of neutral and ionized centers were obtained from the Hall effect analysis. The total mobility was obtained simply from the sum of the reciprocals of the individual mobilities. The solid line of Fig. 8 shows the mobility (total) compared with the data. It appears that either the impurity concentrations obtained from the Hall analysis are not sufficient to account for the scattering at low temperatures, that our simplified application of impurity scattering theory to ZnO is too crude, or that μ_a/μ_0 is smaller than indicated in Fig. 8. Some justification for the latter alternative is illustrated in Fig. 10 where the same mobility analysis has been applied to two highly doped samples. The mobility is seen to drop at least qualitatively in agreement with the prediction of the impurity scattering theories. However, the concentration of donors in sample 52 is so high that the distance between ionized donors is less than the wavelength of a thermal electron, a situation which probably invalidates the present theory of impurity scattering. In the foregoing, no heed has been paid to the subtleties of the relation between the Hall and microscopic mobilities as the scattering mechanism changes with temperature, or to the errors inherent in summing the reciprocal mobilities obtained from different scattering mechanisms. It is felt that such refinements are as yet unwarranted in view of our present limited knowledge of the band structure of zinc oxide.

ACKNOWLEDGMENTS

The author is grateful to Dr. C. Herring and Dr. M. Lax for helpful discussions. Mr. George Foulds deserves special recognition for his able assistance in taking the data and for his patience and skill in assembling the apparatus and mounting the samples.

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Copper-Doped Germanium as a Model for High-Resistivity Photoconductors

P. J. van Heerden
General Electric Research Laboratory, Schenectady, New York

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In the electrical behavior of high-resistivity copper-doped germanium the nature of the electrodes plays an essential role. Three different types of space-charge contacts can be distinguished. For two types of contacts only primary photocurrents are observed, for the other both primary and secondary photocurrents. The secondary photocurrent is observed only in samples with the electrodes prepared in such a way that they show the space-charge-limited current. A simple theory on the magnitude of the secondary photocurrent is confirmed experimentally. Also, some observations are given on the space-charge-limited current and some experiments which throw light on the mechanism of electrical breakdown in this material.

1. INTRODUCTION

In a previous article[1] the author derived a condition under which primary photocurrents can be observed in photoconduction. This condition (already derived earlier by Ryvkin[2]) is that the time T required for a carrier to traverse the photoconductor is small with respect to the dielectric relaxation time ($\rho\epsilon$), so: $\beta\equiv T/\rho\epsilon\ll 1$. It was proposed then to study copper-doped germanium, because it would be possible in that material to vary the resistance in one sample, by varying the temperature, from a high resistance in which the above condition is satisfied to a resistance where β becomes of the order of or larger than unity. This should give the rise of the secondary photocurrent from an unobservably small value at liquid nitrogen temperature to a magnitude comparable to that of the primary photocurrent at room temperature. An investigation of copper-doped germanium has now been carried out and is reported in this paper. However, the experimental results changed the author's views somewhat and the experiments presented here are different therefore from the one he had originally in mind. The reason is the following: the original condition for the observation of the primary photocurrent was derived for an *ohmic* contact, defined as one in which the Fermi level in the electrode material is exactly equal to the one in the photoconductor. Since this is only a point in an infinite spectrum of possibilities, in which the Fermi level in the electrode material lies either higher or lower, this condition can in practice "hardly ever" be realized. Now many authors have used the term "ohmic contact" for contacts in which the Fermi level in the electrode material lies higher than the one in the photoconductor, so that free entry of electrons into the latter is possible. This terminology is correct for all practical purposes in the case of low-resistivity photoconductors like germanium and silicon at room temperature, since this contact leads to an "ohmic" current, that means a current obeying Ohm's law and determined by the resistivity of the photoconductor. However, in high-resistivity photoconductors (and "high resistivity" will

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[1] P. J. van Heerden, Phys. Rev. **106**, 468 (1957).

[2] S. M. Ryvkin, Doklady Akad. Nauk S.S.S.R. **106**, No. 2, 250 (1956).

be defined here as identical to $\beta<1$), this no longer holds true. In the case of the Fermi level in the electrode being higher than in the photoconductor, a space charge of electrons results in the material at the contact, and the current varies as the square of the applied voltage. This is the space-charge-limited current, which was first described theoretically by Mott and Gurney[3] and which only rather recently was observed, by Smith and Rose[4] in cadmium sulfide. For this reason, this kind of contact will always be called a "space-charge contact" or "n^+ contact" and the name "ohmic" contact will be reserved only for the theoretical case defined before.

Now the case in which a pure space-charge-limited current—proportional to the square of the voltage—flows in the material, is again a rather theoretical one, since the material has to be free of traps. In that theoretical case the condition for observing the primary photocurrent is no longer satisfied. Any positive space charge formed by the trapping of holes in the photoconductor will immediately be compensated by the electrons from the space-charge region. The primary photocurrent is equal to the secondary photocurrent and no experiment can separate them. However, Redington[5] has pointed out that if one defines $di/dV \equiv 1/R$, where i is the space-charge-limited current and V the voltage on the photoconductor, and subsequently calls RC the "dielectric relaxation time" of the sample, where C is the capacity, then this relaxation time is only one-half of the transit time. In other words, the material in this state no longer has a high resistivity from the experimental point of view.

This now is the key to a useful extension of the original definition of β. In our experiments on copper-doped germanium with space-charge contacts, $(di/dV)_{\mathrm{s.f.}} \equiv 1/R_{\mathrm{s.f.}}$ [$R_{\mathrm{s.f.}}$ is R-step function], defined as the initial change in current for a small step function in the bias voltage, was usually much smaller than one can expect for the space-charge-limited current, and much larger than one can expect from the resistivity of the material. But it is this quantity $R_{\mathrm{s.f.}}$ which should determine the initial secondary current Δj. Therefore, defining β, previously defined for pure ohmic contacts only, as $\beta \equiv T/R_{\mathrm{s.f.}}C$, one then has a natural extension of the original definition, and the relation between the secondary photocurrent Δj and the primary current j_p, $\Delta j = \beta j_p$ for $\beta<1$, holds for both ohmic and space-charge contacts. This is the reason why the originally proposed experiment was replaced by experiments tending to prove that this more general formula is valid.

It will be shown that in the behavior of a high-resistivity photoconductor the nature of the contacts plays an essential role. The statement in the previous paper[1] that the secondary current pulses from α particles observed in cadmium sulfide by Frerichs and Warminsky[6] could only be observed in low-resistivity material is no longer held to be true. They were observed by the author in high-resistivity germanium provided with the proper space-charge contacts.

2. PREPARATION OF THE SAMPLES

The photoconductors studied were round germanium disks about $2\frac{1}{2}$ cm in diameter and 1 mm thick. They were commercially available[7] in that form as about 4-ohm-cm n-type material. To give this material very high resistivity at liquid nitrogen temperature, they were doped by copper diffusion as described by Woodbury and Tyler.[8] First the Hall coefficient[9] R_L of the starting material was determined with the aid of four platinum wires soldered to the edge of the disk about 90 degrees apart.[10] An easy and quite satisfactory way for soldering on the leads in air is with the sample on a heating plate, using indium containing some arsenic as a solder and the ordinary red liquid flux.[11] This results in good n^+ contacts which can easily be removed with a knife without damaging the sample. The starting material always gave a Hall coefficient $R_L=1.49\times10^4$ cm^3/coul, indicating good uniformity of the material. This corresponds to an initial electron concentration of 4.9×10^{14}/cm^3. From this number can be calculated the temperature to which the sample has to be heated to obtain the desired degree of compensation. The graph given by Woodbury and Tyler[8] (Fig. 1) was used for this purpose and complete agreement with their results was found, except that corresponding results were obtained for a temperature lower by about 5°C. For instance, after diffusing in copper at a temperature of 605°C an $R_L=0.6\times10^4$ cm^3/coul was found (n-type) in a magnetic field of 1600 gauss. The time for heating the sample was always 20–24 hours and no indication of inhomogeneity of the samples was found.

The samples prepared were always studied as "sandwich cells," that means with the two electrodes covering the major part of the two flat sides of the disk. Essentially *three different types of space-charge contacts* were made, and these three different types lead to three different kinds of behavior of the samples, as will be described later.

The first type was made by diffusing arsenic into the surface simultaneously with the copper diffusion. From the data given by Saby and Dunlap[12] one can estimate

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[3] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), p. 170.

[4] R. W. Smith and A. Rose, Phys. Rev. **97**, 1531 (1955); see also M. A. Lampert, Phys. Rev. **103**, 1648 (1956).

[5] R. W. Redington (private communication).

[6] R. Frerichs and R. Warminsky, Naturwiss. **33**, 251 (1946); **33**, 281 (1946).

[7] Obtained from General Electric Semiconductor Products Department, Clyde, New York.

[8] H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 84 (1957).

[9] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 213.

[10] It should be noted here that the theory predicts that the resulting Hall coefficient is completely independent of the shape of the sample and the position of the leads as long as the sample is of uniform thickness.

[11] "Special X Soldering Flux," Industrial Service Laboratories, 710 West National Avenue, Milwaukee, Wisconsin.

[12] J. S. Saby and W. C. Dunlap, Phys. Rev. **90**, 630 (1953).

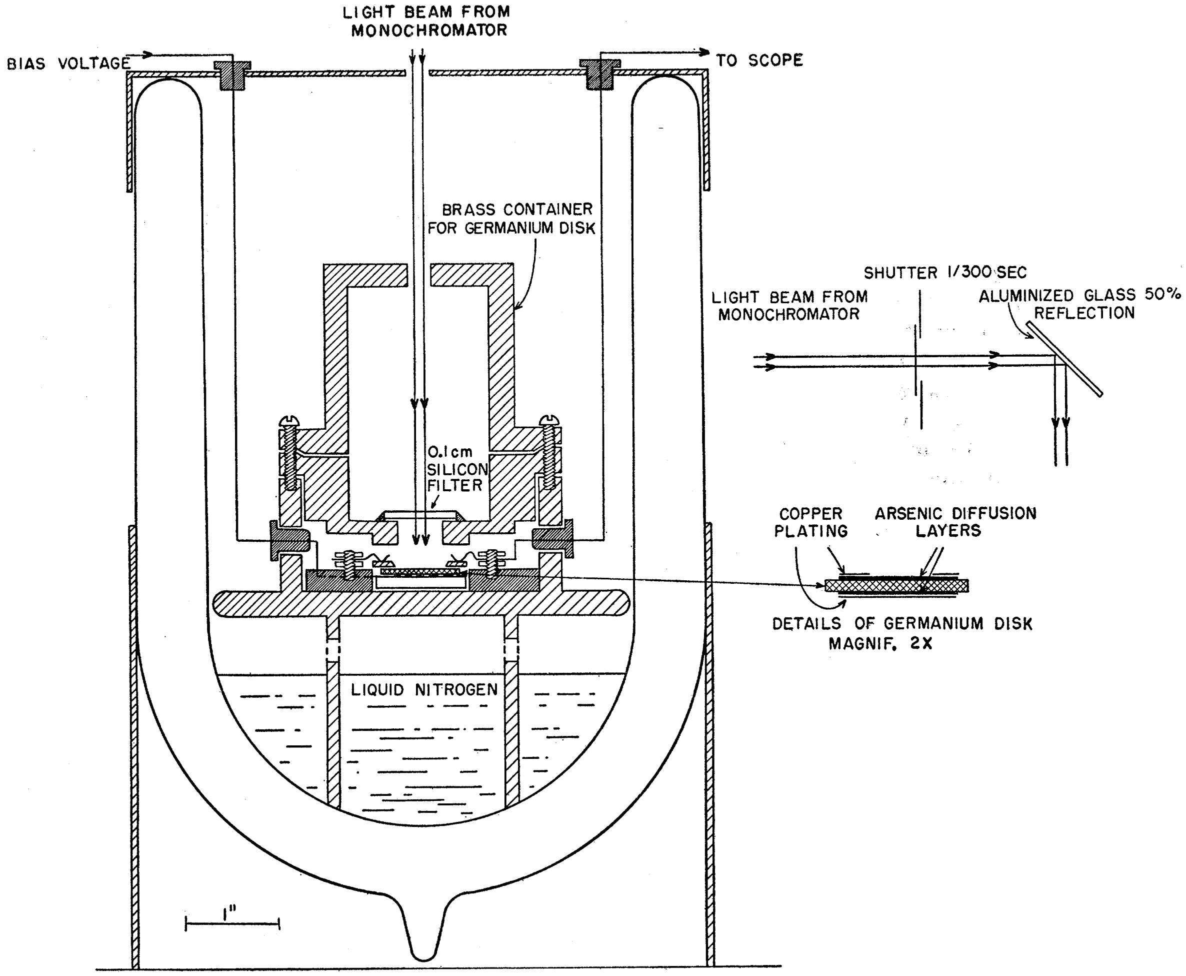

Fig. 1. Experimental arrangement for irradiation and dark-current observations.

that at about 600°C and for a time of 20–24 hours, the arsenic will diffuse in about 5 microns. This therefore will convert the surface layer into a low-resistivity *n*-type region, which will form the electrode for the high-resistivity material inside. When preparing these samples, the germanium disk was smoothed by hand-grinding with 260- and 600-mesh carborundum in water on a glass plate, etched with 80% nitric, 20% hydrofluoric acid, and rinsed in distilled water. It was then copper-plated in a solution of copper sulfate, sodium hydroxide, and sodium potassium tartrate,[13] rinsed in distilled water, and dried. The sample was then sealed in a quartz tube and the tube was baked out under vacuum at about 500°C, after which a few grains of arsenic were dropped in and the tube was filled with 20 cm of hydrogen and sealed off. The baking-out procedure was taken just as a precaution, but it is essential that the arsenic be of high purity,[14] since the use of arsenic of doubtful quality caused completely erratic results. The sealed-off quartz tube was then heated in an oven with the thermostat set at the desired temperature. The vapor pressure of the arsenic was determined by the coldest point in the tube, about 475°C, corresponding to 1.5 mm pressure. After 20–24 hours the sample was quenched by pushing the tube out of the oven into a room-temperature water bath. The sandwich cell was then prepared by removing the low-resistivity layer from the edge of the disk with emery paper. The whole sample was then copper-plated again, the two flat sides covered with ceresin wax to protect the copper, it was etched, the wax removed, and the sample was ready for use in the experiments (Fig. 1).

The second method of preparing the contact layer was like the first, except that the strongly *n*-type layer was removed from the flat sides by etching, leaving only a weakly *n*-type layer.

The third type of space-charge contact prepared may be called the "abrupt" *n*-type contact as contrasted to the two previously described "gradual" *n*-type contacts

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[13] S. F. Field and A. D. Weill, *Electroplating* (I. Pitman and Sons, London, 1951), p. 259.

[14] 99.99+% arsenic vacuum-sealed in Pyrex capsule, American Smelting and Refining Company, Research Department, South Plainfield, New Jersey.

obtained by diffusion. Now the material is copper-doped without the arsenic vapor present. This is simpler since it can be done in an open quartz tube closed with silicone rubber stoppers and in which a flow of say 0.5 cubic feet/hour of hydrogen is maintained. The sample is simply quenched by dropping it from the tube[8] on a piece of quartz wool (after having replaced the hydrogen with nitrogen to prevent explosion). The copper, which now looks grey in color due to alloying with germanium, is removed from the surface by nitric acid or the etching solution. A layer of very roughly 0.3 micron of arsenic and 3 micron of indium is then evaporated on one side of the sample in a vacuum bell jar (10^{-5} mm pressure). After that, the sample is heated in a hydrogen atmosphere to about 400°C. The originally grey-looking evaporated indium layer then acquires a shiny liquid-like appearance in melting and alloying itself with the germanium. The sample is then cooled off and copper-plated where desired. This method is essentially the same as the usual method of making a good n^+ soldered contact to n-type germanium, but by the evaporation process a thin layer is obtained which readily transmits infrared light and α particles. The formation of a space-charge contact in this process seems to happen in the following way[15]: When the sample is heated, the indium melts and starts to dissolve the arsenic and also some of the germanium, to form a solution. When the sample is cooled down again, the dissolved germanium crystallizes back out on the germanium crystal but retains an amount of arsenic larger than the amount of indium, thus forming a thin n-type layer. This layer forms necessarily an abrupt transition to the intrinsic material inside, since the temperature is too low to give an appreciable diffusion of arsenic.

3. THE EXPERIMENTS

The samples prepared as described were mounted in a brass box (Fig. 1) which was placed at the bottom of a Dewar vessel, a setup very much like the one used by the author in studying silver chloride.[16] All observations were made at liquid-nitrogen temperature. The oscilloscope and preamplifier for observation of current pulses were the same as used in the experiments on cadmium sulfide,[1] except that for many observations the model-50 preamplifier could be omitted. In this setup the current pulses were observed from polonium α particles, Co^{60} γ radiation, light flashes from a Perkin-Elmer monochromator equipped with a 1/300-second shutter, and simply voltage pulses on the crystal. The copper-doped germanium samples were either high-resistivity p- or n-type since no essential difference in behavior could be expected in this type of experiment, because the free-carrier concentration is negligibly small.

The samples with the first type space-charge contacts described above were by far the most interesting and showed the kind of behavior with which this investigation was mainly concerned. On the two other types of space-charge contacts only a few observations were made, by no means exhaustive, but enough to clarify their main features. They will be discussed first.

The sample with the *second type* contact, the weak space-charge contact, shows a resistance of about 10^{11} ohms. Three hundred volts can be put on the crystal without breakdown. No space-charge-limited current is observed. When the crystal is irradiated through the cathode with α particles, the current pulses are primary current pulses, as described in cadmium sulfide[1] and silver chloride.[16] The pulse height becomes saturated at about 20 volts. No current pulses are observed when the anode is bombarded, instead of the cathode, indicating motion of electrons only and not of holes. The small "schubweg" of holes can be understood from the studies of Woodbury and Tyler.[8] The polonium α-particle pulses have a rise time too short to be observed, for 45-volt bias, that means shorter than 0.04 μsec, as can be expected from the high mobility of the electrons. For $1\frac{1}{2}$-volt bias, however, the rise time is about one microsecond, which again agrees with a mobility of the order of 10^4 cm^2/volt sec. The pulse height is far from uniform, probably due to roughness of the surface, but the maximum pulse height corresponds to 10^6 electron-hole pairs formed, in agreement with observations by McKay.[17] When the sample is heated up from liquid nitrogen temperature, the α-particle pulses can be observed until a resistance of about 50 000 ohms is reached; the crystal then breaks down and a noisy current results. Essentially, the behavior is quite similar to that of a high-resistivity manganese-doped sample obtained from Tyler and equipped with evaporated-gold electrodes in a preliminary experiment. The difference, however, is that the sample with simple gold electrodes breaks down after receiving a relatively small dose of radiation, while the present sample can be irradiated indefinitely. The nature of this latter breakdown is not completely clear, but it is quite similar to the breakdown observed by the author in silver chloride[16] for an overdose of radiation. The breakdown current is very noisy and appears on the oscilloscope as if breakdowns are continuously taking place. This current was already reported on and studied by Lehfeldt.[18] Although this breakdown phenomenon is not understood, one can at least explain the absence of breakdown in the samples studied presently if one assumes that the breakdown is initiated by holes trapped very close to the cathode. This will gradually build up a field strong enough to cause electron emission, possibly field emission, from the cathode. In the present samples with diffused

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[15] R. N. Hall, General Electric Research Laboratory Report 1039, 1954 (unpublished).

[16] P. J. van Heerden, thesis, Utrecht, 1945 (unpublished); Physica **16**, 505 (1950); P. J. van Heerden and J. M. W. Milatz, Physica **16**, 517 (1950).

[17] K. G. McKay, Phys. Rev. **84**, 829 (1951).

[18] W. Lehfeldt, Göttingen Nachr. Fachgruppe II, **1**, 14, 171 (1935).

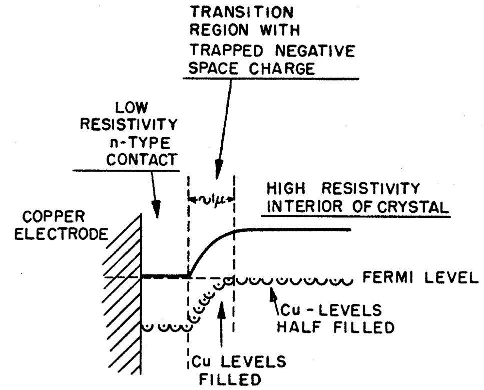

FIG. 2. The shape of the conduction band in an abrupt space-charge contact.

arsenic, the electrode is protected from breakdown by the weak *n*-type space charge in front of it, which will recombine with any trapped holes and thus prevent the build-up of a strong field. Further investigation is necessary to clarify this issue.

The third type of space-charge contact, the "abrupt" *n*-type layer, behaves very much like the second type described above. There is no space-charge-limited current and α particles cause primary current pulses. However, the crystal breaks down already at 10–100 volts, and the breakdown current then shows a regular noise very much like ordinary shot noise. How is it possible that this supposedly strongly *n*-type contact shows only primary photocurrent and no space-charge-limited current? When this was found, first the experimental procedure to make the contact was tested by making such a contact to low-resistivity *n*-type germanium. It then makes an excellent n^+ contact even at liquid nitrogen temperature. Then, in thinking about it, it becomes clear that this behavior on high-resistivity samples is quite understandable (Fig. 2). When no bias voltage is applied to the sample, the Fermi level in the interior is lined up with the (second or third) copper level, 0.3–0.4 ev below the conduction band, while in the space-charge region the Fermi level is close to the conduction band. In thermal equilibrium the Fermi levels are lined up, and this means that the conduction band is bending down in the transition region. But this brings the copper levels below the Fermi level, and consequently they are filled by electrons which have migrated from the space-charge region. It is clear that this gives rise to a strong trapped negative space charge, and the width of this barrier is determined by the concentration of originally empty copper levels, which is about $10^{14}/\text{cm}^3$. Calculation shows that a trapped space-charge region about two microns wide is required to establish the desired potential difference of 0.3 ev, and the corresponding field strength is 1500 volts/cm. It is this barrier which prevents the free electrons in the contact region from entering the crystal. A not too high bias field will not lower this barrier significantly. As Redington[19] has pointed out, this kind of contact behaves essentially as a pure ohmic contact for moderate bias voltages, since the concentration of carriers in the free space-charge region with energy high enough to overcome the trapped space-charge barrier is just equal to the carrier concentration in the interior of the crystal.

We come now to the observations on the first type of space-charge contact, the strong but gradual *n*-type contact made by diffusion of arsenic. This type of contact behaves completely differently from the ones already discussed, in that it shows large secondary current pulses for both α particles and light flashes, and gives a space-charge-limited current for pulsed voltages. For α particles irradiating the cathode, for instance, the charge pulses showed a long rise time, indicating currents continuing much longer than the transit time, and the total charge collected was over 1000 times what could be expected from a primary current only. No doubt this is the same kind of phenomenon as reported by Frerichs and Warminsky[6] in cadmium sulfide.

4. SPACE-CHARGE-LIMITED CURRENT

When a bias voltage of, say, 20 volts is suddenly put on the crystal in the absence of radiation, a strong current flows through it which decreases rapidly at first (Fig. 3) and continues to decrease over minutes to reach a value of the order of 10^{-8} amp. The strong initial current is due to the free space charge which is available at the cathode, and the decrease is due to trapping of electrons in the interior of the crystal, which sets up a polarizing field opposing the bias field, until an equilibrium is reached. Therefore this low stationary current is easily understood qualitatively, but hard to describe in exact terms, especially since different kinds of traps may be present. What should be simple, however, is the initial current, since it must be Mott's space-charge-limited current, as has been pointed out by Smith and Rose.[4] Consequently the initial current was measured, in our case simply by putting the voltage from a charged 2-μf condenser on the crystal by closing a mercury switch. The current was measured on the scope as the voltage across a 5-ohm resistance. The crystal was carefully shielded against radiation during the current measurement; however, a second current pulse a few seconds later is always negligibly small compared to the

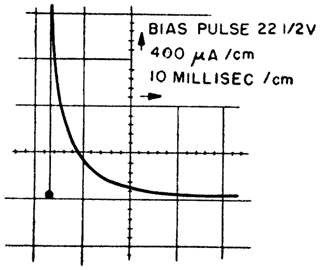

FIG. 3. The decay of the space-charge-limited current with time as observed on the oscilloscope.

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[19] R. W. Redington (private communication).

first one, indicating long depolarization times. To eliminate this, the crystal was irradiated after each measurement with weakly absorbed infrared radiation of about 1.6 microns. This neutralizes the polarizing field and makes the measurements reproducible. The initial current *versus* voltage curve is given in Fig. 4. Also shown in Fig. 4 is the current to be expected theoretically from Mott's square-law formula.[2,3] One observes that for sufficiently high voltages the experimental curve seems to approach the theoretical one, both in slope and in absolute magnitude. In trying to explain the deviation, one must take into account that there is still a potential hill to climb for the electrons in the free space charge to enter the crystal. If one assumes that there is a constant slope to this potential hill, then there is a constant field opposing the bias field, and this suggests as a first-order experimental correction the addition of a fixed voltage to every point of the theoretical curve. This is carried out in the figure for a value of 7 volts, representing the best experimental correction for bringing the theoretical curve close to the experimental one. Now one has to compare this experimental value with what one can expect theoretically from the slope of the barrier. An exact theory of the shape of this barrier is rather involved, but a rough estimate puts the length of the slope equal to one diffusion length, which is 5 microns, while the height is known to be about 0.3 ev. This results in a barrier field of $0.3/5\times10^{-4} = 600$ volts/cm. This rough theory therefore predicts a correction of 60 volts for the 1-mm thick sample, while, as said before, the best experimental fit is only 7 volts, a factor of 10 different. It was thought at first that this discrepancy might be explained by the illumination between two measurements. This will tend to break down the barrier. (This, by the way, is the reason that Smith and Rose needed a bias light during their observations of space-charge-limited current.) It may take a long time to rebuild this barrier, because of the extremely small trapping cross section of the negatively charged copper traps.[8] For that reason, some observations were made of the space-charge-limited current by waiting a long time after depolarization, while keeping the crystal carefully "in the dark." For a 20-volt bias pulse, for instance, the current pulse was reduced after 5 minutes waiting to one-third of the original value, but it did not seem to decrease after that. Therefore, one must conclude that, while there is this effect of breaking down and rebuilding the barrier, it is not large enough to explain the difference between the theory and the observations.

In Fig. 3 one can see that the current decreases in 1–2 milliseconds to less than half of its initial value. This cannot be due to the trapping in the copper levels, since, because of the small cross section of 10^{-23} cm^2, it would at least take 10 seconds to reach that value. Therefore, the traps which determine the initial current decrease must be different. They must lie above the copper levels, since they must be normally empty. Traps with a cross section of 10^{-16} cm^2, in a concentration of 10^{11} to 10^{12}/cm^3, would satisfy the requirements. The nature of these traps is unknown.

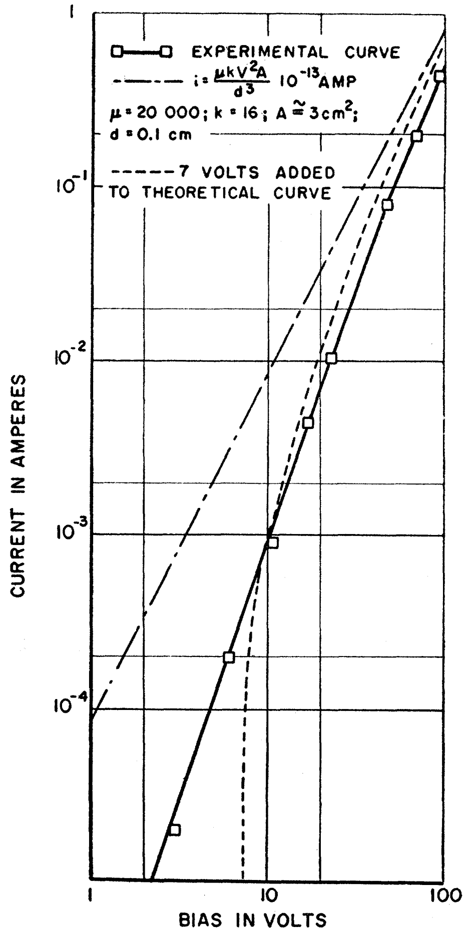

FIG. 4. Space-charge-limited current *versus* bias voltage for a crystal with diffused-arsenic contacts.

5. ELECTRICAL BREAKDOWN IN THE SAMPLES

When a voltage of 50 to 100 volts is put on the crystal, the sample breaks down. Huge currents are observed, which seem only to be limited by the external impedance of the circuit. For instance, for 300 volts bias 20 amperes are drawn through the crystal, while the external impedance was about 15 ohms. The breakdown phenomenon of these high-resistivity crystals was reported by Tyler[20] and can be understood only in terms of injection of minority carriers from the electrodes. These holes will get trapped in the interior, thus forcing more electrons to enter to maintain space-charge neutrality, and this lowers the resistance to a very low value. The surprise at first sight is that in our case the *n*-type contacts can inject holes. This can be explained, how-

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[20] W. W. Tyler, Phys. Rev. **96**, 226 (1954).

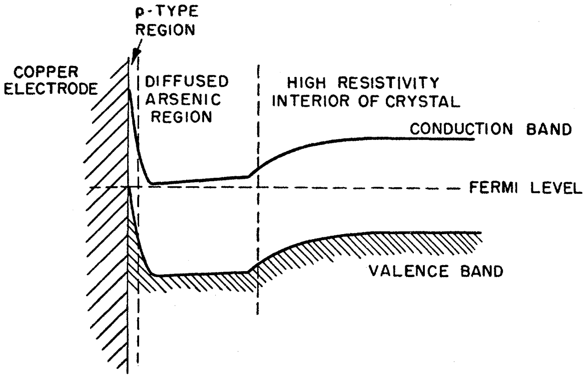

FIG. 5. The shape of the conduction band in a diffused-arsenic contact.

ever, in the following way (Fig. 5). The copper plating on top of the n-type layer actually forms a barrier-layer contact to n-type material, as was found by copper-plating a low-resistivity n-type germanium crystal. Consequently, the layer close to the copper, which may be as thin as 1000 A, is really p-type. When a voltage is put on the crystal, these free holes at the anode cannot escape into the interior of the crystal, since this is prevented by the steep potential hill that they would have to climb towards the n-type region. But as soon as the voltage is put on, the space-charge-limited current starts to flow from the cathode. The electrons in this current will reach the n-type region at the anode, but cannot go further owing to the steep barrier towards the p-type region mentioned before. They will therefore charge up the capacity of this layer until the field in this barrier is compensated. But then at the same time the path is free for the free holes to enter the crystal and start the breakdown. This hypothesis was rather nicely confirmed by observing the breakdown pulse more closely (Fig. 6). When a sudden bias voltage of 45 volts is put on the crystal, first the ordinary space-charge-limited current is observed to flow for, in this case, 30 microseconds. Then the current suddenly jumps to the breakdown-current value. The time during which the space-charge current flows is rather reproducible and decreases with increasing bias voltage, that is, with increasing space-charge current. This suggests that the total charge required to flow before breakdown is constant, indicating the charging up and breaking down of an originally insulating capacity. From the duration and magnitude of the space-charge-limited current the breakdown field in this capacity can be estimated, and the experiments indicate a value of 30 000 volts/cm required to break down this barrier between p- and n-type layers near the anode. This is too low to expect Zener emission or field ionization.

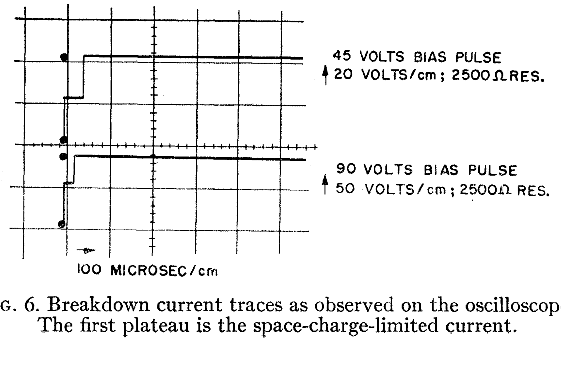

FIG. 6. Breakdown current traces as observed on the oscilloscope. The first plateau is the space-charge-limited current.

This delayed breakdown enables one to follow the space-charge-limited current into the region of breakdown. For 90 volts, however, the delay is only 3 microseconds and beyond that the delay was too short for the means of observation. The high breakdown voltage in the weak n-type contact, mentioned before, may be explained by the absence of the space-charge-limited current.

6. SECONDARY PHOTOCURRENT

The quantitative study of the secondary photocurrent was done with flashes of light, obtained with a 1/300-second shutter in the light beam from a Perkin-Elmer monochromator. Light of a wavelength around 1.58 microns was used, since it is rather weakly absorbed in the crystal. From the absorption curves of Dash and Newman[21] one finds that 30% of the light is absorbed. The crystal was irradiated through the top electrode (Fig. 1), where a 1-cm^2 area of the copper plating was removed. The difference in the primary and secondary photocurrent is well demonstrated in Fig. 7. It can be expected that for very small bias voltages on the crystal the bias field is not able to overcome the barrier in front of the space charge. In that case only a primary current is observed, which flows only during the opening of the shutter. The first part of Fig. 7 gives the reproduction of such a pulse. The second part is a reproduction of a pulse given only 10 seconds later, while in between the barrier has been broken down by shining light on the crystal. This is the secondary photocurrent.

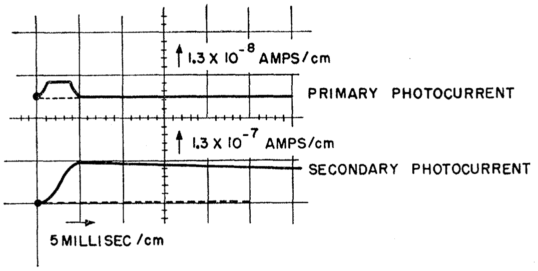

FIG. 7. A primary and a secondary photocurrent pulse, as observed on oscilloscope. The pulses are from light flashes of equal size. The secondary current pulse was obtained after shining in light for a few seconds to break down the barrier at the cathode. The primary current has quantum efficiency of about $\frac{1}{2}$, as it should have for weakly absorbed light.

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[21] W. C. Dash and R. Newman, General Electric Research Laboratory Report 55-RL-1320 (unpublished).

Here the current continues to rise during the time the shutter is open, and flows for a considerable time after that. As will be discussed later, the quantity β defined in the introduction is still very small with respect to unity. This may cause the question to arise as to how then the secondary photocurrent can be larger than the primary, as it obviously is in the figure, while the theory demands that it be smaller by a ratio β. The answer is that the theoretical derivation was given for a δ function of irradiation, or at least an irradiation time smaller than the transit time. In this experiment the exposure time is 1/300 second, and therefore the secondary current is the integral over many δ functions of radiation given successively.

In Fig. 8 a reproduction is given of a secondary photocurrent pulse. It is seen that the current decays with a time constant of one second, and the decay must be due partly to the increased polarization of the crystal by trapping of electrons and partly to recombination of trapped holes. We are interested here only in the initial value. In Fig. 9 a graph is given of the initial secondary photocurrent *versus* the intensity of the light. It is observed that for low intensities the dependence of the current on light intensity becomes practically linear. This should be expected: for very low light intensity the effect of every absorbed light quantum is independent of that of the others. Therefore, in this linear region, one may with some confidence divide the current pulse by the number of light quanta absorbed and so obtain the effect of the "average single light quantum."

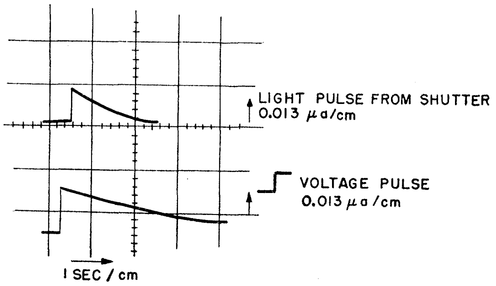

FIG. 8. The decay in time of the secondary photocurrent and of the current caused by a voltage step-function.

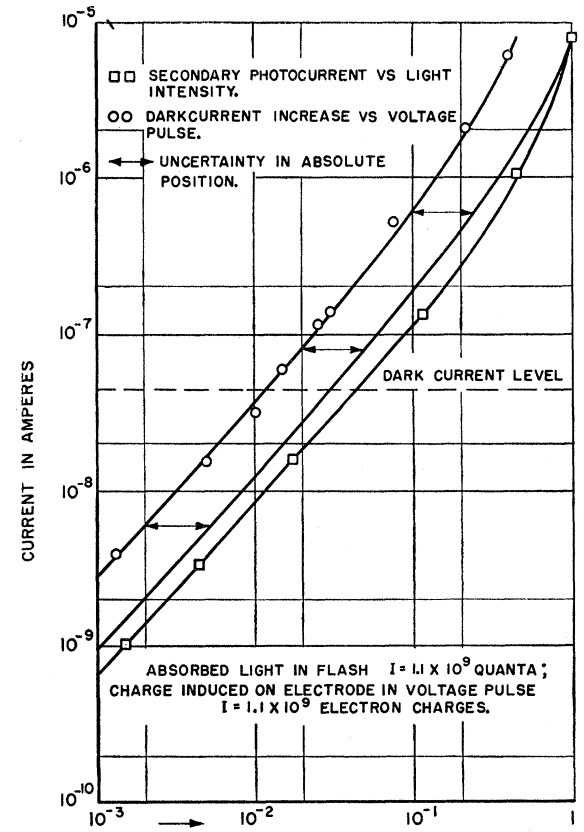

FIG. 9. The secondary photocurrent *versus* light intensity and the current due to a voltage step-function. The abscissas are made to coincide where the trapped positive charge caused by the light pulse is equal to the charge on the electrode in the voltage pulse. There is an experimental uncertainty of a factor of 3 in the active area of the crystal in the voltage-pulse experiments.

Now, to explain the results of Fig. 9, one has to apply the theory of the magnitude of the secondary current as mentioned in the introduction. It is felt that it is a reasonable assumption, even if the crystal is obviously polarized by the negative trapped space charge, that every electron that is drawn out of the cathode layer will reach the anode with a very high probability. Consequently, in considering the secondary photocurrent, just as in the simple ohmic case discussed in the previous paper,[1] the rise in field at the cathode caused by the trapped holes is the simple cause of this current. Only in this case one cannot say *a priori* how much current will result from a certain increase in field at the cathode. One cannot take the dc "resistivity" (voltage divided by current) as a measure, as in the pure ohmic case, nor can one take the pure space-charge-limited current, since one does not even know what the initial field at the cathode is. The thing to do, therefore, is to measure the effect of a small field increase at the cathode experimentally by superimposing a small voltage step-function on the bias voltage and measure the current increase (Fig. 8). In that case our simple theory predicts that if the total extra charge put on the anode in the voltage step-function is equal to the total trapped charge in the light flash, the initial current increase should be the same. This statement needs a slight correction, in that since in weakly absorbed light the average hole is trapped halfway through the crystal, the effect is also one-half of an equal charge on the anode. (See the derivation in reference 1.) This is experimentally checked in Fig. 9, where the result of the voltage step-function experiment is plotted together with the secondary photocurrent experiments. The abscissas are made to coincide for equal charge, so that the theory predicts that the voltage step-function curve lies a factor of 2 higher. There is an uncertainty of about a factor of 3 in the active part of the crystal capacity, and therefore no exact quantitative agreement can be claimed; but on looking at the figure it seems that the evidence is strong enough not to make one doubt what one could expect in the first place: that the secondary photocurrent is caused by the field generated by the trapped holes.

It should be remarked that $[(di/dV)_{\mathrm{s.f.}}=1/R_{\mathrm{s.f.}}]$, the initial change in current for a step-function obtained from Fig. 9, can be much larger than the "dc conductivity" calculated as: $i/V=1/R_{\mathrm{dc}}$. In this case, $R_{\mathrm{s.f.}}=5.8\times10^6$ ohms, while $R_{\mathrm{dc}}=2.4\times10^8$ ohms, a ratio of 40.

The quantity β, defined by the extension of the original definition as discussed in the introduction: $\beta=T/R_{\mathrm{s.f.}}C$, comes out to be about 10^{-4} (since $R_{\mathrm{s.f.}}=5.8\times10^6$ ohms, $C\cong64$ $\mu\mu$f, $T\cong5\times10^{-8}$ second), and therefore it is still small with respect to unity. It was not stressed enough in the first paper[1] that even if β is small, and therefore the secondary current small with respect to the primary, still the quantum efficiency, or gain as it is called by Rose,[22] may be considerable, provided the decay time of the secondary current is long. However, instead of this gain being equal to the ratio of trapping time of the holes to the transit time of an electron, as in the case of low-resistivity photoconduction ($\beta\gg1$), in the case considered here ($\beta\ll1$), the gain is equal to the ratio of the duration of secondary currents to the time ($R_{\mathrm{s.f.}}C$). In the measurements of Fig. 9, for instance ($R_{\mathrm{s.f.}}=5.8\times10^6$ ohms, $C=64$ $\mu\mu$f, duration of secondary current$=1$ second), the gain is about 3000.

Finally, the author wants to mention the difference which seems to exist between his viewpoint and that expressed by Rose.[20] In his paper, Rose rather severely criticizes the applicability of the concept of primary and secondary current to photoconductors. The author's viewpoint, on the other hand, is that primary and secondary photocurrent are the basic concepts by which the photocurrent can be analyzed and that his experiments tend to demonstrate this. It seems likely that this difference of opinion is not basic. Rose in his paper deals with photoconductors where space-charge neutrality is maintained ($\beta\gg1$) and specifically excludes from his discussion the case where this no longer holds ($\beta\ll1$) (reference 22, page 7, last paragraph). The case $\beta\ll1$ is just the one with which this paper is concerned and for which these concepts were originally developed by Pohl. There is another difference. The primary photocurrent, whether observed in the original experiments by Pohl and his school with light, or in the later crystal-counter experiments with corpuscular radiation, was always essentially the initial response to a pulse of radiation. It is in pulse experiments that a sharp distinction between the basic concepts becomes possible, as Rose himself has demonstrated for the space-charge-limited current. The stationary photocurrent is quite a different matter. It is a very complicated phenomenon, the general explanation of which can be attempted only after the response to pulses (step-functions or δ functions) is understood.

7. CONCLUSION

It is shown in this paper that in the electrical behavior of high-resistivity copper-doped germanium the nature of the electrodes plays an essential role. The primary and secondary photocurrent can be sharply distinguished experimentally and form the basic concepts for an explanation of the photocurrent. The secondary photocurrent can be quantitatively expressed in terms of the primary photocurrent and the variation of the dark current with a voltage step-function. It is believed that the study of this particular photoconductor has an application to high-resistivity photoconduction in general. Also, observations are given on the space-charge-limited current and some light is thrown on the mechanism of electrical breakdown.

ACKNOWLEDGMENTS

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[22] A. Rose, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954* (John Wiley and Sons, Inc., New York, 1956).