Hole Trapping in Germanium Bombarded by High-Energy Electrons

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On the basis of an investigation of n-type germanium bombarded with high-energy electrons, it is herein concluded that a particular set of temporary hole traps is created by the bombardment. The bombardment centers which remained in the samples at room temperature were measured by resistivity changes and found to agree with the densities of traps. Different samples with trap densities varying from 5×10^{12}/cc to 5×10^{14}/cc were studied.

An analysis of the trapping kinetics, essentially similar to those previously reported by Haynes and Hornbeck and by Fan, permits the energy of the traps to be determined as 0.28 ev above the valence band while the cross section for capture is 6×10^{-15} cm^2 at 200°K.

INTRODUCTION

MOBILE charges in a nonmetallic solid may be temporarily immobilized when captured by trapping centers. Trapping centers have been known to exist for some time in alkali halides.[1] Haynes and Hornbeck[2] have recently demonstrated minority carrier trapping effects in silicon at room temperature and have indicated the presence of traps in germanium at low temperatures. Fan[3] and his co-workers have reported finding traps in germanium in the vicinity of dry ice temperature. Here we present a detailed study of the origin and properties of a particular set of traps in n-type germanium introduced by high-energy electron bombardment.

The trapping reaction is shown in Fig. 1. We shall confine our discussion to hole trapping in order to conform to our experiments. Energies in this figure and the following discussion will be electron energies. Of course, a similar formulation applies to electron traps. The hole trapping process is the capture by the trap of a hole from the valence band. The rate of capture will depend upon the rate constant for trapping k_1, as well as upon the populations of the various levels. The rate constant k_1 for trapping holes can be expressed as a product of the cross section for capture σ times the thermal velocity of the holes, or $k_1=\sigma v$. Corresponding to this capture process, holes are liberated to the valence band with a characteristic rate constant k_2. The equation for the time rate of change of trapped holes, P_t, is

$$\partial P_t/\partial t=k_1p(N_t-P_t)-k_2P_t, \tag{1}$$

where p is density of holes in valence band and N_t the total density of traps which are assumed to be located at one energy ϵ_t. While k_1 and k_2 designate the trapping process in Fig. 1, the wavy arrow describes a Shockley-Read type recombination process which comprises a parallel path for the minority carriers. Through these localized electronic energy states, called recombination centers, holes and electrons annihilate each other. For the present, recombination and trapping will be considered as separate processes.

THEORY

In our experiments minority carriers are injected by a pulse of light and the time-dependent photoconductivity measured. An analysis of a simple trapping event is presented in Appendix A where Eq. (1) is solved with appropriate boundary conditions. It is assumed that an injected minority carrier, after being trapped once and released, subsequently recombines. In other words, the analysis ignores multiple trapping where carriers are trapped and released more than once before recombining. Since the experiments indicated multiple trapping, it will be shown in the text how these formulas for the simple trapping case may be used to interpret multiple trapping.

The solutions of Eq. (1) are

$$k_1=\frac{1}{p_1}\left[\frac{1}{\tau_0}-\frac{1}{\tau_g}\right]=\sigma v, \tag{2-a}$$

$$k_2=1/\tau_g, \tag{2-b}$$

$$\frac{P_t^{\infty}N_v}{p_1(N_t-P_t^{\infty})}=e^{(\epsilon_t-\epsilon_v)/kT}, \tag{2-c}$$

$$N_v\sigma v\tau_g=e^{(\epsilon_t-\epsilon_v)/kT}, \tag{2-d}$$

where P_t^{∞} is the steady-state density of trapped holes when p_1 mobile holes are maintained by the light source, ϵ_v the energy at the edge of the valence band, N_v the effective density of states, τ_0 the time constant of hole capture, and τ_g the time constant of release.

Haynes and Hornbeck[2] have described multiple trap-

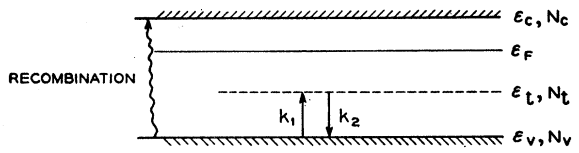

FIG. 1. Energy level schematic for single trapping process.

[1] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), second edition, p. 128.
[2] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953); J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).
[3] H. Y. Fan, Phys. Rev. **92**, 1424 (1953).

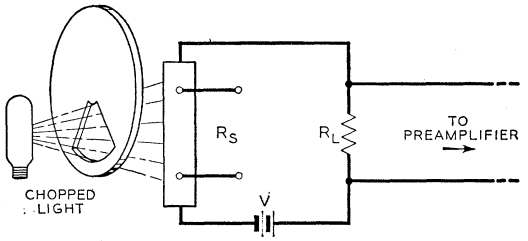

FIG. 2. Circuit diagram of apparatus used to detect photoconductivity.

ping as well as the simple trapping discussed here. Multiple trapping will decay rapidly at first approaching an exponential decay after a time long compared to the reciprocal of the initial rate of decay. At these long times they have shown that

$$\tau_\infty \cong \tau_r \tau_g / \tau_t = \tau_r N_t \sigma v \tau_g, \tag{3}$$

where τ_∞ is the measured exponential decay time, τ_r the recombination time, and τ_g the release time from the traps described in Eq. (2) and actually observed in simple trapping. The mean time that a hole spends in the valence band before it is trapped is τ_t, where $\tau_t = 1/N_t \sigma v$. Therefore, in order to know the value of $\tau_g \sigma v$ required in Eq. (2-d), one measures instead the more convenient ratio of τ_∞/τ_r and uses the equations already presented for the simple trapping case. Equation (3) can be interpreted rather simply. It says that, with τ_r as the recombination time and τ_t as the time of trapping, on the average each hole will be trapped τ_r/τ_t times before recombining. Furthermore, each of these τ_r/τ_t trapping events will have a decay time of τ_g so that the observed decay time will be as indicated. It is also clear that changing the relative values of τ_r and τ_t can alter τ_∞. From this we see that although the decay time of photoconductivity is probably the most apparent property of a trap, it is not an intrinsic property of the trapping center and the temperature. The two intrinsic properties of trapping centers are their cross sections for capture and their energies. It is noteworthy that trapping measurements furnish information about two independent properties of the imperfection acting as a trap, whereas most measurements which have previously been used to identify imperfections measure only the energy. The errors in measuring energies are larger for levels near the center of the forbidden gap in both Hall measurements and optical measurements. The errors in measuring energies from trapping experiments, however, are independent of the position of the trap in the gap. In this manner electronic energy levels near the center of the gap are determined more accurately from trapping experiments, when conducive to measurements of this sort. Bearing in mind, then, the potential advantages of trapping measurements for understanding and identifying deep-lying localized electronic levels over the methods previously employed, we turn to the experimental results on traps caused by bombardment.

EXPERIMENTAL METHOD

Measurements of trap densities and properties were made by observing the time-dependent photoconductivity of germanium rods and bridges. Figure 2 is a schematic diagram of the apparatus. When germanium rods were used as samples, designated by R_s, the photoconductivity was transmitted to the amplifiers by measuring the voltage drop across a matching load resistor R_L. When bridges were used, in order to eliminate transient contact effects, R_L was increased so as to provide a constant current and the voltage measured across the bridge arms. For transient effects in the range 10^{-6} to 10^{-2} second a Tektronix model 121 A preamplifier was used in conjunction with a Tekronix 514 A oscilloscope. This combination contributed only a negligible distortion for exponential time constants between 10^{-3} and 10^{-6} second. For time constants larger than 10^{-3} second a correction was applied to compensate for amplifier distortion.

A typical oscilloscope pattern is shown in Fig. 3. When the light is turned on, the mobile-hole density increases to p_1 in a time of the order of a recombination time. It is maintained at that steady-state value until the light is removed. These additional concentrations of holes and neutralizing electrons cause the conductivity of the sample to increase at the same rapid rate to a value $\Delta\sigma_1 = q\mu_p p_1(1+b)$, where b is the ratio of electron mobility to hole mobility. The nonequilibrium density of holes increases the net trapping rate and holes begin to fill the traps. The rate of filling can be changed by adjusting the light intensity and thereby increasing or decreasing p_1. Trapped holes are immobile and cannot contribute to the conductivity. However, the additional electrons required to neutralize the trapped holes will contribute to the conductivity and their effect is noted in Fig. 3 as $\Delta\sigma_t$. The relation $\Delta\sigma_t = q\mu_n P_t^\infty$ enables one to calculate P_t^∞. When the light is turned off, the concentration of trapped holes decays from its steady-state value to its equilibrium value of P_t^0. The conductivity decreases at the same rate. Depending upon whether or not the system shows multiple trapping, this decay time will be determined by the trap properties as shown in Eqs. (2) or (3).

The experiments have had two objectives: first, to ascertain in what manner the trap densities are determined by the amount of room temperature bombardment; second, to measure the properties of the traps.

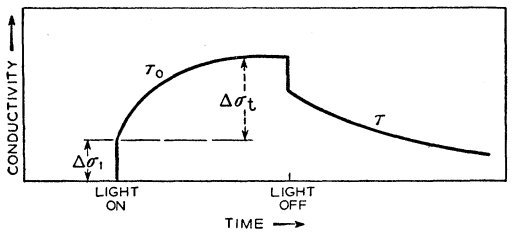

FIG. 3. Typical oscilloscope pattern illustrating trapping.

All bombarded samples were kindly supplied by W. L. Brown and R. C. Fletcher of these Laboratories. They had been bombarded in the Massachusetts Institute of Technology Van de Graaff accelerator through the cooperation of K. A. Wright. Bombarding electron energies were 3 Mev. All samples were bombarded at room temperatures and most were kept at room temperatures until they were studied. Some had been heated at 100°C for ten minutes. It is necessary to emphasize the past history of the samples because Brown and Fletcher[4] have recently observed trapping effects in bombarded germanium which are removed by annealing above −140°C. The trapping centers discussed here are stable at temperatures somewhat above room temperature.

Table I compares trap densities with densities of acceptors introduced by bombardment for eleven different samples. The densities of bombardment acceptors are based upon earlier resistivity measurements by Brown and Fletcher of a cross section for acceptor formation. Densities of acceptors listed in the table are calculated from these experimentally determined cross sections and from the integrated electron flux. The trap densities in bombarded samples were consistently many times higher than in the unbombarded. Although the agreement between trap densities and acceptor densities is not quantitative, it is striking enough to permit the reasonable hypothesis that the traps are formed by the bombardment.

Samples were alternately etched and sandblasted in an attempt to see if these differences in surface condition would affect the traps. The only effects noticed could be accounted for by the change of lifetime. This indicated that the trapping was a volume phenomenon.

EXPERIMENTAL RESULTS—DETERMINATION OF $(\epsilon_t-\epsilon_v)$

Intensive measurements were made of the trap properties in sample 91 *A*. This sample showed multiple trapping. The decay of photoconductivity was not a single exponential. Additional confirmation that the trapping was multiple will be found below in the measured and computed values of τ_t and τ_r. In order to use Haynes and Hornbeck's solution where $\tau_\infty/\tau_r = N_t\sigma v\tau_g$, we plot $1/\tau_\infty$ *vs* $1/T$ in Fig. 4. The solid points are experimental results while the open circles represent these values after a correction for the measured amplifier response time has been applied. In addition to the values of τ_∞, it was also necessary to measure τ_r which varied smoothly from 5.5 μsec at 170°K to 8 μsec at 225°K. These values of τ_r have been incorporated in the formulas where necessary. Equation (2-d) shows that both the absolute value of $N_t\sigma v\tau_g$ at any temperature and its temperature dependence may be used to calculate $\epsilon_t-\epsilon_v$. For the temperature range 180°K to 220°K, we find from the slope that $(\epsilon_t-\epsilon_v)$ = 0.25 ev, while the absolute values yield $\epsilon_t-\epsilon_v=0.30$ ev. These measurements were made on a rod and confirmed by measurements across bridge arms soldered to the sample. In this fashion transient contact effects were eliminated as the cause of these observations.

TABLE I. Density of traps (N_t) compared with density of bombardment centers.

Sample	ρ ohm-cm after bombardment	N_B density of bombardment acceptors at 300°K	N_t density of traps before bombardment	N_t density of traps after bombardment	
95*B*	18.1	5×10^{12}	$<4\times10^{11}$	5×10^{12}	
94*B*	18.6	5×10^{12}	3×10^{11}	3×10^{12}	
51*B*	4.7	5×10^{12}	9×10^{11}	1×10^{12}	
54*B*	4.0	5×10^{12}	3×10^{11}	3×10^{12}	bars
33*B*	2.3	5×10^{12}	9×10^{11}	2×10^{12}	
34*A*	3.5	4×10^{14}		5×10^{13}	
35*A*	3.5	4×10^{14}		5×10^{13}	
91*A*	22.2	5×10^{13}		3×10^{13}	
A-20	1.5	1.5×10^{15}		3×10^{14}	
A-23	3.0	5×10^{14}		7×10^{13}	bridges
A-24	3.2	5×10^{14}		9×10^{13}	

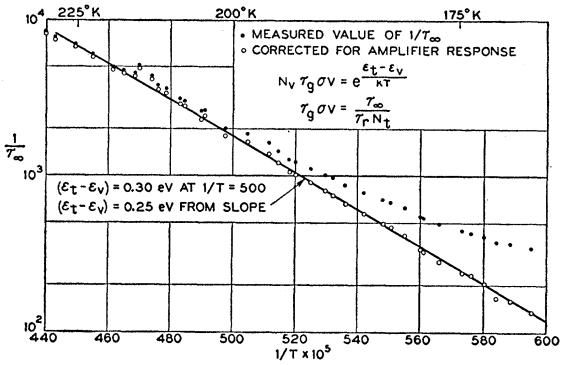

FIG. 4. Inverse of final decay time $1/\tau_\infty$ plotted *versus* $1/T$.

DETERMINATION OF CAPTURE CROSS SECTION

When the light intensity and temperature are adjusted for any particular sample so that $\tau_0 \ll \tau_g$ then Eq. (2-a) reduces to $\sigma v = 1/\tau_0 p_1$. This permits the direct measurement of σv which is presented in Fig. 5 for sample 91 *A*. There seems to be a small temperature dependence of the cross section of the order of 0.05 ev. As mentioned above the absolute value of the cross section combined with the value of N_t will determine τ_t through the relation $\tau_t = 1/N_t\sigma v$. For sample 91 A, $N_t = 3\times10^{13}$ and at 169°K, $\sigma v = 4\times10^{-8}$, hence $\tau_t = 0.8$ μsec. Since the measured value of τ_r was 5.5 μsec at this temperature, carriers will be trapped approximately seven times before they recombine. From Fig. 4 the τ_∞ at $T = 169$°K is seen to be about 5500 μsec. For these values of τ_∞, τ_t, and τ_r we can calculate that τ_g should be about 800 μsec. Now τ_g can also be measured directly. If the decay is measured immediately after a very strong light is turned off, one measures the time constant of a system where nearly all the traps are still

[4] Brown, Fletcher, and Wright, Phys. Rev. **96**, 834(A) (1954).

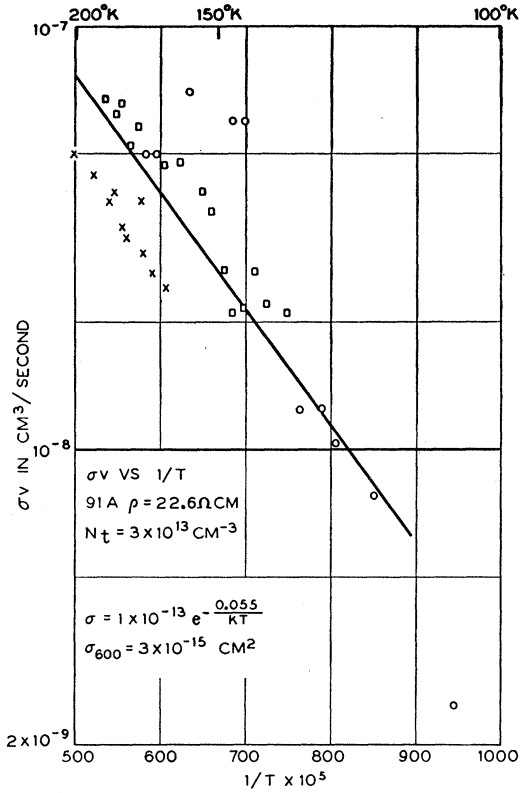

FIG. 5. Product of cross section, σ, and thermal velocity v plotted *versus* $1/T$. The value of v is about 10^7 cm/sec in this temperature range.

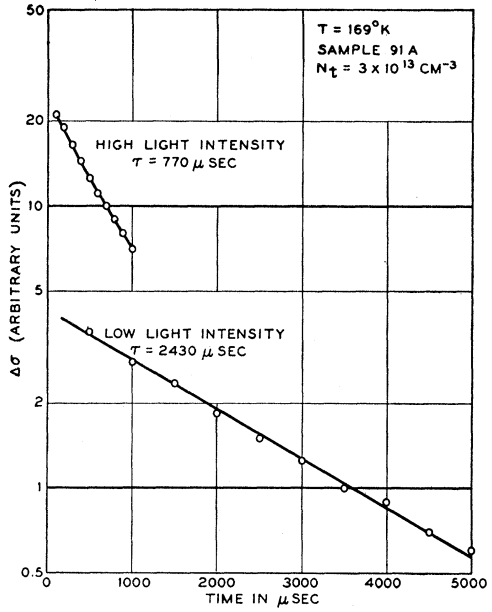

FIG. 6. Plot showing dependence of decay time upon light intensity. The upper curve, showing a decay of 770 μsec, illustrates a case where all traps are essentially still filled and multiple trapping cannot occur. The lower curve results from traps essentially empty, allowing multiple trapping.

filled with holes. Therefore the probability that a hole will be trapped again after it is liberated is small and the holes, once liberated, will recombine. The time constant of the first part of the decay curve is then equal to the liberation time τ_θ. Figure 6 shows the decay in photoconductivity for sample 91 A at $T=169$°K under the two conditions of strong chopped light which essentially fills all the traps and weak chopped light which fills a negligible fraction of them. The strong light decay curve is 770 μsec in excellent agreement with the preceding calculations while the weak light gives a decay time of 2430 μsec. When this latter decay time is corrected for the response time of the amplifiers one obtains the aforementioned value of 5500 μsec. Therefore the trapping picture presented is confirmed by this additional self-consistency of the results.

ACKNOWLEDGMENTS

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APPENDIX A

It is assumed that the traps do not affect the valence band hole concentration which, when the light is on, is determined by

$$dp/dt = l - r(p - p_0),$$

where l is rate of generation of hole electron pairs by the light and p_0 is the equilibrium density of mobile holes. With the light on, the hole density rapidly (in the order of the recombination time) reaches a steady state value $p - p_0 = l/r$, and in the same time after the light is off it reaches the equilibrium value p_0. The first solution then is for the light-on case.

Here the mobile hole concentration is maintained at an arbitrary value $p = p_1$. The solution of Eq. (1), subject to the initial condition that $P_t = P_t^0$ at $t=0$, is

$$P_t = \frac{k_1 p_1 N_t}{k_1 p_1 + k_2} + \left(P_t^0 - \frac{k_1 p_1 N_t}{k_1 p_1 + k_2} \right) e^{-(k_2 + k_1 p_1)t}.$$

The steady-state density of trapped holes is then $P_t^\infty = k_1 p_1 N_t/(k_1 p_1 + p_2)$, and the time constant of trapping is $\tau_0 = 1/(k_1 p_1 + k_2)$.

When the light is turned off, $p = p_0$. Once again Eq. (1) is solved, using this time the initial condition that $P_t = P_t^\infty$ at $t=0$. (Here $t=0$ now refers to the moment the light is extinguished.) The time constant for the decay of $(P_t - P_t^0)$ is $\tau_\theta = 1/(k_1 p_0 + k_2)$.

In addition, the principle of detailed balance at equilibrium supplies another relation among the variables and introduces the trap energy. At equilibrium,

$dP_t/dt=0$ and Eq. (1) becomes

$$k_1 p_0(N_t-P_t^0)=k_2 P_t, \qquad \text{(A-6)}$$

where

$$p_0=N_v e^{-(\epsilon_F-\epsilon_v)/kT}$$

and $(N_t-P_t^0)=N_t[1-e^{-(\epsilon_F-\epsilon_t)/kT}]$. In this equation, $N_v=(2\pi mkT/h^2)^{\frac{3}{2}}$, and it is the effective density of states at the edge of the valence band. Furthermore, it is assumed that ϵ_t is far enough below ϵ_F, the Fermi level, to validate the Boltzmann approximation. By assuming $(p_1-p_0)\cong p_1$, these equations can be rearranged to give Eq. (2).

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Copper in Germanium: Recombination Center and Trapping Center

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The time-dependent photoconductivity of copper-doped *n*-type and *p*-type germanium bridges has been measured between 130°K and 293°K. Temporary hole traps were found in the *n*-type samples at the lower temperatures but no traps were observed in the *p* type. Trap concentrations agreed with the density of copper atoms to within a factor of two and were at least 100 times higher than undoped crystals. The trappings levels are 0.2 ev above the valence band; the capture cross section for holes, σ_p, is 10^{-16} cm^{-2} and independent of temperature while the capture cross section for electrons, σ_n, is temperature-dependent with an activation energy greater than 0.1 ev. As a result of this temperature dependence of σ_n, the 0.2-ev copper level changes from a recombination center at room temperature to a hole trap at lower temperatures.

INTRODUCTION

INJECTED minority carriers in semiconductors have been shown to interact with localized centers whose electronic energy levels lie in the forbidden gap. The kinetics of these reactions have been discussed by several authors under the two classifications of recombination[1] and trapping.[2,3] While it has been convenient for experimental and theoretical reasons to separate these processes, it has also been realized that both are closely related. In this paper, we shall present measurements of hole trapping by the 0.2-ev copper level in *n*-type germanium at low temperatures. Since this level has been shown to act as a recombination center in germanium at room temperature,[4] it will be necessary to examine the relation between recombination and trapping. In general, the results may be anticipated by considering the system represented in Fig. 1.

Recombination centers are represented by triangles within the forbidden gap and trapping centers by squares. The arrows representing transitions to both bands from the recombination centers indicate that electron and hole capture and release rates are important. In other words, an electron or hole in a recombination center has ready access to either band. An electron or hole, after capture, attracts a carrier of the opposite type resulting in a mutual annihilation. If either of the rate constants becomes very small compared to the other, a recombination center will become a trapping center. We have found that the 0.2-ev copper level changes from a recombination center at room temperature to a trapping center at low temperatures, presumably because the rate of electron capture (or hole release to the conduction band) decreases with temperature. This means the probability that a trapped hole will attract an electron is decreased and that the hole usually remains in the center until it is thermally excited back to the valence band.

DETERMINATION OF TRAPPING CENTER PROPERTIES

The trapping center properties were found to be qualitatively similar to those of the bombardment traps[5] described in the previous paper. Experimental techniques were identical with those described in reference 5. In brief, we measured the time dependence of the photoconductivity. Chopped white light was used to illuminate germanium bridges and the conductivity was measured across noncurrent carrying arms.[6] A Tektronix 514 oscilloscope and 121 pre-

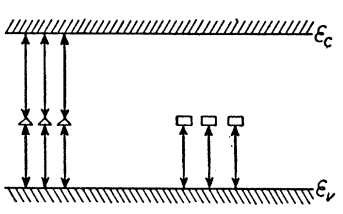

FIG. 1. Schematic energy level diagram. The arrows on the left indicate that recombination centers can capture holes from valence and conduction bands and that captured holes may be released to either band. The arrows on the right indicate that trapping centers interchange holes only with the valence band.

[1] W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).
[2] J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953); J. A. Hornbeck and J. R. Haynes, Phys. Rev. **97**, 311 (1955).
[3] H. Y. Fan, Phys. Rev. **92**, 1424 (1953).
[4] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 102 (1953).
[5] R. G. Shulman, preceding paper [Phys. Rev. **102**, 1451 (1956)].
[6] At low temperatures extreme care is necessary to prevent interference from transient photoresponses arising at the contacts. All our samples were bridges with gold-antimony bonded contacts which at low temperatures were more often ohmic than any other contacts we tried.