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Photosensitization of PbS Films*

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The effect of O_2 on the photoconductive response of evaporated PbS films has been experimentally investigated. The dark conductance g, the photoconductance Δg, and the time constant τ for the photoconductive response of PbS evaporated films vary when the films are exposed to oxygen. Initially g decreases several orders of magnitude when an outgassed film is exposed to oxygen; it reaches a minimum and then increases. The thermoelectric power changes from negative to positive at the minimum in conductance. Δg and τ are given as a function of g. Δg decreases with increasing oxygenation, reaches a minimum near the minimum in g and then increases as g increases after the film becomes p-type; $\Delta g/g$ is a maximum, however, near the minimum in g. On the other hand, τ increases steadily as the film changes from n- to p-type.

These results are attributed to the effect of two oxygen surface states. A low-lying O^- state alters the Fermi level of the originally n-type film. The surface charge thus formed lowers the effective carrier mobility. A higher energy O^{--} state, when empty, traps photoelectrons and hence enhances the hole photoconductivity.

INTRODUCTION

It is generally accepted that the photoconductive effect in PbS-type films can be attributed to the creation of excess current carriers by the action of light. Recently, Rittner and Fine[1] and Humphrey[2] have suggested that high sensitivities and long time constants in these films might be explained by a mechanism whereby the photocarriers are trapped. Minden[3] has pointed out that oxygen adsorbed onto the microcrystalline surfaces of a PbS film can act as an electron trap. He has also shown how such traps can produce the changes in conductivity and thermoelectric power, which are experimentally observed when PbS films are exposed to oxygen.[4] The notion that adsorbed oxygen can act as an electron acceptor is not new. Gibson[5] has attempted to explain the photoconductive effect in PbS films by assuming the light excites electrons out of the oxygen surface traps, thereby lowering the surface space charge barrier to conduction. This particular barrier modulation theory has been disproved on a number of points, but there is still evidence that oxygen surface states play an active role in the photoconductive process.

The present paper reports experiments in which evaporated PbS films were treated with O_2. The consequent changes in the magnitude and time constant of the photoconductive response were observed. Changes in the dark conductance and the sign of the thermoelectric power were simultaneously measured, and a definite correlation was made between the dark conductance and the photoconductive response. A theory for the correlation is proposed in terms of the effect of adsorbed oxygen. Although oxygen acts to reduce the effective carrier drift mobilities, it also enhances the lifetime of the photoholes by trapping the photoelectrons.

Experimental Methods and Results

The apparatus and the general procedures of evaporating lead sulfide films have been described previously.[3] Films evaporated in vacuum and through oxygen were investigated. The cell was kept in a circulating water bath at room temperature during the evaporation. The oxygen pressure was kept constant kinetically at about 500 μ during evaporation for the oxygen evaporated films. Both the fresh vacuum and fresh oxygen evaporated films were p-type as determined from thermoelectric measurements. The films were quite easily made n-type by outgassing in vacuum at temperatures usually less than 250°C. Once a film was n-type, it was exposed to oxygen and the changes in the dark conductance and photoconductance were observed as the film went from n- to p-type. It was possible to follow these changes at room temperature when oxygen was added to a n-type oxygen evaporated film. However, the vacuum evaporated films sometimes had to be heated gently in the presence of oxygen in order to obtain significant changes in the film conductance. Alternatively, a p-type film may be outgassed in steps. That is, by heating the film in vacuum for brief periods of time and then cooling it, the variations in the film conductance and photoconductance can be observed as the film goes from p- to n-type.

The photoconductive response was measured by exposing the cell (see Fig. 1) to light square-wave modulated at 90 cps. The signal developed across the load resistor was amplified and measured with a vacuum tube

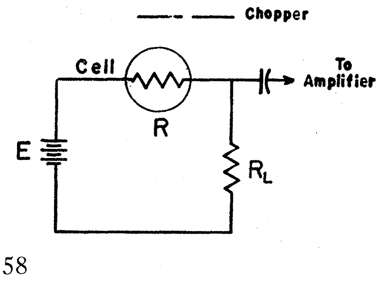

Fig. 1. Measuring circuit for photoconductance.

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* This work was supported in full by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[1] E. S. Rittner and S. Fine, Phys. Rev. **98**, 545 (1955).

[2] J. N. Humphrey, Naval Ordnance Laboratory Report NAVORD-3922, 1955 (unpublished).

[3] H. T. Minden, J. Chem. Phys. **23**, 1948 (1955).

[4] H. T. Minden, J. Chem. Phys. (to be published).

[5] A. F. Gibson, Proc. Roy. Soc. (London) **B64**, 603 (1951).

voltmeter. The light source used for the oxygen evaporated films was a 2-watt tungsten filament lamp, and a microscope lamp was used for the less sensitive vacuum evaporated films.

The cell time constant was determined using a concentrated arc source. The light was modulated at a frequency comparable with the reciprocal of the time constant. The signal was displayed on an oscilloscope screen after it was passed through a wide band amplifier. Photographs of the oscilloscope trace were taken and analyzed.

The photoconductive circuit is shown in Fig. 1. The photocurrent, Δi, is given by

$$\Delta i = E g_L^2 \Delta g / (g+g_L)(g+\Delta g+g_L), \qquad \text{(a)}$$

where Δg = the photoconductance, $g=1/R$ = the cell dark conductance, $g_L=1/R_L$ = the load conductance, and E = the bias voltage, usually 45 v. The signal or photovoltage, Δv, developed across the load is

$$\Delta v = \Delta i / g_L = E g_L \Delta g / (g+g_L)(g+\Delta g+g_L). \qquad \text{(b)}$$

Experimentally, it has been found that Δg is very much less than g or g_L so that Eq. (b), solving for Δg reduces to

$$\Delta g = \Delta v (g+g_L)^2 / E g_L. \qquad \text{(c)}$$

The photoconductance was calculated from Eq. (c).

Figure 2 shows plots of Δg *vs* g for a vacuum evaporated film and for two oxygen evaporated films. The absolute values of g and Δg changed from run to run for the oxygen evaporated films. Moreover, their sensitivity tended to decrease from run to run. These changes were associated with the heating of the film during the oxygen treatment. The curves were normalized at the point of minimum Δg. Figures 2(A) and 2(C) have the same general shape. When the film was *n*-type and oxygen was added, Δg decreased steadily to a minimum at the minimum conductance. Once the minimum in g was passed and the film was *p*-type, Δg increased as the film became more *p*-type, and this increase was greater than when the film was *n*-type. On the other hand, in Fig. 2(B) when the film was *n*-type and oxygen was added, Δg initially decreased, then increased slightly, before it decreased again to a minimum near the minimum in g. After the film became *p*-type, Δg increased regularly like the films described above. For still another film Δg was constant in the *n* range.

Figure 3 shows a plot of the sensitivity, $\Delta g/g$ *vs* g. The maximum sensitivity may occur either on the *n*- or the *p*-type side of the conductance minimum. The sensitivity always decreased more slowly with increasing g in the *p* range than in the *n* range. In fact, it was observed that the sensitivity can be constant for a considerable range of *p*-type conductivity. It should be emphasized that the signal Δv is proportional to $\Delta g/g$ and not Δg. Therefore, with constant bias voltage, the signal is a maximum at the maximum sensitivity. This maximum sensitivity at the minimum conductance has also been observed by others.[6] Moreover, the oxygen evaporated films were about 10 to 20 times more sensitive than the vacuum evaporated films. However, the most sensitive oxygen evaporated films were about 100 to 1000 times less sensitive than an Eastman Kodak cell.

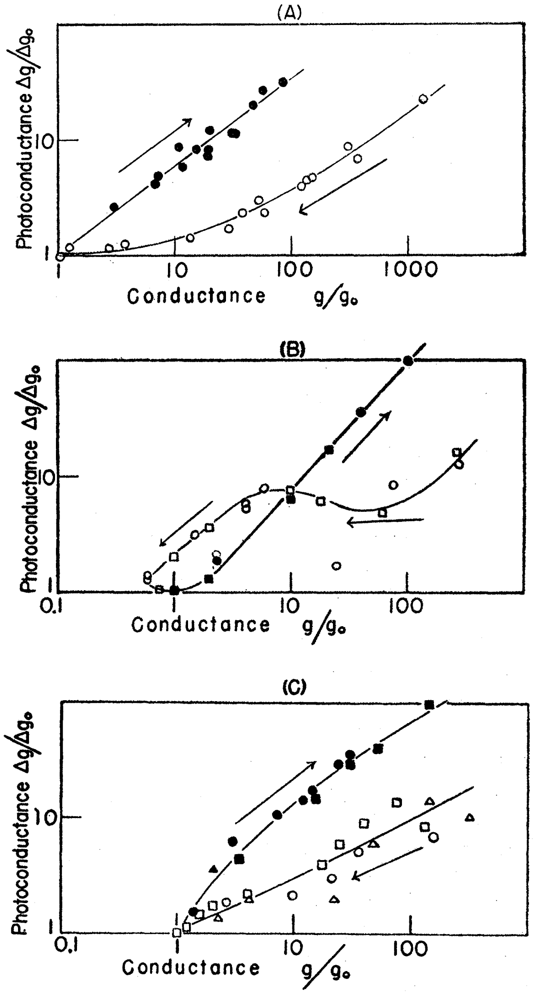

FIG. 2. Photoconductance *versus* conductance. Open points indicate *n*-type conductivity; filled points, *p*-type. Arrows indicate direction of increasing oxygenation. (A) Vacuum-evaporated film V-9. $g_0=3.3$ μmho, $\Delta g_0=650$ $\mu\mu$mho. (B) Oxygen evaporated film A-19. Circles, $g_0=0.72$ μmho, $\Delta g_0=20$ $\mu\mu$mho; squares, $g_0=1.0$ μmho, $\Delta g_0=27$ $\mu\mu$mho. (C) Oxygen evaporated film A-18. Circles, $g_0=0.065$ μmho, $\Delta g_0=5.7$ $\mu\mu$mho; squares, $g_0=0.059$ mho, $\Delta g_0=7.1$ $\mu\mu$mho; triangles, $g_0=0.46$ μmho, $\Delta g_0=58$ $\mu\mu$mho.

Analysis of the oscilloscope traces showed that the signal decay was exponential. Therefore, the time constant was taken as that time where the signal had decayed to e^{-1} of its maximum value. Figure 4 shows how the time constant changed as an oxygen evaporated film was converted from *n*- to *p*-type as a result of oxygen treatment. For this film Δg was constant when the film was *n*-type and rose as the film became *p*-type.

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[6] Sosnowski, Starkiewicz, and Simpson, Nature **159**, 818 (1947). For the same effect in PbTe films, see D. Bode and H. Levenstein, Phys. Rev. **96**, 259 (1954).

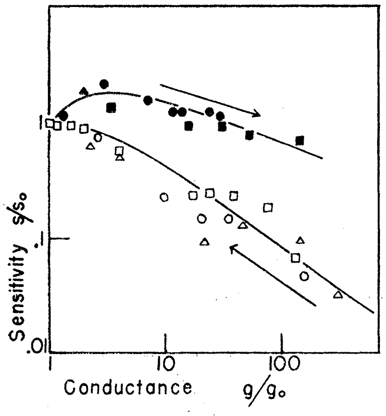

FIG. 3. Sensitivity $\Delta g/g$ *versus* conductance; oxygen evaporated film A-18. $s_0=\Delta g_0/g_0$, [see Fig. 2(C)]. Open points indicate n-type conductivity; filled points, p-type. Arrows indicate direction of increasing oxygenation.

The time constant increased on the n-type side until the film became intrinsic, then it increased still further and became constant when the film was very p-type. Smollet and Pratt[7] also have observed that for p-type films the time constant increases initially, then remains practically constant as the film becomes very p-type.

DISCUSSION

The basic concept used to explain the above results is a duality in the nature of photoconduction in PbS films. First there is what might be called the conventional intrinsic photoconductivity associated with pure PbS. In addition, there is an excess hole photoconductivity due to the trapping of photoelectrons in oxygen surface states. Besides providing surface traps, oxygen adsorbed onto the microcrystalline surfaces of the film also lowers the Fermi level much as do conventional bulk acceptors. Finally the adsorbed oxygen somehow blocks the transmission of current carriers from one microcrystal to the next, reducing the effective carrier mobilities.

To develop the theory, assume first the simplest model of a semiconducting photoconductor. The conductivity and the photoconductivity are given by

$$\sigma=q(\mu_n n_0+\mu_p p_0) \tag{1}$$

and

$$\Delta\sigma=q(\mu_n\Delta n+\mu_p\Delta p), \tag{2}$$

respectively, where n_0 and p_0 are the dark free electron and hole concentrations and Δn and Δp are the changes in the concentrations caused by the action of light.

Outgassed evaporated PbS films are always n-type. The adsorption of oxygen changes not only n_0 and p_0,[3,4] but also the effective mobilities μ_n and μ_p. The reduction in mobilities by oxygen adsorption affect σ and $\Delta\sigma$ alike. On the other hand, the effect of changing n_0 and p_0 on Δn and Δp is more complex, but it can be explained in terms of conventional recombination theory when the film is n-type. The generation equations for electrons and holes are

$$(d\Delta n/dt)=-(\Delta n/\tau_n)+f, \tag{3}$$

$$(d\Delta p/dt)=-(\Delta p/\tau_p)+f, \tag{4}$$

where f is the rate of electron hole pair creation by the light. For low light levels the time constants τ may be assumed independent of Δn and Δp. The steady-state solutions are

$$\Delta n=f\tau_n, \tag{3a}$$

$$\Delta p=f\tau_p. \tag{4a}$$

The Shockley-Read theory of recombination via bulk traps[8] concludes that $\tau_n=\tau_p=\tau$. Substituting Eqs. (3a) and (4a) in Eq. (2),

$$\Delta\sigma=qf\tau(\mu_n+\mu_p). \tag{5}$$

As pointed out above, the reduction in mobility caused by the adsorption of oxygen reduces $\Delta\sigma$. On the other hand, according to the Shockley-Read theory, as the Fermi level is lowered (in this case by the surface oxygen acceptors) τ remains fairly constant while the material is still strongly n-type, rises to a maximum near the intrinsic range, and finally decreases to a constant value in the p-range. Hence while the film is still n-type, μ and τ have opposite effects on $\Delta\sigma$ with increasing oxygenation. For vacuum evaporated PbS films μ decreases faster than τ increases, so that $\Delta\sigma$ decreases steadily as shown in Fig. 2(A). For films evaporated through oxygen, μ initially decreases faster than τ, but there is a slight maximum in $\Delta\sigma$ near the intrinsic point corresponding to a maximum in τ. This effect is shown in Fig. 2(B). In general, for oxygen evaporated films the variation of Δg with g when they are n-type seems to be less reproducible from film to film than the variation when they are p-type. Figure 2(C) shows a case where, with increasing oxygenation, μ decreases faster than τ increases throughout the whole n range. On the other hand, for film A-21 of Fig. 4 the increase in τ just balances the decrease in μ so that in the n range Δg is constant.

In any case, according to the present theory, the sensitivity $\Delta g/g$ is not affected by changes in the mobility. Since τ either increases or remains fairly constant when the Fermi level is lowered from E_c to E_i, while n_0 decreases exponentially as the Fermi level goes

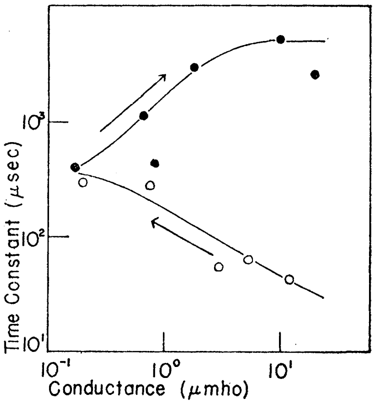

FIG. 4. Time constant for photoconductive decay *versus* conductance; oxygen evaporated film A-21. Open points indicate n-type conductivity filled points, p-type. Arrows indicate direction of increasing oxygenation.

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[7] M. Smollet and R. G. Pratt, Proc. Roy. Soc. (London) **B68**, 390 (1955).

[8] W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

down, $\Delta g/g$ should increase with increasing oxygenation in the n range. This is shown in Fig. 3.

The proposed mobility decrease with increasing oxygenation is somewhat of a mystery. Crude calculations indicate that the barrier height of the negative surface ion layer predicted by Minden[3] is only 10^{-4} volt. Even if the oxygen layer is assumed to be polarized, the dipole barrier is 0.01 volt, unless an unusually large polarization occurs. In this connection, Goldberg and Mitchell[9] have observed that the work function of a PbS film rises from about 5 ev when outgassed to over 6 ev upon exposure to oxygen.

Even if the oxygen acceptors are absorbed into the interior of the microcrystals, the predicted mobility change based on impurity scattering theory is not enough to account for the experimental results on conductivity. This question has already been discussed by Minden.[4] Finally, it is not at all certain that scattering from the surfaces of the microcrystals significantly reduces the mobility. The indications are that the mean free path is about $\frac{1}{10}$ that of the particle size. Perhaps the best suggestion that can be offered at present is that a surface negative ion layer strongly scatters those important carriers which transmit current from one microcrystal to another.

To return to the discussion of photoconductivity, it is assumed here that PbS films are composed of small spherical microcrystals on the surface of which oxygen acceptors are adsorbed. Each oxygen atom has two acceptor levels. The O^- level has an energy in or below the valence band; this level is assumed to be occupied always. The O^{--} level is assumed to be somewhere in the forbidden zone, presumably below the mid-energy (see Fig. 5). As noted above, the films are strongly n-type in the absence of oxygen. Adsorbed oxygen traps electrons from both the conduction and valence bands into the deep O^- state. The Fermi level in each small PbS particle is lowered as oxygen is adsorbed. While the Fermi level is above the O^{--} energy, the O^{--} states are also occupied; but when the Fermi level drops below this energy, these upper states are emptied. These empty states can then trap photoelectrons. It is assumed that recombination does not readily take place from these states. For recombination of electrons trapped in these states to occur, they must first be liberated into the conduction band where they can then recombine fairly quickly. This trapping of electrons gives rise to a long hole lifetime, and therefore an enhanced hole photoconductivity. The O^{--} states are not unlike the "activating centers" described by Rose.[10]

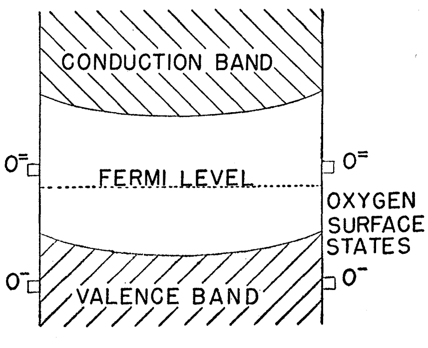

Fig. 5. Energy band diagram of a small PbS particle, showing two classes of oxygen surface states.

Let n_s = the surface concentration of occupied O^{--} states, and N_s the total surface density of these states. The rate of liberation of electrons from these states is

$$g=Bn_sn_1, \tag{6}$$

where $n_1=N_ce^{-(E_c-E_s)/kT}$, E_s = the energy of the O^{--} levels, and $N_c=2(2\pi m_nkT/h^2)^{\frac{3}{2}}$. The trapping rate is

$$r=B(N_s-n_s)n, \tag{7}$$

where n = the free electron concentration near the surface. In the dark,

$$Bn_{s0}n_1=B(N_s-n_{s0})n_0. \tag{8}$$

In the presence of light

$$\begin{aligned}(d\Delta n_s/dt)&\\ &=r-g\\ &=B(N_s-n_{s0}-\Delta n_s)(n_0+\Delta n)-B(n_{s0}+\Delta n_s)n_1.\end{aligned} \tag{9}$$

The steady-state solution is $g=r$, or, using Eqs. (8) and (9),

$$\Delta n_s=(N_s-n_{s0})\Delta n/(n_1+n_0+\Delta n). \tag{10}$$

Substituting Eq. (3a) for Δn,

$$\Delta n_s=(N_s-n_{s0})f\tau_n/(n_1+n_0+f\tau_n). \tag{11a}$$

For low levels of excitation, this becomes just

$$\Delta n_s=[(N_s-n_{s0})/(n_1+n_0)]f\tau_n. \tag{11b}$$

Assume that the potential variation within the microcrystals is small. The requirement of charge conservation is

$$(4/3)\pi a^3(\Delta p-\Delta n)=4\pi a^2\Delta n_s,$$

or

$$\Delta p=\Delta n+(3/a)\Delta n_s, \tag{12}$$

where a is the radius of the microcrystalline sphere. Substituting Eqs. (3a) and (11b) for Δn and Δn_s, respectively,

$$\Delta p=f\tau_n(1+\alpha), \tag{12a}$$

$$\alpha=(3/a)(N_s-n_{s0})/(n_1+n_0). \tag{12b}$$

If the Fermi level is several kT above E_s, $N_s-n_{s0}=0$ and $\Delta p=\Delta n$, as was assumed above. When the Fermi level drops several kT below E_s, $N_s-n_{s0}=N_s$ and $\Delta p\gg\Delta n$. To estimate the magnitude of this effect, assume $a=5\times10^{-8}$ m, $N_s=10^{16}$ m^{-2}, and that $E_s=E_i$, the mid-energy of the forbidden zone. The microcrystals are strongly p-type under these conditions, so that $n_0\ll n_1$ and $n_1=N_ce^{-(E_c-E_i)/kT}\equiv n_i\approx10^{21}$; $\alpha\approx10^3$. This large rise in α as the Fermi level drops below the trap

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[9] A. E. Goldberg and G. R. Mitchell (unpublished work).

[10] A. Rose, Phys. Rev. 97, 329 (1955).

energy is thought to account for the rise in photoconductivity in the p-range of conductivity. This rise can be seen in Fig. 2. Owing to the mobility decrease discussed below, the rise in Δg is not as rapid nor as great as is calculated from the trapping theory. Since the rise in Δg occurs when the film is p-type, it is concluded that the O^{--} level lies slightly below E_i. Further evidence for this is shown in Fig. 3. In the p-range $\Delta g/g$ decreases more slowly with increasing g than in the n-range, and it may even remain constant in the p-range.

Woods quantitatively measured the effect of illumination on the Hall coefficient and resistivity of sensitive PbS films.[11] It can be concluded from his experiments that the photoconductivity might be explained by a one-photocarrier model. This observation corroborates the above theory which predicts that for sensitive films $\Delta p \gg \Delta n$. Equation (11a) predicts that at high light intensities there should be a saturation effect in sensitive films (for which n_1+n_0 is small). This effect has indeed been observed in Eastman Kodak chemically deposited PbS photocells.[12]

In the p-range, the time constant for the decay of the hole photocurrent is just the time it takes for the excess electrons to be liberated from the traps after the light is turned off. To evaluate the transient decay in photocurrent, we expand Eq. (9) and use Eq. (8).

$$(d\Delta n_s/dt)=B[(N_s-n_{s0})\Delta n-(n_1+n_0+\Delta n)\Delta n_s]. \quad (9a)$$

Δn may be neglected as small compared with n_i+n_0. Assuming Δp is not large enough to alter τ_n appreciably, Eq. (3) can be solved.

$$\Delta n = f\tau_n e^{-t/\tau_n}. \quad (3b)$$

Substituting Eq. (12) for Δn_s, and Eq. (3b) for Δn, one can solve for Δp. To a good approximation,

$$\Delta p = f\tau_n(e^{-t/\tau_n}+\alpha e^{-t/\tau_s}), \quad (13)$$

where

$$\tau_s=[B(n_0+n_1)]^{-1}. \quad (14)$$

For film A-21, there could be distinguished only one time constant, and this steadily increased with increasing oxygenation as shown in Fig. 4. When the film is n-type, $\alpha=0$ as discussed above and the time constant is τ_n. As the film becomes intrinsic, τ_n increases. Eventually, however, α and τ_s become appreciable, apparently before τ_n decreases in the p-range. Since only one time constant was observed, evidently $\tau_s \approx \tau_n$ when $\alpha \approx 1$. As the film becomes more p-type, τ_s becomes dominant because of its own large value and also because of the large value of α which masks the intrinsic photoeffect. In the limit, $\tau_s \rightarrow (Bn_1)^{-1}$.

Rittner and Fine observed that the photoeffect in PbS films is highly localized. Although the time constants they measure were large, the photocarrier drift lengths they measured were about an order of magnitude shorter than they calculated from the time constants.[1] The time constant in sensitive films is predicted to be high by the above theory. Furthermore, a very low mobility for both electrons and holes in a sensitive film is essential to the argument of the present work. It appears, then, that in estimating the drift length, Rittner and Fine merely assumed too high an effective mobility.

The trap depth E_s may vary from one film to another. If the microcrystalline surfaces of a given film are fairly perfect, then one would expect the O^{--} levels to be fairly high on the average, because the ions would be relatively loosely bound to the surface.[13] On the other hand, if the surface is very imperfect the traps will have a fairly low energy. It can be shown that $\alpha \propto e^{-E_s/kT}$; hence, high-energy traps contribute little to the enhancement of the photoeffect. It is the difference in energy of the surface traps, then, which is thought to account partly for the variation in sensitivity from film to film.

CONCLUSION

Pure PbS is a poor photoconductor, both in bulk and in film form. The carrier mobilities are low and the lifetimes of the photocarriers are short. The presence of oxygen is necessary to render a PbS film appreciably photosensitive. Moreover, oxygen is a unique sensitizing agent for PbS type films. According to the theory presented here, oxygen alone has two trapping levels which are properly situated with respect to the valence and conduction bands so that the hole lifetime can be enhanced. It is doubtful whether oxygen would sensitize any but a limited group of compounds which now includes PbS, PbSe, PbTe, and Tl_2S. In fact, the sensitization of PbS type salts by oxygen seems so coincidental, that it is improbable that a similar sensitizing agent could be found for other semiconductors. Generally, semiconducting films have high extrinsic carrier concentrations, while the mobility and lifetimes are small. In order to prepare a photoconductor to rival PbS-type films, single crystals would probably be necessary. In the absence of traps the "intrinsic" lifetimes and the mobilities would have to be high compared to those found at room temperature for bulk PbS or Ge in order even to approach the sensitivity of an oxygen-treated PbS-type film. So far these conditions have begun to be realized only in single crystals of InSb and of Au-doped Ge at low temperatures.

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[11] J. F. Woods, Phys. Rev. **99**, 658 (1955).

[12] Kodak Pamphlet No. U-2, Eastman Kodak Company, Rochester, New York.

[13] See reference 4 for a discussion of the relationship between oxygen binding energy and trap depth.