vaporizer currents to deposit a visible film of each metal in approximately 2 minutes. The measurements were carried out in sequences of the type A_1B_1, A_1B_2, A_2B_2, where $A_1A_2\cdots$ and $B_1B_2\cdots$ represent, respectively, successively deposited films of gold and barium. This scheme of single-surface renewal provided information concerning the aging characteristics of the individual films of gold and barium; it was varied occasionally by renewing both surfaces simultaneously.

RESULTS

Sixteen pairs of gold-barium surfaces were measured. The barium films showed their usual high reproducibility and long-term constancy throughout the measurements. In the first four depositions of gold, the initial contact potential values were erratic and marked drifts in contact potential occurred on aging for periods of one to two days. With deposition of the fifth gold film, the variation in the initial readings and the drift with aging disappeared simultaneously. All measurements on the last 12 gold surfaces, including those taken immediately after deposition and after aging periods extending to 48 hours, gave contact potential values within the extreme limits 2.29–2.32 volts. For this group, all measurements on freshly deposited gold surfaces fell within the limits 2.31–2.32 volts. Aging of the gold films for 24–48 hour periods generally, though not invariably, lowered the observed contact potential by 0.01 to 0.03 volt. The variability of gold films 1–4 was probably due to incomplete coverage of the tantalum substrate resulting from agglomeration and piling up of the gold about crystallization nuclei.

Taking 2.31 volts as the contact potential value best representing these measurements and 2.52 ev as the work function of barium,[8] we obtain 4.83 ± 0.02 ev as our value for the work function of gold vapor-deposited on smooth tantalum. This value is in excellent agreement with the Morris-DuBridge photoelectric determination of Au.[4]

[8] N. C. Jamison and R. J. Cashman, Phys. Rev. **50**, 624 (1936).

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Polarization Processes in Partially Illuminated Photoconducting Insulators

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A quantitative analysis of polarization phenomena in photoconducting insulators is presented for the case in which a strip of the sample is illuminated far from the electrodes. It is shown that if the drift length of the photo-excited carriers is small compared with the dimensions of the dark and illuminated regions, the photocurrent decays exponentially during both the buildup and release of polarization. The decay constant is essentially independent of the characteristics of the contacts and the applied voltage, and can be expressed in terms of geometrical factors and the photoconductance of the illuminated strip. The conclusions of the analysis are checked in colored single crystals of NaCl. The experimental results are found to be in satisfactory agreement with the theory presented.

INTRODUCTION

It is well known that photocurrents in insulators frequently exhibit polarization effects.[1] Following a relatively rapid initial rise, the photocurrent decays slowly with time of illumination as the polarization builds up, until a fairly constant "saturation" value is reached. Further, on the removal of the external field, a short-circuit photocurrent appears which subsequently decays to zero as the polarization is released. The buildup of polarization is associated with the accumulation of space charge in the sample as a result of the drift under field of the photo-excited carriers. Such an accumulation can materialize only when the discharge of current carriers between the space-charge regions and the electrodes is insufficient to neutralize the space charge formed. This may arise from contact effects and/or nonuniform illumination. In either case, to maintain the given voltage across the sample, the constant-voltage source must supply additional charge to the electrodes at a rate determined by that of the space-charge accumulation in the sample. The measured photocurrent is given by the rate at which the charge is induced at the electrodes, superimposed on any discharge current between the electrodes and the space-charge regions that may be present. The initial photocurrent and its subsequent decay are associated with the self-limiting rate of space-charge formation. The saturation value of the photocurrent represents the discharge current which, under steady-state conditions,

[1] E. G. R. Hilsch and R. W. Pohl, Z. Physik **87**, 78 (1933); R. C. Herman and R. Hofstaedter, Phys. Rev. **59**, 79 (1941); A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. **22**, 1021 (1954).

just balances the rate of space-charge formation. The short-circuit current during the release process is associated with the rate of space-charge neutralization by the drift of photo-excited carriers under the internal polarization field.

In photoconductivity measurements uniform illumination of the whole sample is generally employed. Polarization may then arise from the blocking nature of one or both of the contacts which prevents or limits the discharge current. In general, contacts applied to insulators are unavoidably of this type. The primary objective in such experiments is the measurement of the photoconductance under specified conditions of illumination. For this measurement it is necessary to determine both the photocurrent and the electric field in the sample. The presence of polarization renders the determination of the field difficult if not impossible. Attempts have therefore usually been made to eliminate polarization effects from the measurement. If, on the other hand, it were possible to analyze polarization phenomena, the latter could be specifically invoked to furnish quantitative information on basic electronic processes in insulators.[2] Such an analysis, however, is rendered difficult and uncertain wherever contact effects are predominant.

It is shown in this paper that if only a strip of the sample is illuminated, rather than the whole sample, the polarization process can be subjected to a straightforward quantitative analysis provided that the insulator is characterized by strong trapping. Under these conditions the accumulation of space charge is due to the trapping of photo-excited carriers in the *dark* regions adjacent to the edges of the illuminated strip. The discharge current is then limited by the high resistance of the dark regions as well as by contact resistance, where present. With a number of simplifying assumptions, the photocurrent is shown to follow an exponential curve whose decay constant can be evaluated in terms of geometrical factors and the photoconductance of the illuminated strip. This decay constant is independent of the applied voltage and is affected to a negligible extent only by the characteristics of the contacts.

The conclusions of the model are checked for the case of colored NaCl crystals which provide a suitable medium. The experimental results are found to be in good agreement with theory as regards both the time dependence of the photocurrent and the electrical field distribution along the sample at various stages of polarization. The field distribution is determined by the use of light probes in the form of narrow illuminated strips. This technique has proved to be a powerful tool in general studies of field distribution in photo-conducting insulators.

[2] H. Kallmann and B. Rosenberg, Phys. Rev. **97**, 1956 (1955).

THEORETICAL CONSIDERATIONS

The discussions that follow will be valid for any photoconducting insulator, irrespective of the detailed electronic processes taking place, provided the following conditions are fulfilled. First, the drift length $w=\mu E\tau$ of both types of carriers should be everywhere in the sample small compared with the dimensions of both the dark and illuminated regions. In the expression for w, μ represents the mobility of either carrier type, τ its mean life in the conducting state, and E the effective field under which it moves. Second, the lifetime in the illuminated region should be constant during the polarization process being considered. For the sake of simplicity of presentation and with no loss of generality the case of a single carrier system will be considered.

Consider a rectangular homogeneous sample of length L and unit cross section in which a uniform electric field is established. Let n_0 denote the electron concentration in the dark. A well-defined strip perpendicular to the length of the sample and of width b is illuminated with penetrating light so as to produce uniform volume excitation of γ electrons per unit volume in unit time, into the conduction band. Under the action of the field each electron drifts on the average a distance equal to the drift-length before leaving the conduction band. When the motion of all the electrons is considered, this process is found to lead to the formation of two space-charge layers at the edges of the illuminated strip. Within a distance of w inside the edge facing the anode, electrons are continually being photo-excited and carried outside of the illuminated strip where they are subsequently trapped. Thus a negatively charged layer of the order of w is formed just outside this edge. At the other edge, facing the cathode, a positively charged layer of approximate width w is formed as the electrons in this region are continually being carried away but not replenished by the dark current. Since the drift length everywhere in the sample is assumed to be negligible compared to the widths of the illuminated and dark regions, these charged layers may be considered as charged surfaces. It can readily be shown that the rate of change of charge density on these surfaces is given by

$$d\sigma_p/dt=e\mu(n_0+\gamma\tau)E_b-e\mu n_0E, \tag{1}$$

where E and E_b are the field intensities in the dark and illuminated regions, respectively. As only charged surfaces are present in the sample, E and E_b are uniform and can be evaluated from the surface divergence of the charge densities:

$$E=(4\pi/\epsilon)\sigma, \tag{2}$$

$$E_b=(4\pi/\epsilon)(\sigma-\sigma_p), \tag{3}$$

where σ and σ_p are the absolute magnitudes of the charge densities at each electrode and at each edge of the illuminated strip, respectively; ϵ is the dielectric constant.

According to Kirchhoff's law,

$$(L-b)E+bE_b=(4\pi/\epsilon)L\sigma-(4\pi/\epsilon)b\sigma_p=V, \quad (4)$$

where V is the applied voltage across the sample, assumed to be constant.

Equations (1) to (4) are sufficient to determine the time dependence of the photocurrent and of the electric field in the dark and illuminated regions. Consider first the simpler case in which the electron concentration in the dark is negligible compared with that under illumination. Under this condition, the terms containing n_0 in Eq. (1) may be omitted. Differentiation of Eqs. (3) and (4) and the use of Eqs. (1) to (4) yields the following relations,

$$dE_b/dt=(4\pi/\epsilon)(1-b/L)e\mu\gamma\tau E_b, \quad (5)$$

$$J\equiv d\sigma/dt=(b/L)d\sigma_p/dt=(b/L)e\mu\gamma\tau E_b, \quad (6)$$

from which the electric field E_b and the photocurrent density J are evaluated as

$$E_b(t)=E_{b0}\exp(-t/T), \quad (7)$$

$$J(t)=J_0\exp(-t/T), \quad (8)$$

where

$$T\equiv\epsilon/4\pi(1-b/L)e\mu\gamma\tau, \quad (9)$$

$$J_0\equiv(b/L)e\mu\gamma\tau E_{b0}, \quad (10)$$

and E_{b0} is the value of E_b at $t=0$. Equations (7) and (8) are applicable for either the buildup or the release processes. Equation (10) is identical with the expression for the photocurrent induced by a light flash as derived by Gudden and Pohl[3] from different considerations.

In the general case where n_0 is not neglected, a similar calculation leads to the following expressions for the field in the illuminated strip and for the photocurrent:

$$E_b(t)=E_{b\infty}+(E_{b0}-E_{b\infty})\exp(-t/T_1), \quad (11)$$

$$J(t)=J_\infty+(J_0-J_\infty)\exp(-t/T_1), \quad (12)$$

where

$$T_1\equiv(\epsilon/4\pi)/e\mu[n_0+(1-b/L)\gamma\tau], \quad (13)$$

$$E_{b\infty}\equiv(V/L)\{n_0/[n_0+(1-b/L)\gamma\tau]\}, \quad (14)$$

$$J_\infty\equiv e\mu(n_0+\gamma\tau)E_{b\infty}, \quad (15)$$

$$J_0\equiv e\mu n_0(V/L)+e\mu\gamma\tau(b/L)E_{b0}. \quad (16)$$

It is seen that in the presence of a dark current ($n_0\neq0$), J again decays exponentially during both the release and the buildup processes, but in the latter process it reaches a nonvanishing saturation value. Thus, if this saturation value is taken into account, the general decay characteristics of the polarization phenomena are not altered by the dark conduction. It is only the value of the decay constant that is affected. The effect of n_0 becomes important in poor insulators and under conditions of weak illumination in good insulators.

The partially illuminated sample can be simulated by an electrical analog consisting of a combination of capacitators and resistors, as shown in Fig. 1. The onset of illumination is equivalent to the closing of the switch S. The charging or discharging currents become identical with the corresponding photocurrents during the buildup or release processes provided the following correspondence holds true. The three capacitances C_1, C_2, and C_3 are, respectively, equal to the geometrical capacitances between the cathode and the left-hand edge of the illuminated strip, between the two edges and between the right-hand edge and the anode; the resistances R_1, R_2, and R_3 are equal to the dark resistances of the corresponding three regions; and the resistance r is equal to the photoresistance of the illuminated strip.

The assumptions underlying the above analysis will now be discussed.

(a) The carrier drift-length is negligible compared with dimensions of the dark and the illuminated regions. This is often the case in insulators where strong trapping is the general rule. In colored NaCl crystals, for example, $\mu\tau$ is of the order of 10^{-8} cm^2 volt^{-1}, so that at fields of several thousand volt/cm this assumption is perfectly valid. The drift length may, however, become appreciably larger when the carriers swept out of the illuminated strip can saturate the traps in the dark regions. A calculation for this case, to be published in a future paper, shows that the photocurrent deviates from an exponential curve but the over-all decay time is not very different from that when no saturation of the traps takes place.

(b) The lifetime in the illuminated region is constant throughout the polarization process. This assumption will be valid if the change in trap occupation is negligible. This is indeed the case in colored NaCl crystals for not too high light intensities such as those employed in the present measurements.

(c) It has been assumed for simplicity that prior to illumination the electric field in the sample is uniform. It can be shown that this provision is not necessary in

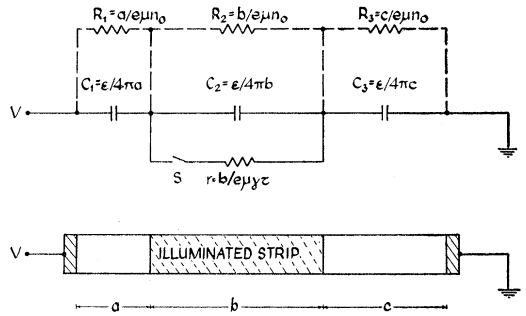

FIG. 1. The equivalent electrical circuit of a partially illuminated photoconducting insulator.

[3] B. Gudden and R. W. Pohl, Z. Physik **16**, 170 (1923); **17**, 331 (1923).

the dark regions. This is also seen from the electrical analog, in which nonuniformity in the field will simply be reflected in the value of R_1, R_2, and R_3. In a homogeneous sample departures from uniformity in the field can arise only from contact effects. Hence, if the illuminated strip is well removed from the electrodes, the conclusions of the model are essentially independent of the nature of the contacts.

EXPERIMENTAL

The experimental results obtained on colored single crystals of NaCl will be subsequently described and discussed. The initial photocurrent and the decay constants during both the buildup and the release processes were measured as a function of the width of the illuminated strip, the intensity of illumination, and the applied voltage. The distribution of the effective electric field along the sample under various conditions was also measured.

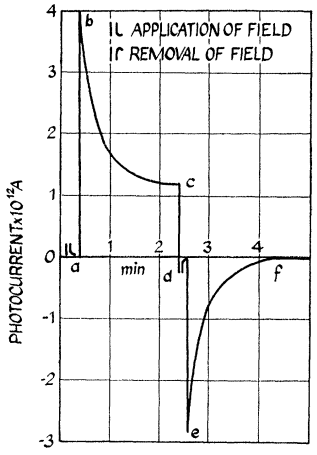

FIG. 2. A typical cycle of measurements showing polarization in a partially illuminated photoconducting insulator. (a) application of an external field, (b) illumination of a strip on the sample, (c) shutting off the illumination, (d) removal of the applied field, (e) re-illumination of the same strip, and (f) shutting off the illumination.

(a) Techniques

The samples studied were rectangular plates of about $10\times4\times2$ mm^3, cleaved from synthetic single crystals of NaCl grown by Harshaw Chemical Company. They were irradiated by x-rays, care being taken to ensure homogeneous coloring throughout their volume. The density of F centers, as derived from the absorption coefficient in the F-band, was found to lie between 10^{16} and 10^{17} cm^{-3} in the samples studied.

The specimen was placed in a closed chamber with a 10×4 mm^2 surface facing a camera window. Indium foils pressed tightly to the 4×2 mm^2 faces served as electrodes. The chamber was mounted on an optical bench and fitted with a mechanism by means of which it could be moved perpendicular to the bench. With these arrangements it was possible to illuminate well-defined strips of variable width anywhere along the sample. In all the measurements the sample was illuminated with white light.

The photocurrent was measured by means of an electronic electrometer, the output of which was connected to a Philips recorder. Voltages up to 1800 v were applied to the sample. In general the experiments were carried out in cycles with the following sequence of operations: (a) application of an external field, (b) illumination of a strip on the sample, (c) shutting off the illumination, (d) removal of the applied field, (e) re-illumination of the same strip, and (f) shutting off the illumination. Before each new cycle performed on the same sample, the whole crystal was illuminated, with the field removed, long enough to achieve total release of polarization and return the crystal to its initial state. The bleaching of the color centers even after many such cycles was negligible.

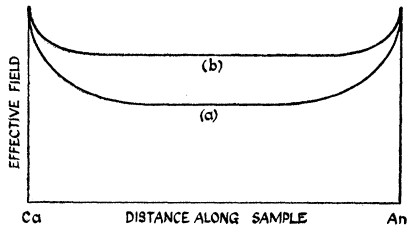

FIG. 3. The electric field distribution along the sample due to the application of an external voltage. (a) With silver paint electrodes, and (b) with indium electrodes.

Typical polarization phenomena are illustrated in Fig. 2 which presents the results of a conventional cycle of measurements. In this experiment, a strip of 4 mm width at the center of a 10-mm long sample was illuminated.

(b) The Initial Photocurrents; Light Probe Investigation of Effective Fields

The initial photocurrent was found to vary linearly with the width of the illuminated strip, the intensity of illumination, and the applied voltage. This is in full agreement with Eq. (16).

Since the initial photocurrent, at constant strip width and light intensity, is strictly proportional to the electric field, it may serve as a measure of the mean effective field inside the strip. Consequently, by using a narrow illuminated strip, the effective field at any point along the sample may be probed. Examples of light probing of various field distributions are shown in Figs. 3 and 4. They demonstrate the usefulness of this technique. Figure 3 shows the field distribution along

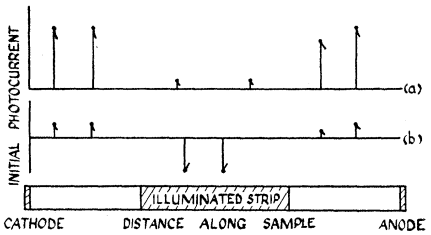

FIG. 4. The effective field distribution along the sample following the buildup of polarization. (a) With the applied voltage on, and (b) with the applied voltage removed (internal field).

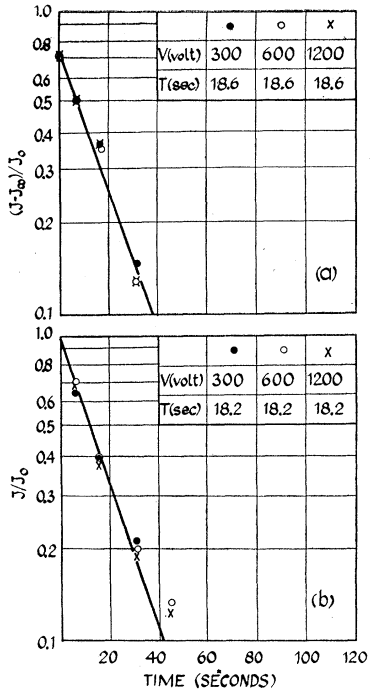

FIG. 5. Plots of $\log[(J-J_\infty)/J_0]$ *versus* time of illumination for three values of the applied voltage. (a) For the buildup phenomena, and (b) for the release phenomena. T denotes the decay constant.

the sample in the dark due to the application of an external voltage and its dependence on the nature of the electrodes. It is seen that the field is not uniform along the sample but increases towards the electrodes, being fairly symmetrical about the center. The variation of the field along the sample was found to be strongly dependent on the nature of the electrodes. Two extreme cases are shown here, one with silver paint contacts (a), and the other with indium contacts (b). It is seen that with indium electrodes the nonuniformity in the field is much smaller and is concentrated in the near vicinity of the electrodes. This is in accordance with the known small work function of indium. It is for this reason that indium electrodes are used in the measurements described here.

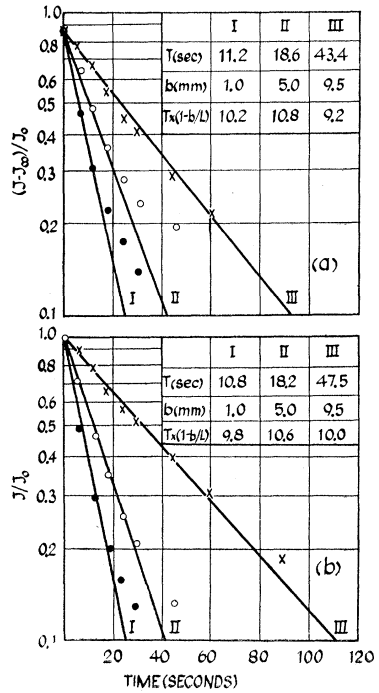

FIG. 6. Plots of $\log[(J-J_\infty)/J_0]$ *versus* time of illumination for three values of the width of the illuminated strip b. (a) For the buildup phenomena, and (b) for the release phenomena. The length of the sample L is 11.8 mm. T denotes the decay constant.

Light probe measurements of the electric field at various locations on the sample, following the buildup of polarization, are shown in Fig. 4. Polarization was produced by illuminating a strip of 4 mm at the center of the sample. Light probes of 1 mm were used. The initial photocurrent due to a light probe is shown for the cases where the latter is applied at points, (i) inside the previously illuminated strip, (ii) between the strip edge and the cathode, and (iii) between the strip edge and the anode. Figure 4(a) shows the results of measurements on the effective field in the presence of the applied field, while Fig. 4(b) presents results of measurements on the internal field, i.e., with the applied field removed. It is seen that the field distributions are in complete agreement with the implications of the proposed model except in the region between the strip edge and the anode, where the field is seen to fall off slightly as the probe approaches the previously illuminated strip.

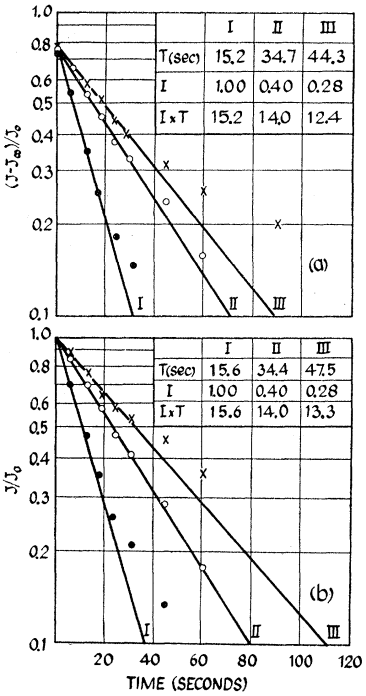

FIG. 7. Plots of $\log[(J-J_\infty)/J_0]$ *versus* time of illumination for three different light intensities I (relative values given). (a) For the buildup phenomena, and (b) for the release phenomena. T denotes the decay constant.

(c) Decay Constants

According to Eq. (12) the photocurrent density should decay exponentially with time of illumination to a saturation value J_∞. Semilogarithmic plots of $(J-J_\infty)/J_0$ *versus* t, for various values of the applied

voltage, strip width, and light intensity, are shown in Figs. 5, 6, and 7, respectively, for both the buildup and the release phenomena. The three curves shown in each of these figures correspond to different values of the respective parameter, the other variables having been kept constant. It is seen that in all cases the curves are exponential over a considerable portion of the decay process; the decay constant is independent of the applied voltage, while its reciprocal varies fairly linearly with $(1-b/L)$ and light intensity. These results are in satisfactory agreement with theory.

The value of J_∞ in the buildup process observed in these experiments is appreciably larger than the dark current. This must be attributed to the effect of scattered light on the conductivity of the dark regions, as no particular precautions were taken to eliminate its presence completely. The deviations from the exponential curve may be associated with some spreading-out towards the anode of the space-charge of trapped electrons. This view is supported by the results presented in Fig. 4 which indicate the presence of a small space-charge of trapped electrons outside the illuminated strip on the anode side. The nature of this spread-out is now being investigated.

(d) Estimation of $\mu\tau$

From the expression for the decay constant, Eq. (9), the value of $\gamma\mu\tau$ can be calculated since all other quantities are measurable. Thus in curve I of Fig. 7, for example, $b=0.5$ cm, $L=1.2$ cm, and the decay constant is 15.4 sec. The value of $\gamma\mu\tau$ calculated from this data is 3.8×10^5 sec^{-1} cm^{-1}. Alternatively, $\gamma\mu\tau$ can also be calculated from the value of the initial photocurrent, according to Eq. (10), if the initial field in the sample is assumed to be uniform. The value obtained in this way from the data of the same experiment is 3.5×10^5 sec^{-1} volt^{-1} cm^{-1}. The agreement between the two values is good.

The value of γ as estimated from the intensity of the light source, taking into account the geometrical configuration, is of the order of 10^{13} cm^{-3} sec^{-1}. Accordingly $\mu\tau$ is of the order of 10^{-8} cm^2 volt^{-1}. Values of $\mu\tau$ reported in the literature for alkali halides are of the same order of magnitude.[4]

[4] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), p. 127. For KCl with 5×10^{16} F centers per cc, $u\tau\simeq10^{-8}$ cm^2 volt^{-1}.

CONCLUSION

The success of the rather simple model presented here in accounting satisfactorily for polarization phenomena in insulators stems largely from the condition that a strip, rather than the whole sample is illuminated. For the common case of low dark conduction and small carrier drift length the polarization process is determined by well defined quantities, namely the photoconductance of the illuminated strip and three geometrical capacitances. These parameters are independent of the nature of the contacts and of the applied voltage within wide limits. When the whole sample is illuminated, on the other hand, the polarization process will depend on a poorly defined quantity involving the space-charge capacitance associated with the contacts. A simple analysis in this case is feasible[5] only when the carrier concentration under illumination prior to the application of the field is uniform throughout the sample and for applied voltages in the millivolt range.* The limitation of the measurements to such low voltages makes them extremely difficult. Moreover, the condition of uniform carrier concentration is rarely, if ever, satisfied in insulators because of the difference in the work functions of the electrode and sample materials and, possibly, the presence of surface states on the insulators. Such a nonuniformity in concentration is indicated, for example, in Fig. 3 by the nonuniformity of the field distribution near the electrodes.

The analysis presented can be extended to cover situations where saturation of traps in the dark regions can take place during the buildup of polarization. Under these conditions the drift length may become appreciable compared to the sample dimensions giving rise to deviations of the photocurrent decay from exponential characteristics, as well as to nonuniformity in the field distribution in the dark regions. It is believed that in such cases the time dependence of the photocurrent combined with the field distribution as determined by the light-probing technique will furnish valuable information on trapping kinetics in insulators.

[5] J. R. MacDonald, Phys. Rev. **92**, 4 (1953); J. Chem. Phys. **23**, 275 (1955); J. Chem. Phys. **23**, 2308 (1955).

* *Note added in proof.*—An analysis of space-charge capacity associated with contacts for large signals has recently been carried out by J. R. MacDonald [J. Chem. Phys. **29**, 1346 (1958)].