hypothesis that the electrical conduction in n-CdTe is due to electrons in the conduction band characterized by a spherical constant energy surface with the energy minimum at $k=0$.

The data on the resistance and Hall coefficient as a function of hydrostatic pressure up to (1.2×10^{10} dyn/cm^2) indicate additional complications in the conduction band. Our results are inclusive about this additional mechanism responsible for inhibiting the electrical conduction in n-CdTe at higher pressures. The observed instability in the data (especially at 195°K) above 8.5×10^9 dyn/cm^2 and hysteresis in R and R_H versus pressure data at 300°K could not be attributed to any structural defects in our samples.[27]

ACKNOWLEDGMENTS

The authors wish to thank Dr. B. Segall for his very thorough and critical review of this work, and Dr. P. R. Emtage, Dr. M. Pollak and Dr. R. C. Miller for many useful discussions on this work.

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Photo-Hall Effect in Anthracene

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The Hall mobility for photogenerated carriers has been measured in anthracene crystals in the temperature range from −40 to 60°C. Two-carrier effects were found to dominate, so that only lower limits could be calculated for the mobility. Near room temperature, the Hall mobility exceeds 50 cm^{2}V^{-1}sec^{-1} for electrons and 30 cm^{2}V^{-1}sec^{-1} for holes, compared with values close to 1 cm^{2}V^{-1}sec^{-1} measured for the drift mobility. The most likely explanation for this difference is a change in transport properties with illumination level. The existence of the anomalous Hall effect predicted by LeBlanc and Friedman could not be verified.

INTRODUCTION

THIS paper describes the measurement of the Hall mobility μ_H for photogenerated electrons and holes in anthracene crystals. Anthracene, which can be considered a prototype material for investigation of the charge-transfer mechanism in organic crystals, has been the subject of extensive experimental and theoretical studies in recent years. In particular, the drift mobility μ_D has been measured by several investigators[1–4] yielding values for both holes and electrons of the order of 1 cm^{2}V^{-1}sec^{-1}. It is now believed that conduction in anthracene can be described by band theory[5–7] rather than by tunneling through intermolecular barriers[8,9] or by a thermally activated hopping process. Band-structure calculations using the tight-binding approximation[5,10] have yielded bandwidths for excess electrons and holes of approximately 0.02 eV, which is compatible with the low measured values of μ_D. It has been predicted that these narrow bands would result in the measured values of μ_H being anomalously large in magnitude and reversed in sign for the temperature range $kT>0.1\ W$ where W is the bandwidth.[7,11] It has been suggested by LeBlanc[11] that an experimental determination of μ_H/μ_D as function of temperature might offer a test of the narrow-band theory. The present measurements were undertaken for this purpose. Because of two-carrier effects, it was not possible to perform this test. However, it was established that the Hall mobilities for both electrons and holes are at least of the order of 50 cm^{2}V^{-1}sec^{-1}. These values are large not only with respect to μ_D, but also compared at the values of μ_H predicted by the theory of the anomalous effect.

EXPERIMENTAL PROCEDURE

Some of the problems encountered in performing Hall-effect measurements in very resistive materials have been discussed in a previous paper,[12] which also describes the electrometer bridge used in the present experiments. Our measurements are an extension of conventional dc techniques; as shown below, the carriers are photogenerated in the anthracene and not injected at the contacts.

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The samples were cut from single-crystal boules melt-grown from synthetic anthracene (Eastman H-480) which had been treated by chromatography and repeated zone refining. Plates a few mm thick were obtained by cleaving along the *ab* plane or by sawing in a plane normal to the *ab* plane. The plates were then etched in benzene and rinsed in acetone until microscopic examination under polarized light showed a minimum of surface defects. Measurements attempted on unetched surfaces yielded very low values for μ_H. In experiments where the carriers are created close to the surface, these defects also generate a spurious signal to the Hall probes, proportional to B^2, which may be much larger than the Hall voltage.[13]

The geometry of the experiment is shown in Fig. 1. The electrode structure consists of thin lines of Se–Te alloy (40% Te by weight) applied by vacuum evaporation. The calculation of μ_H for this electrode geometry, whose use was dictated by the high resistivity and fragility of the crystals, is discussed in the Appendix. The crystal surface was illuminated by a 200-W point-source Hg arc through a $H_2O\cdot CuCl_2$ filter, giving an incident flux of $J=5\times10^{17}$ quanta/cm^2 sec in the spectral region 3500 to 4500 Å. It was found that fluctuations in the illumination level constituted a major source of noise in the Hall signal; the lamp was therefore fed from a constant-current regulator of stability better than 1%. In this experiment, the mobility is measured in a thin layer parallel to the surface. Since the maximum potential applied to the current electrodes is 48 V, space-charge-limited currents do not play a role in these measurements.

The Se–Te alloy was selected as electrode material because of ease of application and because, under the intense illumination used, it furnishes carriers freely to the anthracene. The Ohmic character of these contacts is demonstrated by the experiment of Fig. 2, where four parallel electrodes, 0.2 mm wide and separated by 1.2 mm, were deposited on the crystal surface. The figure shows the potential distribution in the sample for three temperatures. There is no evidence of a potential drop at the current electrodes, and the potential distribution remains unchanged after passing currents of the order of 10^{-10} A for 1 h. The same result was obtained upon reversing the current direction. None of the samples used for the Hall measurements showed evidence of polarization at the current contacts under illumination.

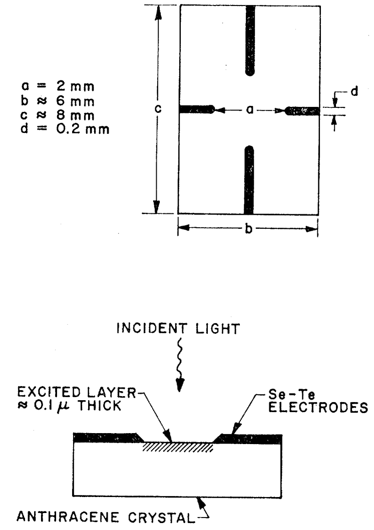
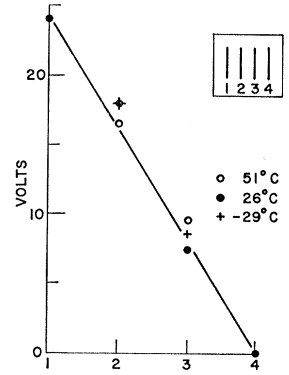


FIG. 1. Geometry of the experiment.

FIG. 2. Potential distribution under illumination in a crystal having four parallel electrodes of Se-Te alloy. There is no appreciable potential drop at the current electrodes 1 and 4. The current level is approximately 10^{-10} A.



All measurements except one were performed with the crystal in a He atmosphere. The effects of adsorbed oxygen on the surface photoconductivity of anthracene are well known.[14–17] Upon illumination in He, most of the surface oxygen is desorbed; a small part, however, is permanently bound in the form of anthraquinone. Since anthraquinone is highly insulating and not photoconducting,[16] one would expect it to be electrically inert and to affect the measured mobility perhaps only through changes in the band bending at the interface or roughening of the interface. As shown below, no first-order changes in the magnitude of μ_H were detected when a layer of anthraquinone was intentionally grown on the illuminated surface. After the crystals were irradiated for a few hours in He at room temperature, they became coated with a translucent white substance. The photocurrent and mobility were also found to decrease slowly with time. The surface coating was identified by D. L. Ross of this laboratory as an anthracene polymer, linked at the 9-10 carbon atoms. It is apparently produced under intense illumination in an inert atmosphere, but not in the presence of oxygen. The deterioration of the surface proceeds rapidly above 70°C, which set the upper limit to the temperature range of these measurements. The lower limit of about −40°C was determined by the increasing resistivity of the crystal upon cooling. In these experiments, there-

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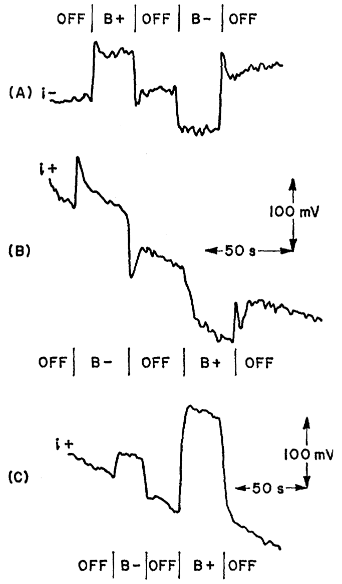

Fig. 3. (A) Tracing of n-type signal showing reversal with direction of magnetic field; (B) same measurement performed after reversing current direction; (C) effect of surface inhomogeneities, resulting in a spurious signal proportional to B^2 superimposed on a p-type Hall effect.

fore, the crystals were illuminated only during the time actually needed to perform a measurement.

EXPERIMENTAL RESULTS

In Fig. 3, curves (A) and (B) are tracings of a typical set of measurements taken on a crystal showing n-type conductivity. The Hall voltage shows the proper behavior under reversal of current direction and magnetic field. The identification of the measured signal as a Hall effect is completed by the curves of Fig. 4 showing the linearity of the signal with magnetic field for two crystals exhibiting, respectively, n and p conductivity. In all cases, the Hall voltage was computed by averaging for the two directions of magnetic field. In some cases, where the noise level was higher than in Figs. 3(A) and 3(B) a graphical integration was performed. Fig. 3(C) illustrates the effect commonly found in the presence of surface defects, with a spurious signal proportional to B^2 superimposed on a p-type Hall signal. In this case, the desired Hall voltage is half the difference between the two peaks. Since this spurious signal can also be caused by local variations in mobility, the type of trace obtained will often vary with light intensity or temperature of the sample.

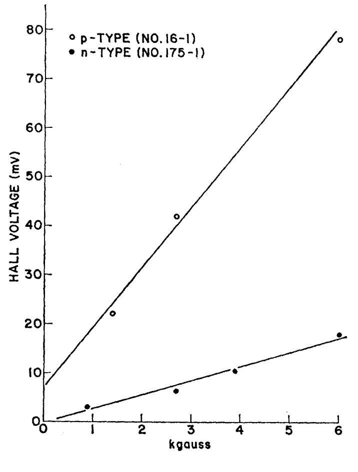

Fig. 4. Dependence of Hall voltage on magnetic-field strength.

It was found that all crystals showed a strong dependence of mobility on illumination level. This is illustrated by the curves of Fig. 5, taken at constant temperature, showing the change of conductivity type from n to p as the photocurrent increases. The transition between the two maxima takes place over a change in the photocurrent of a factor of 3. The decreases in μ_H at both ends of the current range suggest that other reversals of the conductivity type may take place at current levels not accessible to our apparatus. Thus, the mobility can be studied for the p and n modes separately on the same crystal by suitable adjustment of the light level.

Figures 6 and 7 show the dependence of μ_H on temperature, in both conductivity modes, for two crystals, cut, respectively, parallel and normal to the ab plane. These curves were taken at constant light level. Their most salient feature is the magnitude of μ_H which exceeds 60 cm^{2}V^{-1}sec^{-1} at one point. There is a considerable variation of μ_H with temperature, and it is important to note that for both crystals the n- and p-type curves are essentially parallel to each other, i.e., where μ_H increases for holes it decreases for electrons and vice versa. The behavior of the p-type curve in Fig. 6 suggests that a change of sign with temperature may take place above 70°C. Such a change of sign at constant light level was actually observed at 20°C for another crystal in which the highest measured values of μ_H were considerably lower than those presented above (<5 cm^{2}V^{-1}sec^{-1}).

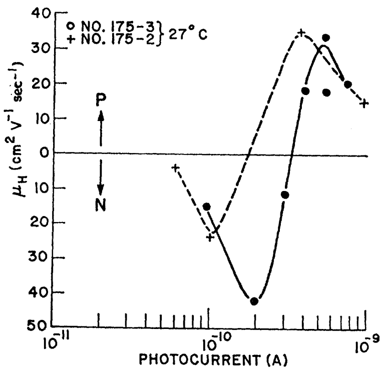

Fig. 5. Dependence of Hall mobility on illumination level at constant temperature.

The photocurrent showed an exponential dependence on temperature with activation energies $0.11 \leqslant E \leqslant 0.16$ eV/kT depending on the crystal and the illumination level. No systematic differences could be found in E for curves taken in the p and n modes on the same crystal. The photocurrents i_l were measured as function of the light intensity J over a range of three decades, including the light level where the photoconductivity type changes sign. A relation of the form $i_l \propto J^n$, where $0.91 \leqslant n \leqslant 1$, was found in agreement with previous reports of a nearly linear dependence.[1,18]

The influence of surface oxygen was studied on one crystal which showed a reversible increase in photocurrent by a factor of 2 upon exposure to oxygen. Figure 8 shows the dependence of μ_H on photocurrent taken in He and also in O_2 after allowing a heavy layer of anthraquinone to form. While the mobilities for this crystal are somewhat less than for those of Figs. 6 and 7, no essential difference is found between the curves in O_2 and He, as discussed above. The shift in the current level at the point where the conductivity changes from n to p is probably due to a change in the lifetime of one of the carriers.

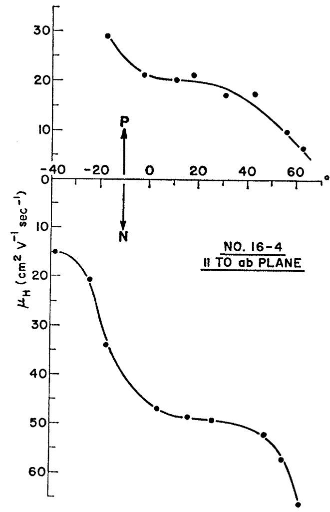

FIG. 6. Dependence of μ_H on T for the n and p modes in a direction parallel to the cleavage plane.

DISCUSSION

From the curves of Fig. 5, showing the change in conductivity type with illumination level, it is clear that two-carrier effects must be considered and that the measured Hall mobility must be interpreted by the expression

$$\mu_H = (p\mu_p^2 - n\mu_n^2)/(p\mu_p + n\mu_n).$$

An assumption that at the extrema of mobility in the curves of Fig. 5 the current is nearly a one-carrier current would indicate that electrons and holes have nearly equal mobilities and that the carrier densities at the n-type and p-type maxima are comparable. The two-carrier interpretation of the curves of Figs. 6 and 7 is reinforced by the correspondence of the structures for the curves of μ_H versus T in the n and p modes: Where μ_H increases for electrons, it decreases for holes and vice versa. These inverse variations reflect changes in the recombination kinetics which alter the ratio n/p. In the high-temperature region of Fig. 6, as the p-type signal tends to disappear, the n-type mobility rises above 60 cm^{2}V^{-1}sec^{-1}. It appears, therefore, that the measured mobilities are lower limits and that the true Hall mobility may be considerably in excess of the values shown in Figs. 6 and 7. Large values for μ_H in molecular crystals are not unknown; a mobility for holes in excess of 100 cm^{2}V^{-1}sec^{-1} has been measured in copper-phthalocyanine.[19] The question which requires study is the compatibility of our results with the low values measured for μ_D and with the narrowness of the excess electron and hole bands as calculated by theory.

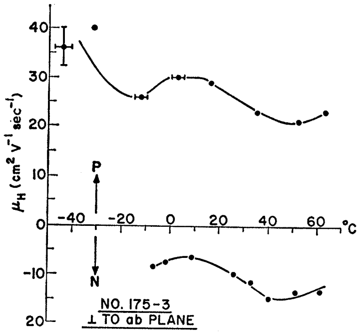

FIG. 7. Dependence of μ_H on T for the n and p modes in a direction normal to the cleavage plane.

The measurements of μ_D by other investigators made use both of melt-grown and of solution-grown crystals and were performed either under space-charge-free[1,3] or space-charge-limited[2,4] conditions. They all agree in yielding values of μ_D close to unity, which decrease as the temperature increases. The most commonly found mechanism in wide-band-gap materials which accounts for a low value of μ_D/μ_H is the presence of shallow traps. In this case, these traps should have both capture times and thermal-release times under 10^{-6} sec. However, it is clear that there is no trap distribution which can yield the observed dependence of μ_D on temperature, and the reported values of μ_D must be microscopic mobilities.

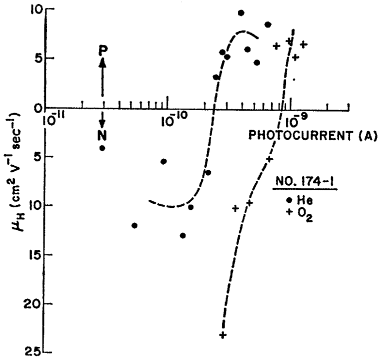

FIG. 8. Dependence of μ_H on illumination in a He atmosphere for a crystal having previously been exposed to O_2, and in a O_2 atmosphere after formation of heavy layer of anthraquinone.

The principal difference in the measurements of μ_D

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and μ_H is that for the former the carriers are photogenerated at a surface and their transport is measured through the unexcited bulk of the crystal; in the latter, transport is measured in a thin surface layer, intensely illuminated. The production of photogenerated carriers in anthracene is known to take place through an intermediate exciton, generally believed to be the lowest excited singlet state.[18,20,21] These excitons, which have a diffusion length of the order of 1000 Å,[18] about the same as the absorption depth of the exciting light, dissociate into a carrier pair upon encountering either the surface or some other imperfection. If we assume that the conducting layer is thinner than 1000 Å, our measurements take place under conditions where the free-carrier density is greater than 5×10^{11} cm^{-3}. It might be argued that the transport properties of anthracene may be different at the surface than in the bulk. Most results of the early workers on the differences between surface and volume photoconductivity have been satisfactorily explained on the basis of electrode and space-charge effects. Moreover, to our knowledge, no case has been reported where proximity to a crystal surface increased the mobility in a semiconductor. The possibility exists that the surface of our crystals may have keen contaminated during the sample preparation. However, no photoconductive effects have been found which were not characteristic of anthracene. Furthermore, it was shown above that a coating of anthraquinone on the crystal surface does not markedly affect the measured values of μ_H.

We now consider the possibility that the measured values of μ_H are anomalous in sign and magnitude as predicted theoretically.[7,11] Physically, this effect arises from the narrowness of the conduction bands, leading to the nearly equal population of the band states. From the curves given in LeBlanc's paper, we find that for a bandwidth of 0.025 eV, $\mu_H/\mu_D\approx-5$ at 300°K. Extrapolation of these curves to values μ_H/μ_D of the order of -50 at room temperature, as required by our measurements, yields a bandwidth $W\approx0.002$ eV, about ten times smaller than predicted by the best theoretical calculations.[5,10] The actual existence of an anomalous effect can only be verified by measuring μ_H/μ_D as function of T separately for electrons and holes, but this could not be done because of the two-carrier effects. Little experimental evidence is available concerning either the width or the location of the conduction band in anthracene. The conduction band is known to lie above the first excited singlet state[22] so that the photoconductive bandgap is at least 3.1 eV and may be greater than 3.7 eV.[23] Some investigators have recently suggested that electron conduction may take place in a band of higher energy and wider than that normally considered.[24,25] For the case of narrow bands, the mobility is given by[26]

$$\mu\approx(e\tau/kT)(Wa/\pi\hbar)^2,$$

where a is the lattice parameter and τ the scattering time. If we assume a bandwidth of 0.02 eV and an average thermal velocity of 10^5 cm/sec as calculated, we find, using our measured value of $\mu\approx50$ cm^{2}V^{-1}sec^{-1}, that $\tau=2\times10^{-12}$ sec and the mean free path $L=40$ Å, in agreement with the value of L determined experimentally by other investigators.[24]

Another possible explanation of the difference between the observed values of μ_H and μ_D is that the transport properties may vary with the conductivity of the crystal. Increases greater than tenfold of μ_H with illumination level have been observed on materials such as CdS, CdSe, InP, and GaAs.[27] These changes have been attributed to the presence of charged impurity centers, which become neutral upon illumination with a consequent decrease in scattering cross section. The giant cross section (10^{-10} cm^2) measured in such cases has led to the idea that these impurities exist in clusters and that macroscopic inhomogeneities surrounded by space-charge barriers which disappear under illumination may also contribute to this effect.[28] Despite the precautions taken in the preparation of our anthracene crystals, the concentration of organic impurities is probably well in excess of one part in 10^6. In addition to impurity clusters, it is also possible that charge-transfer complexes may be present in the crystal, which would also have a large scattering cross section.

Since μ_H can be measured only at the highest light levels, the existence of such a mechanism can only be inferred. Under illumination, one can calculate the position of the quasi-Fermi levels given by

$$E_f=kT\ln[N\rho e\mu],$$

where ρ is the resistivity of the illuminated layer. Taking for the density of states in the narrow bands[29] $N=10^{22}$ cm^{-3}, one finds the quasi-Fermi levels, which must be about the same for both signs of carriers, at 0.63 eV from the band edges. Since the band gap is greater than 3.1 eV, it is reasonable to suppose that the occupancy of most deep states has been altered by illumination. For both carriers, photoconductive life-

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times $\tau_l = 10^{-6}$ sec are obtained,[30] and the density of deep states must be at least as great as the concentration of deep traps, which has been measured at low conductivity levels in the range $10^{14} < N_t < 10^{17}$ cm^{-3}.[31] Thus, one obtains for the recombination cross section $10^{-16} < S < 10^{-13}$ cm^2, a range of values considerably smaller than the Coulomb cross section of 2×10^{-12} cm^2 expected in anthracene, and most of the states lying between the two quasi-Fermi levels (the recombination states) must be neutral. Should the bands be wider than 0.02 eV, with a concomitant increase in the mean thermal velocity of the carriers, the values of S would be proportionately smaller. In the dark condition, we might apply the expression derived by Frohlich and Sewell[26] for scattering by impurities in the case of narrow bands:

$$\mu \approx \frac{e}{kT} \frac{Wa}{\pi h} \frac{1}{SN_i},$$

where N_i is the concentration of impurities. If we assume as before $10^{14} < N_i < 10^{17}$ cm^{-3}, a mobility of 1 cm^{2}V^{-1}sec^{-1} implies $S > 10^{-10}$ cm^2. Such large cross sections could only be associated with macroscopic inhomogeneities. Thus, a model where the mobility is controlled by defects which change their cross section or disappear under illumination may have some validity.

ACKNOWLEDGMENTS

The author wishes to thank Dr. W. Helfrich of the National Research Council of Canada for providing some of the anthracene crystals used in this work. He is also indebted to his colleagues L. Friedman, P. Mark, and M. A. Lampert for helpful conversations and to D. L. Ross for identifying the anthracene polymer.

APPENDIX

The electrode geometry used (Fig. 1) was dictated by the high resistance of the material, even under intense illumination, which necessitates small electrode spacings and by the softness of anthracene which sets a limit on the smallest crystals which can be manipulated without damage. It was found impossible to use standard six-electrode methods or the method of Van der Pauw[32] which requires four electrodes on the periphery of the crystal. The following procedure is useful for cases where there is no appreciable potential drop at the current electrodes (as demonstrated above) and when conduction takes place in a layer thin compared to the electrode spacing. It is easily shown[33] that for such a sample of arbitrary shape having four point-contacts at the periphery, the mobility is given by

$$\mu_{\mathrm{H}} = (V_{\mathrm{H}}/Bi\rho_s) \times 10^8 \text{ cm}^2\text{V}^{-1}\text{sec}^{-1},$$

where V_{H} is the Hall voltage, i the current flowing through the sample, B the magnetic field in gauss, and ρ_s the surface resistivity of the conducting layer in ohms per square. As the electrodes are extended inwards from the periphery as in Fig. 1, the Hall voltage is given to first order by replacing i in this equation by the current flowing between the probes $i' = \gamma i$, where γ is a geometrical factor. A much smaller correction, involving the effect of the loop currents at the electrodes upon application of the magnetic field, will be neglected here. Another geometrical factor β gives the surface resistivity $\rho_s = \beta V_l / i$, where V_l is the potential applied to the current electrodes. For this electrode geometry, where the lines of current flow form a family of confocal ellipses, γ and β can readily be evaluated by a conformal transformation yielding the product

$$\gamma\beta = (2/\pi) \ln(1+\sqrt{2}) = 0.56.$$

The exact size and shape of the crystal boundary do not play a role provided the current flow is not strongly distorted. It is clear that if there is a potential drop at the current electrodes only a lower limit on μ_{H} can be obtained by this method. In such a case, the more complicated method described by Lange,[34] utilizing four surface point-contacts, might be useful.

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[30] In this calculation the quantum efficiency for the primary free-carrier-generating process is arbitrarily assumed to be unity. The values for quantum efficiency quoted in the literature, which are as small as 10^{-6}, are usually measurements of the photoconductive gain and include the effect of free-carrier recombination in the region of generation. [R. G. Kepler and R. E. Merrifield, J. Chem. Phys. **40**, 1173 (1964)].

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