the same dimensions and surface treatment as sample 376D-2 (the specimen studied most extensively), but which contained no detectable density ($<10^8$ cm^{-3}) of either α or β traps. When this specimen was illuminated with the weak light source, its photoconductivity is caused entirely by additional electron-hole pairs in the conduction and valence band, respectively, and hence $l=p/\tau_r$, where p comes from a measurement of the photoconductivity and τ_r is the measured life time in the sample.

The value of l obtained in this way was checked by substituting a p-type sample, having the same dimensions and surface treatment, which contained many deep traps. In this sample, nearly all the electrons produced by the light are trapped before they can recombine, i.e., the sample integrates the light falling on it for weak incident illumination and times short compared to its decay time.

The value of r for specimen 376D-2 was obtained in a straightforward way as described in Part I. With these procedures and the formulas described[11] in Appendix I, the capture cross section of the β traps was measured as a function of the temperature.

EXPERIMENTAL RESULTS AND DISCUSSION

In this section, we present the results of the measurements as a function of temperature on the β traps. We shall show that the measurements of the β trap density, N_β, determine the energy level of the traps with respect to the conduction band, that measurements of the capture cross section together with measurements of the decay time, τ, when interpreted properly determine the trap energy level with respect to the valence band, and that these results are consistent with the principle of detailed balancing. From this interpretation, we also obtain information on the rate of recombination in the β traps.

Capture Cross Section

Using the procedure described in the last section, we have determined the capture cross section S of the β traps as a function of temperature T. The results are shown in Fig. 6, which is a plot of ln S as a function of T^{-1}. The circles represent values of S obtained by using the n-type silicon sample (containing no measurable trap density[12]) to evaluate l, whereas the squares represent values obtained by using the p-type sample for the same purpose. Within experimental error the data fall on a straight line represented by $S=S_0 \exp(-2100/T)$ with $S_0=8\times10^{-15}$ cm^2. The activation temperature 2100°K corresponds to an energy of 0.18 ev.

At room temperature, $S=8\times10^{-18}$ cm^2, a value twice that obtained for the α traps. The small value of S explains the almost complete lack of multiple trapping

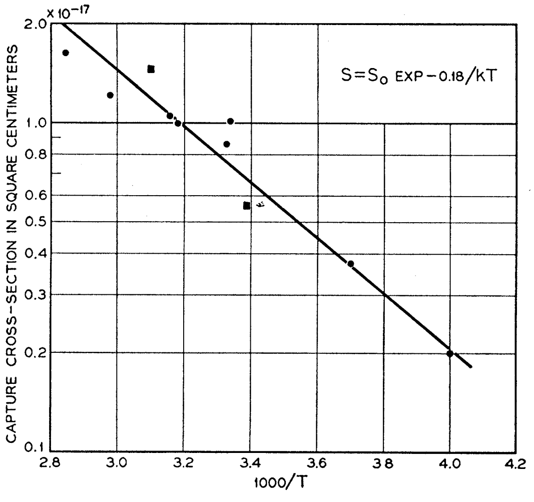

FIG. 6. Capture cross section of β traps as a function of temperature. The solid circles were obtained using a sample containing no detectable traps for the determination of l. The squares were obtained using a p-type sample with a high trap density for this purpose.

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[11] Corrections to the simple formula used in the case of the α traps are discussed in the Appendix. There the right hand, or long time, portion of Fig. 5 is discussed.

[12] Although we found no measurable density of volume traps in this specimen, we did find that after heating the specimen in an oven in the course of the experiments, small trapping effects showed up that were associated with the surface. If unnoticed, these effects would have affected our experimental results.

in β traps. In specimen 376D-2 at 35°C, the rate of recombination from the valence band is ten times the trapping rate[13] (NSv). In the neighborhood of room temperature in this specimen, a trapped hole has about one chance in ten of being retrapped when all the traps are empty; hence the final decay rate is about 10% longer than the initial decay rate when most of the traps are filled, and there is a small but detectable amount of multiple trapping in β traps.

Energy Level with Respect to the Conduction Band

The energy level of β traps with respect to the conduction band can be obtained by a comparison of the trap level and the Fermi level. This is most easily done with a specimen (such as 376D-2) which has a large trap density and a resistivity which places the Fermi level at room temperature close to the energy level of the β traps. Under these circumstances the sample shows an anomalous behavior of conductivity as a function of temperature. Such data are shown in Fig. 7, which is a plot of sample conductivity as a function of temperature for two conditions, (a) with the sample in equilibrium in the dark, and (b) with all of the β traps filled by illumination. The conductivity obtained with this sample in the dark (curve a) has two inflection points and is quite different from a sample containing relatively few β traps. These "normal" samples show dark conductivity in this temperature range which decreases contiuously as the temperature is increased, as does curve *b*. If essentially all of the impurity atoms are ionized, as is the case for these samples, the decrease in conductivity is caused by the decrease in electron mobility with increasing temperature. The data defining this upper curve, however, are values also attained with sample 376D-2, but with all of the β traps filled with holes produced by illumination, as described previously. From Fig. 7, the concentration, N, of normally empty β traps as a function of temperature shown is therefore given by $(\sigma_b-\sigma_a)/q\mu_-$.

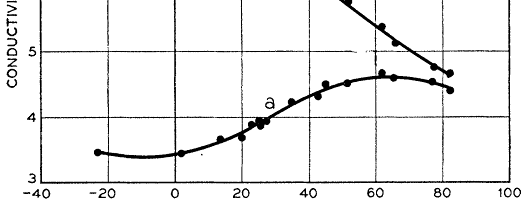

FIG. 7. Conductivity as a function of temperature for sample 376D-2 for two conditions; (a) with the sample in equilibrium in the dark and (b) with the β traps filled with photo-holes.

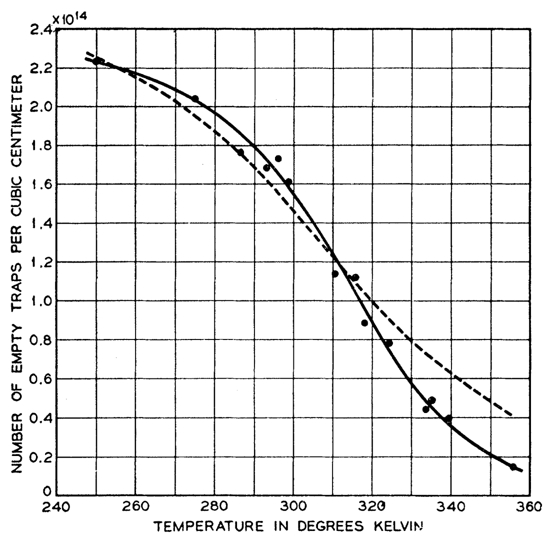

FIG. 8. Density of normally empty β traps as a function of temperature. The solid line is drawn through the experimental data. The dashed line is the expected variation of trap density with Fermi level change. See text for assumptions.

Values of N obtained in this way are shown as circles in Fig. 8 in which we have plotted the normally unfilled trap density as a function of absolute temperature.[14] The trap density may be seen to approach a maximum value of $\sim 2.4\times 10^{14}$ cm^{-3} at low temperature and to drop rapidly in the region of room temperature so that at slightly elevated temperatures (80°C) less than one tenth of the trapping centers remain normally unfilled with holes. This change of trap concentration with temperature is, of course, associated with movement of the Fermi level.

The dashed line in Fig. 8 is an approximate calculation of the variation with temperature of the equilibrium density of empty traps obtained by making use of two well known relations: (a) the Fermi-Dirac distribution which relates the fraction of empty traps to the difference between the Fermi level and the trap energy level, and (b) the relation between the position of the Fermi level and the sample conductivity, which is known experimentally (curve *a* of Fig. 7). In this calculation it was assumed that the product $(g_0/g_1)(m_e/m)^{\frac{3}{2}}=1$, where (g_0/g_1) is the ratio of the

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[13] At lower temperature this latter rate drops because of the decrease in S, and at higher temperature it drops because of the decrease in N.

[14] The values of μ used were obtained by assuming $\mu=1200$ cm^2/volt second at 295°K and $\mu=\text{constant } T^{-2.4}$ as given by the experimental points of curve *b* of Fig. 7 assuming that the number of carriers is constant. This temperature dependence is also in accord with the exponent -2.6 found for pure lattice scattering by F. J. Morin and J. P. Maita [Phys. Rev. **96**, 28 (1954)] with allowance for some impurity scattering.

statistical weight of the trap when it is empty to that when it is filled with a hole and (m_e/m) is the ratio of the effective mass of a conduction electron in n-type silicon to the mass of a free electron. It was assumed, further, that the temperature dependence of the trap energy level[15] was one half that of the total energy gap in silicon, i.e., that in electron volts $E_t(T)=E_t(0°\text{K})-2\times10^{-4}T$, where T is the absolute temperature, and that at 300°C, $E_t(T)=0.32$ ev below the conduction band.

The fit between the two curves, Fig. 8, is not as good as we expected, and we are unable to explain the discrepancy. The fit would be much worse if, instead of a single trapping level, we assumed a band of levels a few hundreds of an electron volt wide. More careful calculations[16] were made in which we assumed (a) the same temperature coefficient and mobility variation as above and (b) the "density of states" electron effective mass as computed from cyclotron resonance experiments,[17] and then looked for the best values of the unknown parameters for the two simple cases $(g_0/g_1)=\frac{1}{2}$ and $(g_0/g_1)=2$, corresponding to the traps being donor-like or acceptor-like, respectively. The donor case fitted better than the acceptor case, and yielded the following results: $E_t(0°\text{K})=0.35$ ev, N_0, the density of trapping centers $=2.6\times10^{14}$ cm^{-3}, and (N_D-N_A), the difference between the densities of "normal" donor and acceptor centers, $=1.1\times10^{14}$ cm^{-3}.

In any case, we believe the agreement between theory and experiment is close enough to warrant the conclusion that we are dealing with a single trap level and that its position relative to the conduction band is known with an uncertainty of only a few hundredths of an electron-volt.

Energy Level with Respect to the Valence Band

The energy level of the β traps with reference to the valence band can be determined by measurements as a function of temperature of the capture cross section and $1/\tau_g$, the rate of thermal release from the traps, and then invoking the principle of detailed balancing. Herring[18] has given a formulation of this principle which we shall employ, *viz.*,

$$1/\tau_g=16\pi m_h^*(kT)^2h^{-3}(g_0/g_1)S\exp[(E_v-E_t)/kT]. \quad (1)$$

Here the symbols are as previously defined with the additions that E_v is the energy at the top of the valence band and m_h^* is an effective mass for holes. Herring has pointed out to us that, strictly speaking, this formula is not applicable to our case because it does not take into account the facts that (1) the top of the valence band in silicon is degenerate, (2) the effective mass to be used at room temperature is different from that obtained from cyclotron resonance experiments because kT is the order of the energy associated with spin orbit splitting. He does not feel, however, that an appreciable error for our purposes will be incurred by ignoring these complications, setting $m_h^*(g_0/g_1)=1$, and employing experimental values of S and τ_g in Eq. (1).

This equation predicts that except for the T^2 effect a plot of $\ln 1/\tau_g$ *vs* $1/T$ should be a straight line. In Fig. 9, we have plotted as circles experimental values of $\ln 1/\tau$ *vs* $1/T$, where τ is the photoconductivity decay constant corrected for a small multiple trapping effect. The fact that these data do not lie on a straight line suggests that there is a loss mechanism from the trap in addition to thermal release to the valence band. A reasonable assumption here is that the additional loss mechanism is recombination of the trapped holes with conduction electrons. If $1/\tau_b$ is this recombination rate, then as in Part I,

$$1/\tau=1/\tau_g+1/\tau_b, \quad (2)$$

and we attempt to draw two straight lines the sum of which fits the experimental data. As shown in Fig. 9, this can be done, for the triangles which fall on a straight line were obtained by subtracting from the data the line having the lower slope. Either line might represent generation out of the trap. The line of lower slope, however, has an activation energy much too low to represent $1/\tau_g$, so we attribute it to $1/\tau_b$.

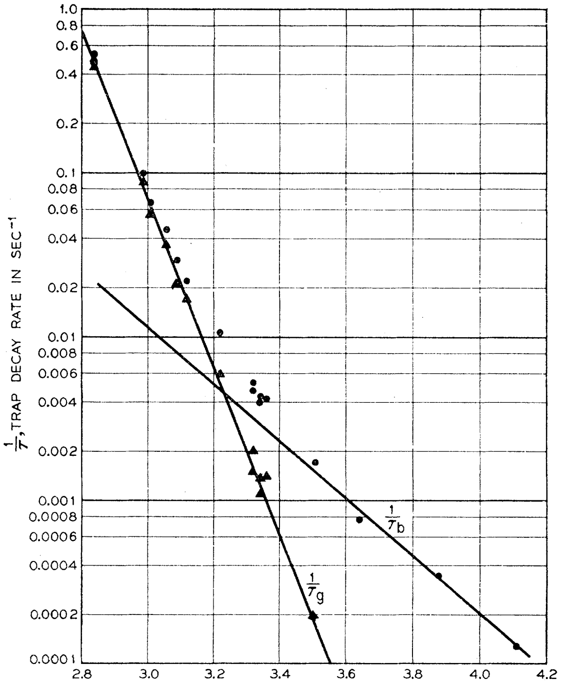

FIG. 9. Reciprocal of the time constant of decay of photoconductivity due to β traps as a function of reciprocal temperature. The data are shown by the open circles. The triangles are the result of subtracting the line of lower slope, labeled $1/\tau_b$, from the data.

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[15] We are indebted to Dr. C. Herring for discussions of this point.

[16] We are indebted to Dr. M. C. Gray for carrying out these computations.

[17] R. N. Dexter and B. Lax, Phys. Rev. **96**, 223 (1954).

[18] C. Herring, *Fundamental Formulas of Physics* edited by D. H. Menzel (Prentice Hall Publications, Inc., New York, 1955), p. 630.

We may now use the detailed balance equation to determine (E_v-E_t) in two different ways from the data: (1) from slope of the line $1/\tau_g$ *vs* $1/T$ (with corrections for the T^2 factor) and (2) from the measured values of S and τ_g at a given temperature. From the slope of the line we obtain the absolute zero difference $(E_v-E_t)=0.79$ ev after taking into account the 0.18 ev activation energy associated with S. Correcting this value to 300°K by using the temperature coefficient discussed earlier (2×10^{-4}), we obtain $(E_v-E_t)_{300°\text{K}}=0.72$ ev. From the measured values of τ_g and S at 300°K we also obtain $(E_v-E_t)_{300°\text{K}}=0.72$ ev, which is somewhat better agreement than we expect. Thus we conclude that the detailed balance principle applies in a consistent fashion to the data on the τ_g process, which gives us confidence in the results and their interpretation.

It should be noted, further, that these results together with the conductivity data predict an energy gap in silicon at 300°K of $(0.72+0.32)=1.04$ ev. This value lies within experimental error of that of 1.1 ev recently obtained by Morin and Maita.[19]

Recombination

The line of lower slope in Fig. 9, which we have attributed to recombination, empirically is of the form $1/\tau_b=\nu\exp-E/kT$. From the data, $\nu=2.2\times10^3$ sec^{-1} and the activation energy $E=0.35$ ev. From the low value of ν it is evident that the process is an improbable one.

More information on the recombination process may be obtained from measurements of decay time on a variety of specimens at room temperature. Since $1/\tau_g$ is known, $1/\tau_b$ can be obtained from $1/\tau$ by use of Eq. (2). The results of these measurements are shown in Fig. 10, in which we have plotted the rate $1/\tau_b$ as a function of the concentration of electrons in the conduction band.

The solid circles were obtained using different specimens while the triangles were all obtained with a single sample. The triangle at the lower left was measured with the sample before heat treatment. The other triangles from left to right were obtained after heating the sample at 460°C for 1, 4 and 10 hours, respectively. This heat treatment increased the majority carrier concentration by more than an order of magnitude while leaving the concentration of β trapping centers substantially constant. The line drawn has a slope of two so that, within experimental error, the recombination rate is found to be proportional to the square of the majority carrier concentration. This is the same dependence found for the recombination rate of electrons in deep traps in p-type silicon (see Sec. I). It must, therefore, represent some general fundamental process.

It has been suggested that this process is the inverse of an Auger-like process in which two slow electrons in the conduction band interact with one of the electrons ending up in the trap, i.e., recombining with a hole, and the other is speeded up, conserving energy.

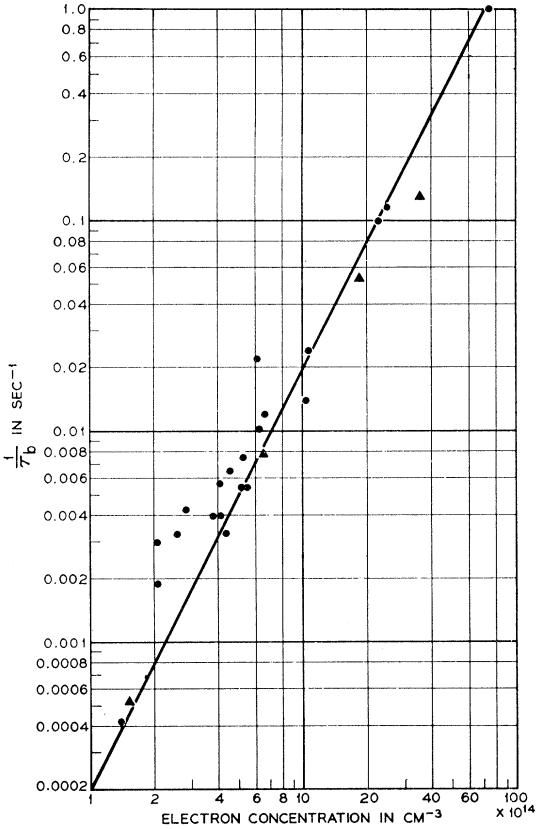

FIG. 10. Recombination rate for holes trapped in β traps as a function of majority carrier (electron) density.

The large spread in the points is to be expected since the carrier concentration was calculated from the average conductivity of the sample. Consideration shows that samples having a nonuniform conductivity will produce data which are shifted downward and to the right from those obtained using uniform specimens. A few data are not shown. These were obtained with samples having time constants nearly two orders of magnitude larger than expected. This large difference cannot be explained on the basis of nonuniform conductivity and it is, therefore, strong evidence for the presence of another deep trapping level (γ traps).

Factors Effecting Trap Density

Densities of α and β traps[20] usually lie in the range of 10^{13} to 10^{14} cm^{-3} for material grown by the method of Teal and Little (crystal rotated while grown) and are approximately two orders of magnitude less for crystals grown in the same way but without rotation. Samples having the lowest trap density are those produced by the floating zone crystal growing technique of Theuerer

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[19] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

[20] Most of the α-trap concentration data were obtained by R. G. Shulman.

and Whelan.[21] One such sample has a β-trap density $<2\times10^{8}$ cm^{-1}. Although samples having high β-trap density usually also have a large concentration of α traps, Shulman has found samples in which the α trap density was more than an order of magnitude less than our measured density of β traps.

The β traps are sensitive to heat treatment. A reduction in trap density of two orders of magnitude can be accomplished by heating a specimen to 800°C for a few seconds, and the original trap concentration can be restored by subsequent heating at 450°C for a few hours.[22]

We have not found it possible, however, to introduce these traps by either bombarding with high energy particles or by bending, twisting, or compressing the material. Neither has it been possible to produce them by adding chemical impurities although a large section of the periodic table has been tried.[23] Accordingly, we know nothing more concerning the origin of β traps than we do of α traps, or the deep and shallow traps found in p-type silicon discussed in Part I.

ACKNOWLEDGMENTS

It is a pleasure to thank many of our colleagues for advice and assistance during this investigation, particularly H. R. Moore, who aided with instrumentation, E. Buehler who furnished silicon crystals, C. Herring, G. H. Wannier, and P. A. Wolff who supplied many valubale discussions, R. G. Shulman for his measurements of α trap density, J. H. Wiley, who measured some of the time constants of β traps and W. C. Westphal who assisted us generally.

APPENDIX: APPROXIMATE FORMULAS FOR USE IN MEASURING CAPTURE CROSS SECTIONS

We are interested here in deriving simple, approximate formulae which may be used in determining the capture cross section S of the α and β traps. These derivations are based in part on the experimental conclusion that the rate of capture of holes in traps is small compared with their rate of capture in deathnium (normal recombination) centers.

We start with the equations of trapping kinetics for a single kind of center as given in the Appendix of Part I:

$$dp/dt=l-rp+gp_1-p(N-p_1)Sv, \tag{3}$$

$$dp_1/dt=-gp_1+p(N-p_1)Sv. \tag{4}$$

Here p = the excess density of holes in the valence band, p_1 = the excess density of holes in traps, $r\equiv1/\tau_r$ = rate of recombination of excess holes in the valence band, $g\equiv1/\tau_g$ = thermal rate of generation of holes from traps, S = cross section for capture of holes in traps, N = density of normally unfilled traps, v = thermal velocity, l = rate of generation of electron-hole pairs per cm^3 by external light, and NSv = rate of trapping of holes when all traps are empty.

Prior to $t=0$, let the specimen be in the dark and all traps empty (i.e., thermal equilibrium). For $t\geq0$ let a light shine on the specimen such that a constant number l of hole electron pairs is produced per cm^3 per sec. Near $t=0$, $p_1\ll N$, and if in addition $g\ll NSv$, then

$$\dot{p}\simeq l-(r+NSv)p, \tag{5}$$

$$\dot{p}_1\sim NSvp. \tag{6}$$

Integrating Eq. (5) gives

$$p\simeq[l/(r+NSv)][1-\exp(r+NSv)t]. \tag{7}$$

That is, in the order of time no longer than the recombination time $\tau_r=1/r$, the density of excess holes in the valence band increases to a value $p=l/(r+NSv)$. The final steady state value of p from Eqs. (1) is $p=l/r$. Thus if $r\gg NSv$, as is generally the case for n-type silicon, the density of holes in the valence band quickly rises essentially to its steady-state value and remains constant.

We have then from Eq. (6) that

$$\dot{p}_1\simeq NSvl/(r+NSv), \tag{8}$$

so that if we measure the initial slope of the change in conductivity with time milliseconds to seconds after the light is turned on, and before p_1 becomes appreciable compared to N, and also measure N, r, and l, then S can be gotten directly from Eq. (8):

$$S=r\dot{p}_1/Nv(l-\dot{p}_1).$$

If $r>NSv$ such that p does not change by more than say 10% after several lifetimes (τ_r), so that it may be known quite well, slightly more accurate values of S may be obtained by using Eqs. (3) and (4) rather than (5) and (6) for $\dot{p}_1$. For according to Eqs. (3) and (4), if p is constant, and we know that $l/(r+NSv)<p<l/r$,

$$\dot{p}_1\simeq NSvl/(r+NSv)-(g+pSv)p_1. \tag{9}$$

By keeping p_1 small so that it never exceeds a few percent of N, then the measurement of the initial slope $\dot{p}_1$ will give a reliable value of S unless g becomes large.[24] This can happen at high temperatures since g is increasing exponentially with T, e.g., $g\propto\exp(-8200/T)$. As long as NSv is still much smaller than r, so that p is essentially constant, we can correct for this g-effect by adding to the measured initial slope the negative of the slope of the decay curve (obtained after the light is turned off) for the same value of p_1, for this slope is

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[21] H. C. Theuerer and J. M. Whelan, Trans. A.I.M.E. (to be published). These data have also been independently derived and described by Keck, Emis, Müller, and others: P. H. Keck, Physica **20**, 1059 (1954); R. Emis, Z. Naturforsch. **9A**, 67 (1954); S. Müller, Z. Naturforsch. **9B**, 504 (1954).

[22] Hannay, Haynes, and Shulman, Phys. Rev. **96**, 833 (A) (1955).

[23] This work was done in collaboration with N. B. Hannay and E. Buehler.

[24] Both correction terms in Eq. (5), viz., $(g+pSv)p_1$ can be computed from the experimental data and applied if one desires.

just gp_1. This is shown schematically in the right hand position of Fig. 5. It was necessary to make this correction only at the highest temperature (62°C) at which the cross section of the β traps was measured.

For the α traps, it is not necessary to measure l and r independently in order to obtain S, for their ratio can be obtained directly from the oscillogram, Fig. 1, as described in the text.

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Precipitation of Copper in Germanium

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The density of dislocations is shown to have a marked effect on the rate of anneal of copper in germanium. At 500°C samples containing high dislocation density ($\sim 10^6/\text{cm}^2$) anneal in about 1 hour in contrast to material of low dislocation density ($\sim 10^4/\text{cm}^2$) which requires about 24 hours. When copper-doped germanium is cooled from a high temperature in regions of high dislocation density, significant precipitation occurs in a cooling cycle of only a few seconds. In this case, in order to prevent precipitation the sample must be quenched from the high temperature in a time of the order of 0.1 second.

INTRODUCTION

WHEN germanium is heated to high temperature without precaution to prevent chemical contamination, impurities diffuse into the crystal. Copper has an appreciable solubility and high diffusivity in germanium[1] and is generally the principal contaminant in most heating procedures. Copper is an acceptor in germanium with an energy level[2] 0.04 ev above the valence band and a higher energy level[3] near the center of the energy gap.

When germanium is heated at a given temperature in the presence of copper at equilibrium, the concentration of the solid solution is characteristic of the temperature only. Except for the temperature range near the melting point where retrograde solubility occurs,[4] the solubility increases with increasing temperature. Hence except for retrograde solubility effects, as soon as the temperature is lowered from this equilibrium temperature, the copper solution immediately becomes supersaturated; and the copper concentration, as inferred from resistivity measurements, will drop from the high-temperature value to that characteristic of the lower temperature. A study[1] of this annealing process with techniques using radioactive copper showed that the copper precipitated at various places in the crystal. The extent to which this copper precipitates depends mainly on the cooling cycle and the density of nucleation sites.

In the experiments reported here, it is shown that precipitation of copper is extremely rapid in regions of the crystal of high dislocation density ($\sim 10^6$ dislocations/cm^2). In such samples significant precipitation occurs in a few seconds, and in order to prevent precipitation the sample must be quenched from the high temperature in a time of the order of 0.1 second. In addition, complete annealing at 500°C will occur in about 1 hour in contrast to a time of about 24 hours in material of low dislocation density ($\sim 10^4$ dislocations/cm^2).

In these experiments, dislocations associated with plastic deformation are introduced into germanium by bending at high temperature. The copper solubility in these samples, determined from resistivity measurements, shows a marked dependence on the density of dislocations. In regions of high dislocation density ($\sim 10^6/\text{cm}^2$), the density of acceptors due to copper is much lower than in regions of low dislocation density ($\sim 10^4/\text{cm}^2$). This phenomenon gives rise to an apparent decrease in copper solubility (as inferred from resistivity measurements) in regions of high dislocation density.

EXPERIMENTAL PROCEDURE

In these experiments, rods of dimension 0.06 in.×0.1 in.×1.0 in. were cut from a single crystal of germanium which had a room temperature resistivity of about 0.8 ohm-cm, n-type. The rods were bent about the (111) crystal axis, without introducing chemical contamination, by a method devised by Pearson.[5] This method consists of (1) cleaning the rod,[6] (2) clamping it between molybdenum electrodes, (3) heating it by the joule heat developed by passing current through the rod, and (4) deforming the rod by bending at a high temperature (~800°C). The bent rods were then dipped in an

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[1] Fuller, Struthers, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).

[2] F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

[3] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).

[4] C. D. Thurmond and J. D. Struthers, J. Phys. Chem. **57**, 831 (1953).

[5] Pearson, Read, and Morin, Phys. Rev. **93**, 666 (1954).

[6] R. A. Logan, Phys. Rev. **91**, 757 (1953).

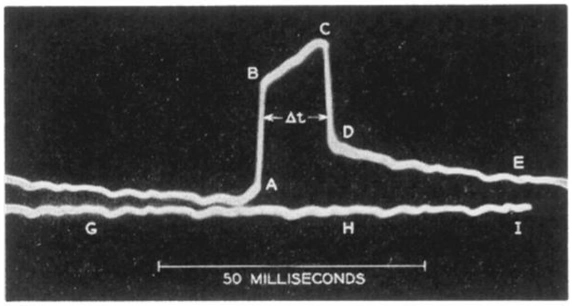

FIG. 1. Photograph of oscilloscope trace showing photoconductivity as a function of time. The sample was illuminated from A to C and the remainder of the time was in the dark. The conductivity difference from H to D was produced as a result of holes caught in α traps.

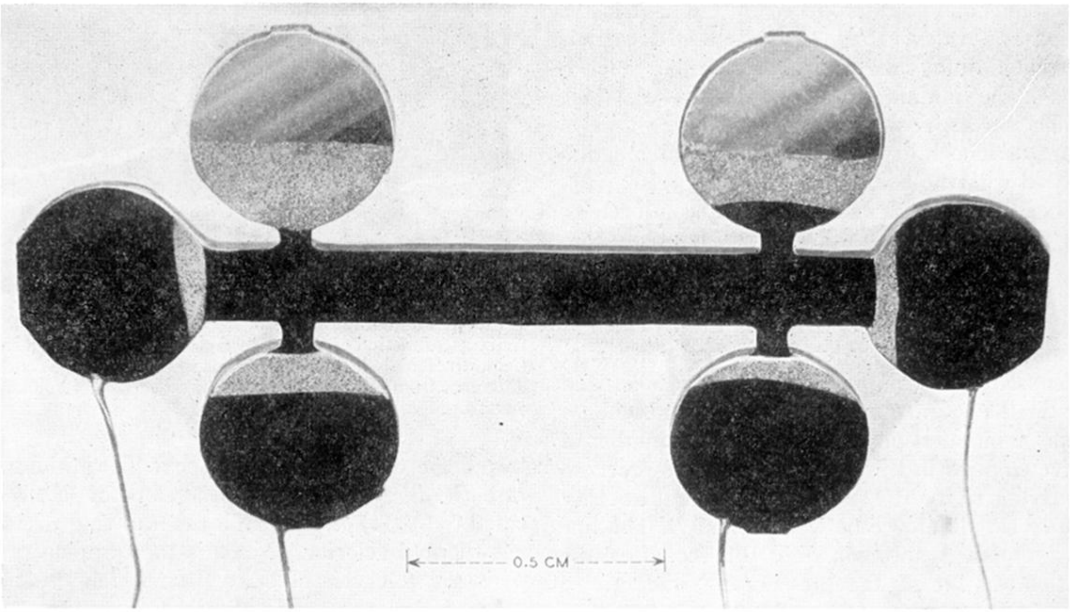

FIG. 2. Photograph of sample 376D-2. The etched surface of the silicon is visible in the central portion of the sample. The upper middle circular sections show the plated areas (top) and the sand blasted regions (bottom). The other four circular sections (with wires attached) are coated with black enamel.