PHOTOELECTRETS

The behavior of active dielectrics and semiconducting materials in external electric fields has today developed into an extremely important branch of solid-state physics. These dielectrics have given rise to a new type of solid-state device in the form of an "electret." Due to their wide applications, electrets are no less challenging than any other growing field of science. On one hand they are becoming important as materials for study of charge storage phenomena, and on the other hand there is rapid application in a wide range of devices.

Some dielectrics, when placed in an external field, get polarized, thereby preserving their polarization for a long time after the external field that has produced this polarization is removed (1). An electret establishes an electric field for a long time in the same way as a permanent magnet sets up a magnetic field. Thus an electret can be thought of as an electric analogue of a magnet (2).

A. Gubkin (3) and G. Skanavi first demonstrated that the electrets could be obtained from various inorganic dielectrics such as titanates of barium, magnesium, zinc, calcium, and so on. The electret effect was also observed in organic dielectrics, namely, polymethylmethacrylate, ebonite, polyetrafluoroethylene, and so on.

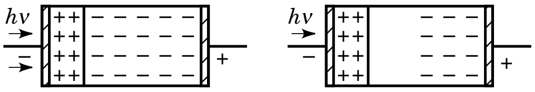
The polarization of the dielectric can also be carried out in many ways depending upon external agency. These electrets are termed "thermoelectrets" (4), "photoelectrets" (5), "magnetoelectrets" (6), or "radioelectrets" (7).

In 1937, G. Nadzhakov (8) discovered the photoelectret. During his investigation on polycrystalline sulfur, he found that the space charges during photoconduction were accumulated and retained for a long time, even after the fields were removed and illumination ceased.

FORMATION OF PHOTOELECTRET STATE

Photoelectrets are formed as a result of the spatial distribution of the photocarriers in the presence of an external field. When an active dielectric is illuminated with light, electron and holes are generated. Electrons get sufficient energy to make the transition across the band. Charge carriers diffuse

J. Webster (ed.), *Wiley Encyclopedia of Electrical and Electronics Engineering*.

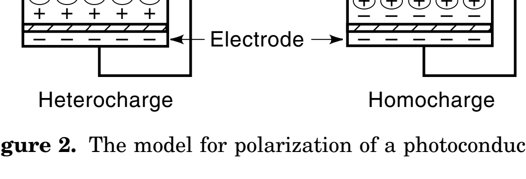


Bulk polarization Barrier polarization

Figure 1. Charge distribution in an electret.

in the presence of the field and get trapped, thereby giving rise to persistent internal polarization even after the illumination ceases and the field is removed. Now, if the electrodes are short-circuited in the dark, a dark depolarization current of stray charge carriers is obtained. Dark depolarization current is due to charge carriers which are trapped at shallow levels. Charge carriers trapped into deep levels give rise to persistent internal polarization if the dielectric is kept in the dark. The prerequisite for photoelectret formation is the presence of deep traps where the charge carriers could be held up. Besides this, the dielectric should be photosensitive because it has high resistive layers at the electrodes and has the capability for strong trapping of one type of charge carrier.

Depending upon the conditions of polarization, the charge of a photoelectret may be a heterocharge or a homocharge. In earlier experiments, only a heterocharge was observed. In this case, the nature of the charge in layers adjacent to the electrodes is opposite to that on the electrodes, while in the case of a homocharge, the surface charge is similar to the charge on adjacent electrode (Fig. 1). It was originally concluded by Kallmann et al. (9) that there might be two types of heterocharge distributions in the photoelectret: a barrier type and a bulk type. In the former case, a distribution of charge carriers is confined only to layers adjacent to the electrodes. However, in bulk-type polarization, charge carriers are distributed throughout the body of the material (Fig. 2). The middle portion of the photoelectret remains quasi-neutral in barrier-type polarization because the thickness of the charged layers is very small compared to the length of the photoconductor. The field in the quasi-neutral region is homogeneous and opposite to the direction of the external electric field. In bulk-type polarization, charges are distributed throughout the length of the body in which no quasi-neutral region may exist. In this case, the internal field is heterogeneous and changes its sign from point to point inside the photoelectret. There exists no quasi-neutral region inside the crystal. The charge distributions are mainly determined by the nature of the electrodes, strength of the electric field, type of radiation, polarity of the electrode being illuminated, and the relative values of the electron and the hole mobilities. In a dielectric, if electrons are more mobile than holes and if the negative electrode is illuminated, the electrons will be distributed throughout the length of the body, while the holes will be trapped near the negative electrode. This gives rise to bulk polarization which appears in ZnS, CdS, and ZnO. But if the dielectric is very thin (~30 to 50 μm), charge carriers are trapped in layers adjacent to the electrodes, thus giving rise to barrier-type polarization.



Heterocharge Homocharge

Figure 2. The model for polarization of a photoconductor.

The dielectric may be in direct contact with its electrodes, or it may be isolated from the electrodes by a mica sheet. In the case of blocking contacts (isolated contacts), the distribution of heterocharges is of the barrier type. When the polarity of the electrodes is changed, the polarity of the heterocharges is reserved. On the other hand, a homocharge is a surface effect whereby the charges come from outside the material. The stability of homocharges and heterocharges can be different. In some cases, after a comparatively rapid drop of the heterocharge, a homocharge is set up which is reduced rather slowly. This happens when the internal field increases steadily during polarization. The electric field between the dielectric interface and electrode may become so high that it causes a breakdown. Under breakdown, charge carriers are transferred from the electrode to the surfaces of the dielectric. These charges are trapped at the surface of the dielectric. The sign of these charges will be opposite to that of previous heterocharges. Thus the charges injected from the electrodes will partially compensate for the previous charges. The sum of these charges having opposite polarity gives rise to the net surface charge. When the electrodes are short-circuited at the end of the forming period, heterocharge still prevails over the homocharge. The amount of heterocharge decreases continuously, while the amount of homocharge increases. When the homocharge just balances the heterocharge, the net surface charge becomes zero. A steady state is obtained when the electret gets a net homocharge.

Contacts

The photoelectret state formation also depends on the nature of the contacts between the photoconductor and the electrode. The contacts may be one of the following three types.

Neutral Contact. A metal semiconductor contact is said to be a neutral contact if the energy bands remain flat throughout the semiconductor and do not bend up or down at the interface. The maximum current that can be drawn from a neutral contact has a limit. The current is set by the thermionic emission from the metal over the potential step into the semiconductor. The saturation in thermionic emission is given by the relation (19)

$$E = \frac{v}{4\mu}\,\mathrm{V/cm}$$

where v is the thermal velocity and μ is the mobility of charge carriers. Departure from Ohm's law was observed when the field exceeded the value ~10^4 V/cm for $\mu = 100$ cm^2/V-s and when $v = 10^7$ cm/s.

Blocking Contact. In the case of blocking contacts, the emission current is saturated. In such cases, the current does not increase with an increase in the field near the contact, unlike in the case of neutral contacts. Photoconductivity gain in this case cannot exceed unity because there is no injection of carriers from the electrodes.

Ohmic Contacts. A contact is said to be ohmic if it obeys Ohm's law. In such cases, there is a reservoir of carriers freely available to enter the semiconductor as needed. A blocking contact acts as an ohmic contact if it is thin enough to permit tunneling of carriers from the metal to the semiconductor.

To achieve an ohmic contact, there are two useful rules to observe:

1. A metal with a smaller work function than that of an *n*-type semiconductor and greater than that of a *p*-type semiconductor gives rise to ohmic contacts.
2. A metal which acts as an impurity in the material with the same conductivity characteristics gives rise to ohmic contacts.

Binders

Binders are useful for holding sensitive material in the form of large-area electret cells. The binders should be largely high solvent polymers with good insulating properties. They should have the ability to wet and disperse the photoconducting powder without reacting with it. They should form a tough, flexible, nontacky film having high electrical resistivity, high dielectric strength, and high dielectric constant. For electrophotography they should have good charge acceptance characteristics, a minimum dipole orientation effect at room temperature to avoid the thermoelectret effect, and slow dark decay and fast light decay characteristics.

Binder should not be added in larger quantities; otherwise it would cause secondary adverse effects. If too little binder such as a resin is present, the particles are not bound sufficiently tightly together for good conduction properties. Thus the proportion of binder to powder should be just sufficient to bind the particles together to form interparticle contact.

The quantitative properties of binder layers are strongly dependent on both type and proportion of binder to powder. However, the qualitative behavior of the binder layer is roughly dependent on the binder.

Polystrene used in some of the investigations is a nonpolar, high-resistant, and transparent binder (10). It does not show any thermoelectret formation or deteriorate the photoconducting characteristics of the photoconductor. These properties make polystyrene a good binder. The other common binders are carnauba wax, chlorestrol, polyvinyl chloride, paraffin, and so on.

The photoconducting properties of binder layers differ from those of single crystals in some respect. This difference is due to the presence of a large surface-to-volume ratio and the presence of interparticle contacts. Potential barriers arise between the interparticle contacts. According to Rose (11), most of the potential drop occurs across the boundaries between granules, and the high-power dependence of the current on the voltage is due to either the lowering of barrier height or tunneling through barriers. All the carriers that strike the barrier will not get through it. Only a fraction crosses over the barrier, and this fraction increases with applied field. An increase in light intensity increases the number of free carriers in a granule, thereby increasing the current in the same proportion. Thus the dark current and photocurrent depend on voltage. The barrier heights are modified in the presence of light.

Sample Preparation

An electret material should have a suitable energy gap and a large number of traps to hold the charge carriers. The majority of the photoelectrets are prepared by oxides and II–IV group compounds. The electret may have a single base or may have mixed composition. The high-purity raw materials are first homogeneously mixed and then fired in crucibles or boats in a furnace under controlled conditions. The temperature is kept near their melting point, ranging up to 1000°C. The various parameters such as firing temperature, firing time, and concentrations are changed to obtain maximum polarization. After firing, the material is suddenly quenched to room temperature and is finely powdered. It is preserved in a desiccator to avoid moisture.

Cell Preparation

For practical purposes the measurement with powdered samples is simple and economical. The electret cells are constructed in the form of a parallel plate capacitor. The electret material is sandwiched in the form of a dielectric layer. A small quantity of finely powdered microcrystalline sample is added to a solution of polystrene in benzene and stirred vigorously to result in a homogeneous suspension. The suspended sample is poured over a clean plane-polished Al plate and kept in a bell jar in a benzene atmosphere for a few hours to let it slowly dry. The plate is then brought out from the container, and a conducting thin glass plate or mica sheet is pressed over the other surface of the layer to make a second electrode. The common binder materials are polyvinyl chloride, carnauba wax, paraffin wax, shellac wax, chlorestral resin, and so on. The glass plate is rendered a conductor by depositing a thin layer of SnO_2 over it by the spray method. One could also use conducting jelly to make temporary conducting electrodes.

Measurement of Photoelectret Charge

The cell is kept in a dark chamber to avoid any undesirable radiation. It is first illuminated in the presence of a high direct current (dc) field (5 kV/cm to 40 kV/cm) which causes polarization of the layer. The cell is then short-circuited in the dark. This creates a dark depolarization current, and the charges are stabilized. This current flows in the opposite direction and is due to stray or shallow charge carriers, which diffuse and recombine inside the sample due to internal field. To measure the photoelectret charge, the cell is again illuminated in the absence of a field. The trapped charges are then released, which gives rise to a photodepolarization current. The current is recorded on a graphic recorder. The time integral of current gives the photoelectret charge. This charge is measured under various parameters such as polarization field, charging time, intensity of illumination, time of depolarization, excitation energy, temperature, and so on. To get the true photoelectret charge, pyro charges are subtracted from it. The pyro charge is recorded by polarizing the sample in the dark only.

Materials

The initial studies of photoelectrets in inorganic materials were made on S, Se, ZnO, and CdS. Pillai and his group (27) did a great deal of work, and mixed lattices were explored. The mixed lattices like $ZnO–TiO_2$, ZnO–CdO, ZnO–CdS,

Table 1. Photoelectret Properties of Inorganic Materials

Substance	Crystal State	Photoconduction		Phosphorescence	Photoelectret State
Sulfur	Polycrystal	Present	Absent	Present	Thermoelectret
Sulfur	Monocrystal	Present	Absent	Present	—
CdS : Cu : Cl	Polycrystal	Present	Absent	Present	—
ZnS : Cu : Cl	Polycrystal	Present	Present	Present	Electroluminescent
Anthracene	Monocrystal	Present	Absent	Present	Thermoelectret
Anthracene	Polycrystal	Present	Absent	Present	—
(Zn, Cd)S	Polycrystal	Present	Absent	Present	—
CdS	Monocrystal	Present	Absent	Present	—
Paraffin wax	Monocrystal	Absent	Absent	Absent	Thermoelectret
ZnO	Polycrystal	Absent	Absent	Absent	—
(Cs, Te)I	Monocrystal	Absent	Present	Absent	—
ZnO	Polycrystal	Present	Absent	Present	Electroluminescent
Se	Polycrystal	Present	Absent	Present	Electroluminescent
$BaTiO_3$	Monocrystal	Present	Absent	Present	Thermoelectret

$PbCrO_4$–ZnO, and $PbCrO_4$–HgO–ZnO have been thoroughly studied by Sadhana Devi et al. (28). By changing the composition, one can tailor the band gap and hence the photoelectret properties of the materials (Table 1). Gubkin and Skanavi made systematic studies on ceramic electrets such as $CaTiO_3$, $MgTiO_3$, $BaTiO_3$, and $BiTiO_3$ (Table 2).

THEORY OF PHOTOELECTRET STATE

Phenomenological theories of photoelectrets have been proposed by Kallmann and co-workers, Fridkin and Zheludev, Chetkarov, and Adirovich. Where the results of Kalabukhov and Fishdev suggest surface trapping of electrons, Kallmann and Rosenberg have suggested the volume polarization in polycrystalline dielectrics.

The kinetics of the photoelectret effect in photoconductors and the depolarization by reillumination can be understood on the basis of band theory. For this purpose, a set of differential equations describing the transition of electrons in a band model, and their movement under the action of an external electric field must be derived.

Tartakovski and Kaminker (12) arrived at the following conclusions on the basis of their study about space charges in photoconductors:

1. Illumination causes generation of electron–hole pairs. Electrons are transferred from the valence band to the conduction band where they move under the action of an external electric field.
2. In the course of their motion, electrons somehow leave the conduction band and get trapped in trap levels just below the lower edge of the conduction band.

Initially the number of electrons in trap levels will increase with time, but later an equilibrium is established when the number of electrons making transitions to the trapping levels per unit time becomes equal to the number of electrons excited per unit time from these levels to the conduction band under illumination. This gives rise to a saturation effect. Also, the electrons are transferred from the valence band to free trapping levels, which increases the dark hole conductivity. This gives rise to a dark depolarization current.

Table 2. Properties of Ceramic Electrets

Ceramic Electret	Permittivity	Resistivity (Ω · m)
$MgTiO_3$	16	10^{11}–10^{12}
$BaTiO_3$	1200	10^{8} –10^{10}
$SrTiO_3$	175	10^{8} –10^{10}
$BiTiO_3$	80	10^{10}–10^{11}

Let h_1 and h_2 be the number of electrons transferred by illumination, per unit time from the valence band to the conduction band and from filled trapping levels to the conduction band, respectively (Fig. 3).

If N is the number of electrons per unit volume in the trap levels, I is the intensity of illumination, and r_1 and r_2 are coefficients of absorption of light quantum yield, then we may set (15,16)

$$h_1 = r_1 I \quad \text{and} \quad h_2 = kN = r_2 IN$$

Now we can write a set of differential equations using all these facts; that is,

$$\frac{dn}{dt} = h_1 + kN - \alpha nP - \beta n(N_t - N) \tag{1}$$

$$\frac{dN}{dt} = -h_2 + \beta(N_t - N)n + Q - \delta NP \tag{2}$$

$$\frac{dP}{dt} = h_1 - \alpha nP + Q - \gamma NP \tag{3}$$

$$P = N + n \tag{4}$$

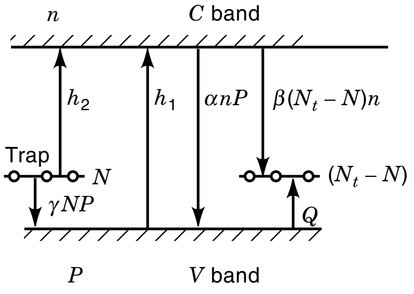


Figure 3. Energy level diagram of a photoconductor and possible transitions.

where

N_t = density of trapping levels
n = density of electrons in conduction band
P = density of holes in valence band
Q = number of electrons transferred per unit volume by thermal motion from the valence band to the trapping levels
γNP = the number of recombinations between electrons at the trapping levels and holes in the valence band per unit volume per unit time

The recombination coefficient α and trapping coefficient β are given by

$$\alpha = \sigma_1 v \quad \text{and} \quad \beta = \sigma_2 v$$

where σ_1 is the effective cross section of capture of a hole by an electron in the valence band and σ_2 is the effective cross section of capture of an electron by a local level. Also, v is the mean velocity of an electron in the conduction band.

Nadzhakov and Kashukeev (13) showed that near room temperature, the dark depolarization proceeds so slowly that terms like Q and γNP in Eqs. (2) and (3) can be neglected. The equations now reduce to the form

$$\frac{dn}{dt} = h_1 + h_2 - \alpha nP - \beta(N_t - N)n \tag{5}$$

$$\frac{dN}{dt} = -h_2 + \beta(N_t - N)n \tag{6}$$

$$\frac{dP}{dt} = h_1 - \alpha nP \tag{7}$$

The formation of an "intrinsic" photoelectret is defined by these equations. The photoelectret charge at any point depends only on exposure $Z = It$, known as the reciprocity law.

We shall assume that Adirovich's solution of Eqs. (1)–(3) describes satisfactorily the kinetics of excitation of an ideal crystal phosphor by illumination. We assume that the necessary and sufficient condition of the validity of Adirovich's solution is the fulfillment of the reciprocity law, which can be formulated as follows: The density of electrons in trapping levels (N) depends on the product of intensity of illumination I and the time of exposure t; that is,

$$N = N(z), \qquad \text{where } z = It \tag{8}$$

When this is substituted in Eq. (6), we get

$$\frac{dN}{dz}I = h_2 IN(z) + b[N_t - N(z)]n \tag{9}$$

Equations (8) and (9) give the electron density in the conduction band, which is given by

$$n = n_0(z)I \tag{10}$$

When Eq. (10) is substituted in Eq. (7), it gives

$$\frac{dP}{dz} = h_1 - \alpha n_0(z)P \tag{11}$$

This equation implies that hole density (P) is also a function of z; that is,

$$P = P(z) \tag{12}$$

Substituting Eqs. (8), (10), and (12) into Eq. (4), we arrive at the first quasi-stationary condition:

$$n \ll N \tag{13}$$

Substituting Eq. (10) in Eq. (5) and using Eq. (13), we get

$$\frac{dn_0(z)I}{dz} = h_1 + h_2N(z) - \alpha n_0(z)N(z) - \beta[N_t - N(z)]n_0(z) \tag{14}$$

Equation (14) shows that the reciprocity law is obeyed only if we neglect the term $\{dn_0(z)/dz\}I$—that is, when the following condition is obeyed:

$$\frac{dn_0(z)I}{dz} \ll h_2N(z) - \beta[N_t - N(z)]n_0(z) \tag{15}$$

This gives the second quasi-stationary condition:

$$\frac{dn}{dt} \ll \frac{dN}{dt} \tag{16}$$

It is clear from Eqs. (13) and (16) that when the reciprocity law is obeyed, the quasi-stationary electron density is low and vice versa.

The system of Eqs. (9), (10), (14), and (4) do not give the electret effect. A strict solution must take into account the following aspects:

1. Transport of conduction electrons by field
2. Diffusion of electrons due to nonuniform distribution in the direction of applied field

To describe the formation of the photoelectret state, current divergence terms must be introduced into Eqs. (5) and (7). In the one-dimensional case, the quantities n, N, and P should be functions of the x coordinate and time t. Introducing these modifications, the following nonlinear equations are obtained:

$$\frac{\partial n}{\partial t} = h_1 + kN - \alpha nP - \beta n(N_t - N) + \frac{\partial}{\partial x}\left(n\mu_n E - D_n \frac{\partial n}{\partial x}\right) \tag{17}$$

$$\frac{\partial N}{\partial t} = -kN + \beta n(N_t - N) \tag{18}$$

$$\frac{\partial P}{\partial t} = h_1 - \alpha nP + \frac{\partial}{\partial x}\left(P\mu_p E - D_p \frac{\partial P}{\partial x}\right) \tag{19}$$

where

E = electric field
μ_n = electron mobility in conduction band
μ_P = hole mobility in valence band
D_n = diffusion coefficient of electrons
D_P = diffusion coefficient of holes

The charge neutrality condition given by Eq. (4) may now be replaced by the charge conservation condition:

$$\int_0^l P\,dx = \int_0^l (N+n)\,dx \tag{20}$$

where the integration was along the length of the photoconductor in the direction of external electric field.

If the external field is E_o and the space charge field is E_1, then

$$E = E_1 - E_0 \tag{21}$$

Also,

$$\frac{\partial E_1}{\partial x} = \frac{4\pi e}{E}(P - N - n) \tag{22}$$

where $(P - N - n)e = \sigma e$ is the charge density at any point in a photoelectret.

The quantity $\sigma = P - N - n$ may be obtained by solving the system of Eqs. (17) to (19); s is a function of time t and the x coordinate. Equations (17) to (19) represent the case of mobile electrons and holes and describe the "pseudo-photoelectret" state in a dielectric.

The hole current divergence is equal to zero when electrons from the activator levels reach the conduction band, and holes are formed at these levels in a crystal subjected simultaneously to illumination and an electric field. Using the above concepts, Eqs. (17) to (19) take the form

$$\frac{\partial n}{\partial t} = h_1 + kN - \alpha nP - \beta n(N_t - N) + \frac{\partial}{\partial x}\left(n\mu_n E - D_n\frac{\partial n}{\partial x}\right) \tag{23}$$

$$\frac{\partial N}{\partial t} = -kN + \beta n(N_t - N) \tag{24}$$

$$\frac{\partial P}{\partial t} = h_1 - \alpha nP \tag{25}$$

This system of equations is also correct when the hole mobility μ_p in the valence band is negligible compared to electron mobility in the conduction band.

Formation of an "intrinsic" photoelectret is given by Eqs. (23) to (25) if the activation energy of the trapping levels is large and there are no direct electron transitions from the valence band to the trapping levels (from activator level to conduction band). A "pseudo-photoelectret" cannot be distinguished from an "intrinsic photoelectret" if the hole mobility μ_p is sufficiently small.

At this stage we may note whether the reciprocity law is obeyed during the process of photoelectret state formation or not.

The reciprocity law means that the photoelectret charge at any point depends only on the exposure $z = it$; that is,

$$\sigma = P - N - n = \sigma(z, x) \qquad \text{when}\, 0 \le x \le 1 \tag{26}$$

where l is the length of the photoconductor.

If we assume that the Eq. (26) is obeyed during the processes given by Eqs. (17) to (19), we find that

$$\frac{\partial}{\partial t}(P - N - n) = \frac{\partial \sigma}{\partial z}I = \frac{\partial}{\partial x}\left(n\mu_n E - D_n\frac{\partial n}{\partial x} - P\mu_p E - D_p\frac{\partial P}{\partial x}\right) \tag{27}$$

since $E = E_1 - E_o = E(z)$ in Eq. (27), it follows from Eq. (26) that

$$P = P_0(z, x)I;\, n = n_0(z, x)I \tag{28}$$

When Eq. (28) is satisfied, the reciprocity law of Eq. (26) is not obeyed, since $\sigma = P_0(z, x)I - N - n_0(z, x)I$ is self-contradictory unless $P \approx N$ or $\sigma = 0$, which are trival cases. Equations (17) to (19) show departure from reciprocity law of Eq. (26). This departure is due to the presence of electric fields.

We may derive the conditions for the reciprocity law which will be valid under the conditions represented by Eqs. (23) to (25):

From Eq. (27),

$$\frac{\partial}{\partial t}(P - N - n) = \frac{\partial \sigma}{\partial z}I = \frac{\partial}{\partial x}\left(n\mu_n E - D_n\frac{\partial n}{\partial x}\right) \tag{29}$$

From this, it can be concluded that

$$n = n_0(z, x)I \tag{30}$$

If we substitute Eq. (30) into Eq. (25) and use $h_1 = r_1 I$, we find a solution $P = P(z, x)$. Similarly, when we put Eq. (30) into Eq. (24) and use $k = r_2 I$, we obtain $N = N(z, x)$. From these two results and from the relation

$$\sigma = P(z, x) - N(z, x) - n_0(z, x)I$$

we find the first necessary condition as

$$|n \ll |P - N|$$

Also when we substitute Eq. (30) into Eq. (23), we obtain the second necessary condition as

$$\left|\frac{\partial n}{\partial t}\right| \ll \left|\frac{\partial P}{\partial t} - \frac{\partial N}{\partial t}\right| \tag{31}$$

Fridkin calculated the temperature dependence of the photopolarization current and found that

$$J_2(t^1) = aI_1E(1-\theta)[(1 - e^{-\theta(1-\theta) - I_1 t_1/\epsilon}]e^{-\theta(1-\theta) - I_2 t_1/\epsilon} \tag{32}$$

where

$\theta = j_1(\infty)/j_1(\mathrm{O})$
I_1 = intensity of polarization radiation
I_2 = intensity of depolarization radiation
j_1 = depolarization current
E = applied electric field

Later Kallmann and Rosenberg calculated the space charge at the electrode, which is given by

$$\sigma_0 = \frac{\gamma K V_0 d_{2g}}{4\pi n d_g (d_{1g} + d_{3g})} \tag{33}$$

where d_2 is grain thickness and d_{1g}, d_{2g}, and d_{3g} are the distances of the charge layers in the three-layer capacitor, and g pertains to grain. Charges mostly concentrate in layers near the electrodes.

The essential conditions for creation of persistent polarization are (a) a surface layer of usually smaller conductivity than that of the bulk material and (b) a sufficient number of traps.

In a polarized photoelectret the thermal release of trapped charge results in dark decay of polarization.

$$\frac{d\sigma}{dt} = -\frac{C_0\sigma_0}{t+\alpha} \tag{34}$$

For (Zn : Cd)S the rate of decay of surface charge is given by

$$\sigma_{\mathrm{dark}}(t) = \sigma_0\left(1 + C_0 \ln\frac{t_0+\alpha}{t+\alpha}\right) \tag{35}$$

where σ_0 is the polarization at $t = t_0$ and C_0 is a material constant. These results suggest bulk polarization for various intensities and voltages, independent of sample thickness. The dark decay of free charge is

$$\left(\frac{d\sigma}{dt}\right)_{\mathrm{dark}} = -\frac{C_2\sigma(t)}{t+\alpha}$$

Decay under illumination is given by

$$\left(\frac{d\sigma}{dt}\right)_{\mathrm{release}} = -C_3\sigma(t) \tag{36}$$

where C_0 and C_3 are constants. It was found by Kallmann that the observed dark decay is faster than the calculated value, while radiation decay is slower than the corresponding theoretical value. This is so because of the assumption that charge displacement is proportional to field strength.

DEPOLARIZATION OF PHOTOELECTRET

When a dielectric after complete polarization is short-circuited in the dark, its polarization decays with time, giving rise to a depolarization current. It has been observed that the dark depolarization at the first stage is rapid; but as time passes, it decays slowly over a long period. It was shown by Kallmann and Rosenberg (9) that dark depolarization of the photoelectret depends not only on the dielectric itself but also on the thickness of the dielectric, the kind of radiation used for polarization, the voltage of the polarizing field, and a number of other conditions.

Complete depolarization of a photoelectret cannot take place in the dark. For total depolarization, the photoelectret should be illuminated with radiation.

The initial drop in polarization in the presence of light is more rapid than dark depolarization. Tartakovski and Kaminker (14) showed that depolarization of a photoelectret during illumination occurs by the formation of free charge carriers and their migration under the action of the internal field of the photoelectret. These free carriers may be created by the transfer of electrons from the valence band to the conduction band, or they may be ejected directly from the trapping levels. Due to thermal energy, carriers are ejected from trap levels, which give rise to dark depolarization current. Thus the dark depolarization current is due to charge carriers which are trapped in shallow levels.

Residual polarization of a photoelectret increases with the increase of the polarizing voltage and the thickness of the electret. Illumination at low temperature will partially discharge the photoelectret. Complete depolarization of a photoelectret can be brought about only when it is heated to the temperature at which it was polarized.

The thermal depolarization current of a photoconductor has several peaks depending on the distribution of traps. Thermally stimulated conductivity (TSC) is obtained from thermal depolarization of the photoconductor.

PARAMETERS CONTROLLING THE PHOTOELECTRET STATE

There are a number of parameters which affect the formation of the photoelectret state. They will be discussed below.

Intensity of Illumination

An increase in intensity of illumination increases the density of free carriers available for trapping. According to Fridkin (17), the nonlinear equation which describes the time dependence of electron concentration in the trapping levels during the process of illumination of the crystal in the presence of an applied field (E_0) is given by

$$\frac{dN}{dt} = -IN_c\nu\exp\left(-\frac{E_a}{kT}\right) + n(N_t - N)vS_t \tag{37}$$

where ν is the escape frequency, S_t is the capture cross section of the trapping center, v is the velocity of electron in the conduction band, E_a is the activation energy of the trap level, N_c is the density in conduction band, I is the intensity of polarization radiation, N is the number of filled traps per unit, and N_t is the total number of traps per unit volume.

At a given value of applied field, polarization of a photoelectret reaches saturation after a certain response time depending on the intensity of illumination (I). When the steady state is reached, a saturation current (J_S) flows through the specimen. At this stage, there is no change in the number of electrons trapped in trapping levels. Thus we have

$$\frac{dN}{dt} = 0 \qquad \text{when} \qquad J_S = -e\mu n_S E \tag{38}$$

where the subscript s denotes the value at saturation.

Also,

$$E = E_0 - E_1 \simeq E_0$$

where

E_1 = field due to polarization of the specimen
E_0 = applied field

From Eq. (38) we have

$$n_S = -\frac{J_s}{e\mu E_0} \tag{39}$$

With the condition $dN/dt = 0$, Eq. (37) reduces to

$$n(N_t - N)vS_n - IN_c\nu e^{-E_a/kT} = 0$$

Using Eq. (38), the above equation reduces to

$$N_S = \frac{J_S N_t}{J_S - N_c I e \mu E_0 e^{-E_a/kT}} \tag{40}$$

where N_S is the number of electrons in the trapping levels at saturation.

Equation (40) shows that with the increase of electric field and intensity of illumination, N_S increases; that is, the charge increases linearly with intensity of illumination when the intensity is low but acquires a saturation value at higher intensities. At saturation, only a small number of traps are filled. This implies that saturation is not due to the filling of all the traps, but to dynamic equilibrium between the trapping levels and the respective bands under the influence of the light-modified Fermi levels.

Polarizing Field

In a photosensitive dielectric, illumination causes generation of the charge carriers to be available for trapping. The polarizing field causes these charge carriers to drift through the dielectric, giving rise to an accumulation of trapping carriers toward the surface of the photoconductor. When we increase the field, the spatial shift of the carriers increases which decreases the recombination probability. According to Kallmann and Rosenberg, the photoelectret charge increases with increasing field. No saturation was observed in their investigations except in the case of CdS. This effect can be explained on the basis that the traps are not completely filled; and as the field is increased, more and more traps are filled.

During the process of polarization, the charge carriers which are trapped in the bulk of the dielectric have longer trapping time because of the reduced probability of their rejection by the absorption of photons, as the photons are being rapidly absorbed within a few microns of the illuminated surface. This explains why the photoelectret charge increases increased voltage.

Polarization of anisotropic crystal may be different for fields applied in different directions. Thus polarization of the polycrystalline photoelectret may change due to field reversal. The polarization of a dielectric also depends upon the type of electrodes being illuminated.

Dark Polarization

In the presence of a field, dark conductivity of a dielectric causes polarization of the dielectric even in the absence of illumination. Photopolarization of a dielectric is always accompanied by dark polarization. Photopolarization for most of the materials (sulfur, anthracene, etc.) has been found to be greater than the corresponding dark polarization. However, for small exposure (It), the photopolarization decreases to such an extent that it may prove to be nearly the same as the corresponding dark polarization. The dark polarization for some dielectrics like electroluminescent ZnS proves to be greater than photopolarization. Photopolarization of a dielectric is taken to be the difference between the total polarization when a photoelectret is formed and the corresponding dark polarization.

Kallmann and Rosenberg observed that a preliminary excitation of anthracene and [Zn : Cd]S with ultraviolet radiation increases the dark polarization. This effect is known as the "excitation effect." Kallmann and Rosenberg studied the effect of direction of the polarizing field on dark polarization. It was observed that reversal of the polarizing field did not always change the sign of dark polarization.

Dark polarization is produced by the thermal liberation of conduction electrons from shallow trapping levels. Ultraviolet radiation transfers electrons from the valence band or from activator levels to the conduction band (excitation level). In this way, electrons fill the trapping levels including the shallow levels responsible for dark polarization, and the electron density in the conduction band rises. The process of filling the trapping levels in the absence of an electric field takes place randomly but fairly uniformly in the dielectric. But when an electric field is applied, it displaces the conduction electrons and causes a nonuniform distribution of electrons or holes and gives rise to dark polarization. Increased energy of excitation increases the electron occupancy of the trapping levels, which causes dark polarization. This explains the rise of dark polarization with increase in the duration of excitation (t) and the energy (It) received during excitation.

Charging Time

A photoconductor has both trapping and recombination centers. The presence of trapping and recombination centers decreases the photoelectret as well as the lifetime of charge carriers. Trapping of carriers is a desirable factor for photoelectret formation, but it is undesirable for photoconductors. As the charging time increases, more and more charge carriers are generated, thus increasing the trapping probability and hence the photoelectret charge. Polarization of a photoelectret reaches saturation when a dynamic equilibrium is established between the rate of generation of carriers and the rate of trapping plus recombination. According to Kallmann and Rosenberg, the dependence of polarization, P, of a photoelectret on the duration of polarization, t, obeys the following empirical law:

$$P = P_{\max}(1 - e^{-t/\tau}) \tag{41}$$

where τ is the response time.

Studies of the formation of the photoelectret state in a dielectric showed that the dependence of the photoelectret charge on charging time (t) at a fixed intensity of illumination is governed by the nature of the dielectric and by the conditions of the polarization (in particular the wavelength of radiation) used. The polarization of a photoelectret depends on exposure (It), for any duration of polarization (t) or intensity of illumination (I). This law is known as the reciprocity law. Some dielectrics show departure from the reciprocity law. Departure from the reciprocity law depends on the nature of the dielectric and its condition of polarization. In the case of low dose rates and long durations of irradiation, departure from the reciprocity law may be due to an increased relative importance of dark depolarization under such conditions.

Energy of Illumination

The formation of the photoelectret state as a function of the energy of illumination was studied by Kallmann and Rosenberg. They observed that the light with wavelength longer than the absorption edge of a given dielectric produced slight photoconductivity and some polarization. This effect is related to the absorption of light by activator atoms in the dielectric, which produce electron transitions from the activator levels to the conduction band. The occurrence of the peak in the photoelectret charge versus λ (energy of illumination) curve at a particular wavelength may correspond to the absorption edge of the dielectric.

Temperature of Polarization

Temperature is also an important parameter which determines the polarization of the photoconductor. At a fixed voltage and intensity of illumination, the number of charge carriers trapped in trap levels will decrease with an increase in temperature. This will decrease the photoelectret charge.

Decrease in photoelectret charge with temperature is given by the relation

$$Q_{\mathrm{ph}} = \frac{Q_0}{T} \tag{42}$$

The temperature dependence of the photoelectret effect is explained by considering the transformation of the trapping center to recombination centers, when the quasi Fermi level shifts toward the conduction band as a consequence of photon irradiation (18). This gives the concept of photoelectret transition temperature (T_{pE}). Thus the photopolarization is not the algebraic sum of the photoelectret polarization and the dark polarization, but it can be given by

$$Q_{\mathrm{pp}} = Q_{\mathrm{pE}} + Q_{\mathrm{dp}}, \qquad T < T_{\mathrm{pE}} \tag{43}$$

$$Q_{\mathrm{pp}} \neq Q_{\mathrm{pE}} + Q_{\mathrm{dp}}, \qquad T > T_{\mathrm{pE}} \tag{44}$$

The photoelectret transition temperature is the temperature at which $Q_{\mathrm{pp}} = Q_{\mathrm{dp}}$. This indicates that T_{pE} depends upon the conditions of polarization; and once these conditions are defined, it will be characteristic of the photopolarization process. Because T_{pE} is governed by the transformation of the trapping centers to the recombination centers, this is an important characteristic of a photoconductor's photopolarization process to correlate the Q_{pp}, Q_{dp} and the type of trap centers.

Photoelectrets are simultaneously thermoelectrets, since illumination of photoelectrets at low temperatures discharges them only partially. Total depolarization occurs in photoelectrets only when they are heated to a temperature at which the polarization was carried out. Conversely, the heating of a photoelectret without simultaneous illumination showed that the total charge could not be liberated in this way.

The effect of temperature on the photoelectret polarization in sulfur monocrystal was studied by Nadzhakov and Kashukeev (19). Nadzhakov and Kashukeev concluded that the reduction of the photopolarization of a sulfur monocrystal at increased temperature is due to thermal transition of electrons from the valence band to the discrete levels. These transitions reduce to photoelectret polarization and increase the hole density in the valence band, causing an increase of the dark conductivity of the crystal.

Another possible mechanism of changes in the photoelectret polarization is the diffusion of charge across the dielectric–electrodes boundary. According to Nadzhakov and Kashukeev, the changes in the photoelectret polarization with increase of temperature are due to volume recombination and diffusion of charge across the dielectric–electrodes boundary. At low temperatures, both processes proceed slowly, and that is why the photoelectret charge is relatively stable.

APPLICATIONS

Electrets find uses in various forms. Perhaps the most significant application of photoelectrets have been for dry photography and in duplicating prints in the form of electrophotography (20). They also find applications in electrostatic measuring instruments, air filters, electrostatic voltage generators, microphones, radiation dosimeters and piezoelectric devices (21), pollution control (22), holographic image intensification (23), and so on.

They have also been used in memory devices for data storage. Photoelectrets are used in prosthetic devices, with wide application in medical science.

Photoelectrets for Holographic Image Recording and Amplification

Photoelectrets prepared from photorefractive crystals of $BaTiO_3$, $LiNbO_3$, $Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$, and so on, have been recently used by Pillai et al. (23) for recording holographic images. When a uniformly polarized photoelectret of a $BaTiO_3$ crystal is exposed to the two interacting subject and reference beams for photographic image formation, periodic illumination of the crystal results, and the eletrons and holes are optically excited from the filled donor or acceptor sites to the conduction or valence band, where they migrate to dark regions in the crystal by diffusion or drift. These transported charges form a space-charge grating in the crystal, the field to which, in turn, modulates the refractive index of the crystal through the electro-optic effect. This space-charge field and the resultant refractive index would be significantly higher in a photoelectret-induced crystal due to its more efficient separation of the charge carriers than in the unpolarized crystal. Researchers have reported an enhanced holographic image amplification gain of over 24,000 at a wavelength of 514.5 mm using $BaTIO_3$ photoelectrets. The amplification gain is found to depend on the beam mixing geometries, the poling conditions, and signal-to pump beam intensity ratio. The amplification is found to increase linearly with the photoelectret-forming field as well as the illumination intensity.

PRINCIPLES OF XEROGRAPHY

Electrophotography is well known in the photocopy industry, where it is rapidly gaining a major portion of the market (23,24,25). However, in addition to photocopying from paper and microfilm, electrophotography has found application in printing and reproduction and in radiology. Applications to such other fields as facsimile, microimage storage and retrieval, data processing and display, and other specialized uses are in various stages of development. Electrophotography in its broadest sense consists of many different processes. These processes involve the interaction of light and electricity as the basic ingredients for image formation. Electrophotographic studies give us useful information about the physical

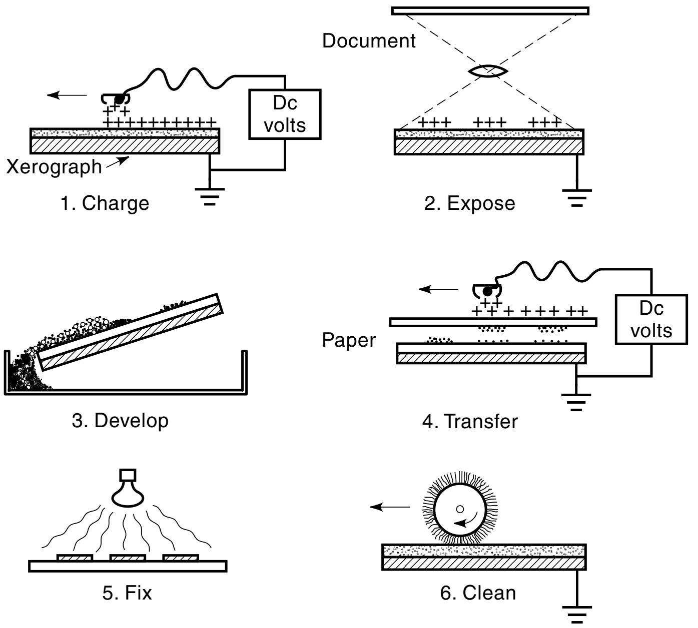


Figure 4. Steps of xerography.

parameters of the material such as light decay, dark decay, charge acceptance, constant potential, and quantum efficiency. At present, xerography is the highly developed field of electrophotography.

Xerography differs from other known photographic processes. It is a dry photoelectric process. No chemical reactions are involved.

Usually five steps are involved in making a print by xerography (Fig. 4):

1. Sensitizing the xerographic plate by electrical charging.
2. Formation of latent image by exposing the plate.
3. Developing the latent image with fine particles.
4. Transferring the developed image to paper or other materials.
5. Fixing the image by fusing.

Sensitizing of Xerographic Plate

Corona Discharge Technique. The electrosensitization of a photoconducting layer is done by the corona discharge technique. A corona discharge can be obtained by applying high voltage to a thin smooth conducting wire, which is mounted along the axis of a long hollow metallic cylinder. A high potential across a wire or point-shaped electrode causes air breakdown. The breakdown is in the form of glow discharge. This discharge in air—atmosphere—is usually called a “corona.” When a positive potential is imparted to the wire with respect to the cylinder, it is surrounded by a hazy sheath, which appears bluish green in air. The application of a negative potential to the wire with respect to the cylinder causes generation of a regularly spaced, short, reddish spray into a continuous sheath.

The high tension wire is given a positive potential in case of a positive corona. By ionization radiation, electrons are formed in the surrounding space which move toward the high-intensity field region near the wire where they gain sufficient energy, thus ionizing the gas molecules. Avalanches are formed by the ionizing process. The positive ions move away from the wire. The field in which they move is a decreasing one. Positive ions carry most of the current in the space outside the glowing envelopes (28,29). Discharge is generally maintained by the photoionization of the gas. The main products of the corona discharge in air are ozone and oxides of nitrogen (30). In the case of a negative corona discharge, positive ions move toward the wire. The positive ions are formed by electron impact near the wire. A self-sustained discharge is maintained when these positive ions produce electrons by bombarding the cathode wire with relatively high energy received from the field. The only current outside the region of ionization is caused by electrons which move toward the anode.

The layer can be sensitized by exposing the plate to corona discharge. The corona unit sprays electrical charges (ions) uniformly over the photoconducting layer. The operation must take place in the dark; otherwise the charge carriers will leak away from the surface. The amount of charge accepted and retained by the layer is an important process because it decides the magnitude of contrast which can be obtained in the image. The total charge accepted by the photosensitive layer depends upon a number of parameters such as grid voltage, charging time, and corona voltage. By adjusting these parameters, the charge accepted by the layer can be increased.

Forming the Latent Image

The sensitizing layer is exposed by using a camera, by contact exposure, or by projection. Electrical charge is conducted away from the plate surface where light strikes the surface. However, the charges are retained in the dark areas of the image. Thus, a latent electrostatic image of the object is formed on the layer.

Developing the Latent Image

The latent image is developed by applying a pigmented resin powder, carrying an electrostatic charge of opposite sign. The developer is a mixture of triboelectrically compatible “dye”-coated resin and “carrier beads” which produce opposite charges on the resin powders due to friction. The developing material is brought very close to the plate surface where the latent image is formed. The powder is attracted and held by the charged areas of the image.

Transferring and Fixing

The powder image is either fixed by melting as in the electrofax system or it is transferred to a fresh sheet of paper as in the transfer electrophotographic system. For this, the paper is kept in contact with the image side of the plate, charging the paper electrically with the same polarity as that of the latent image. Then the paper is stripped from the plate. The charge applied to the paper overcomes the attraction of the latent image for the developer particles and pulls them onto the paper. The image thus obtained on the paper is fixed on the paper by the heat treatment. Thus finally a permanent bright print is obtained which employs no liquid processing. Several copies can be obtained from a single corona charging. In modern xerographic copying machines, continuous charging of a photosensitive drum, subsequent image development, transfer of the image onto ordinary paper, fixing, and so on, are done in few seconds of time. Any number of copies of the original can be taken as per the requirement.

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PHOTOELECTRIC EFFECT. See PHOTOEMISSION.

PHOTOELECTROCHEMICAL CELLS. See SOLAR ENERGY CONVERSION.

PHOTOELECTRONIC PHENOMENA. See PHOTOCONDUCTIVITY.