Photoconductivity of Lead Selenide: Theory of the Mechanism of Sensitization*

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The intrinsic, majority, and minority carrier models of photoconductivity are critically examined in terms of an experimental study of the effect of oxygen, sulfur, selenium, and the halogens on PbSe films. It is concluded that the only model adequately describing these experimental results is the following:

Radiation is absorbed in the crystallites and produces a main-band electron transition. Recombination centers which exist in the film produce a very short photoconductive time constant in a non-sensitized film; at room temperature this time constant is so small in PbSe that no photoconductivity is observed. Treatment with oxygen introduces minority carrier traps which increase the majority carrier lifetime and enhance the photoconductive sensitivity, both at room temperature and at reduced temperatures. Similar treatment with sulfur introduces shallow electron traps, which are effective in increasing the majority carrier lifetime at −195°C but not at room temperature. Selenium and the halogens do not introduce minority carrier traps effective at any temperature studied.

INTRODUCTION

IN a preceding paper,[1] henceforth called I, an experimental investigation of the sensitization of PbSe films was described. The effects of various treatments on the electrical properties of PbSe films were studied. Those results which are significant for the development of a model of photoconductivity are the following:

1. PbSe cells which are photoconductive at room temperature were made by sensitizing with oxygen at high temperatures. Similar procedures with sulfur, selenium, and the halogens did not produce sensitivity at room temperature.
2. Cells which are photoconductive at reduced temperatures (−195°C) could be prepared by treatment with any of the above sensitizers.
3. All sensitizing agents examined produced a change of carrier sign from n type to p type. A resistivity maximum of approximately 30 times the bulk resistivity of intrinsic PbSe occurred at or near the condition of reversal of sign of the thermoelectric power.
4. Oxygen- and sulfur-sensitized films showed three time constants at −195°C. Other sensitizers produced only the fastest and slowest of these responses. Only a single time constant was observed at room temperature. Time constant values decreased with rising temperatures.
5. The long-wavelength limit was found to be independent of the particular sensitization procedure or sensitizer used.

Other results concerned with the effect of film thickness on sensitivity have been discussed in another paper,[2] henceforth called II.

In this paper we shall examine various theories currently under consideration for the lead salts (PbS, PbSe, and PbTe) in terms of these results.

A. BASIC MODELS OF PHOTOCONDUCTIVITY

The two primary processes involved in the photoconductive mechanism are: generation of carriers (absorption), and recombination of carriers (lifetime). Secondary processes may be important in amplifying the primary effect.

We may distinguish two types of generation: (a) main band transitions in which a hole-electron pair is generated, and (b) transitions from impurity levels in which a single type carrier is generated.

We may distinguish three types of lifetimes: (a) intrinsic (hole-electron pair) lifetime, (b) minority carrier lifetime, and (c) majority carrier lifetime.

Because of experimental evidence discussed in I and II, the generation process is known quite definitely to be a main-band transition, and we need not discuss it further.

Our major task then is to select the recombination process which best describes the data. We first describe the characteristics of each model.

1. Intrinsic Carrier Model

In this model the number of electrons and holes are approximately the same; this condition is achieved by compensation in the sensitization process. Holes and electrons combine either directly or through recombination centers; in either case the lifetimes of holes and electrons are the same. This model has been discussed recently by Wood,[3] and previously by von Hippel[4] and Rittner, and others.

A useful way to characterize the photoconductive response is the specific responsivity, R_s, which is defined as

$$R_s=\Delta\sigma/4\sigma J, \tag{1}$$

where $\Delta\sigma/\sigma$ is the fractional change in conductivity per unit radiation flux J (watts/cm²). For the intrinsic model

$$R_s=\eta_s\tau_{\text{pair}}/4ndh\nu_s, \tag{2}$$

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[3] C. Wood, Proc. Phys. Soc. (London) **B69**, 613 (1956).

[4] A. von Hippel and E. S. Rittner, J. Chem. Phys. **14**, 370 (1946); O. Simpson and G. B. B. M. Sutherland, Trans. Roy. Soc. (London) **A243**, 547 (1950–1951).

where τ_{pair} is the lifetime of a hole-electron pair, $n=p$ is the intrinsic number of electrons and holes, d is the film thickness, and η_s is the quantum efficiency at the spectral frequency, ν_s, of the signal radiation. Maximum responsivity is thus achieved by minimizing n and p by compensation, and maximizing the lifetime of hole-electron pairs.

2. Minority Carrier Model

Minority carrier photoconductivity depends upon the presence of p-n junctions. One can show that the responsivity is given by

$$R_s=K_1\eta_s\tau_{\text{min}}/4n_{\text{min}}dh\nu_s, \tag{3}$$

where τ_{min} is the minority carrier lifetime and n_{min} is the minority carrier density.

Secondary amplification can play an important role in this model if an array of p-n junctions is present. The diffusion of minority carriers across the p-n junction results in lowering the space-charge barrier at the junction. This allows more current to flow across the junction, greatly enhancing the responsivity. The factor K_1 in Eq. (3) represents this amplification effect. This model has been discussed recently by Slater *et al.*,[5] and previously by Sosnowski *et al.*,[6] and others.

Maximum responsivity is achieved by virtue of n_{min} being small, by making τ_{min} as large as possible, and by amplification through space-charge lowering of the junction potential barrier. In general, a large value of τ_{min} is favored by high-purity single crystals; recombination centers and minority carrier traps shorten τ_{min}.

3. Majority Carrier Model

The expression for responsivity in this case is

$$R_s=K_2\eta_s\tau_{\text{maj}}/4n_{\text{maj}}dh\nu_s, \tag{4}$$

where τ_{maj} is the majority carrier lifetime and n_{maj} is the majority carrier density.

The denominator of Eq. (4) must always be larger than that in Eqs. (2) and (3) for any given material. However, it is possible that τ_{maj} can be made very large by the phenomenon of minority carrier trapping which is discussed below. Thus a high responsivity can be achieved. This model has been discussed recently by Petritz.[7]

In the normal recombination process of holes and electrons through recombination centers, discussed by Shockley and Read,[8] and Hall,[9] the minority carrier first enters the center, after which the majority carrier quickly recombines with the minority carrier. The rate-determining process is normally the rate of entry of minority carriers into the center, because there are so many majority carriers available to make the second step.

However, if the cross section for the second step is abnormally small the majority carrier will be free for an extended period of time after the minority carrier is trapped. In the limit of a very small cross section, the minority carrier may be thermally excited back to the band before recombination in the center occurs. We call such centers nonrecombining traps (or simply traps) to distinguish them from normal recombination centers. The phenomenon of trapping has been discussed for the cases of germanium,[10] silicon,[11] insulators,[12] and lead salts.[13,14]

After the trapped minority carrier is thermally excited back to the band, hole-electron recombination can occur through a normal recombination center, thus terminating the majority carrier lifetime. The majority carrier lifetime will depend on the time the minority carrier spends in the trap. The dependence of τ_{maj} on the energy level of the trap and on temperature is

$$\tau_{\text{maj}}=\tau_0 e^{-E_t/kT}, \tag{5}$$

where E_t is the energy level of the trap below the conduction band.

Thus minority carrier trapping provides a mechanism for enhancing greatly the lifetime of majority carriers, and thereby increasing the responsivity according to Eq. (4). Maximum responsivity is thus attained by optimizing $\tau_{\text{maj}}/n_{\text{maj}}$. In general τ_{maj} and n_{maj} are interrelated.

Secondary amplification can occur in this model through lowering of intercrystalline barrier potentials by the trapped minority carriers, thus increasing the effective majority carrier mobility.[7] This effect is represented in Eq. (4) by K_2.

B. CRITIQUE OF THE VARIOUS THEORIES IN TERMS OF THE EXPERIMENTAL RESULTS

We shall consider these various theories in the light of the results of our experimental study,[1] and attempt to select the one which best interprets the data.

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1. Intrinsic Model

The intrinsic model in PbSe films would indicate that maximum photoconductivity results when the material is well compensated. Then the equilibrium carrier density is a minimum, yielding a maximum dark resistivity, and the time constant as determined by recombination centers is a maximum.[8,9] The action of a sensitizer would be to drain electrons out of the conduction band and out of any traps in the top half of the forbidden band.

We see from the summary of experimental results that the intrinsic model does not explain the data, since all the materials investigated lowered the Fermi level, raising the resistivity through approximately the same maximum value at room temperature, but only oxygen was able to produce photoconductivity. Thus some further action of oxygen must occur.

2. Minority Carrier Model

In the minority carrier model it is necessary to have p-n junctions present, and a reasonably long minority carrier lifetime. Treatment of an initially n-type PbSe film with the acceptors selenium, sulfur, oxygen, or the halogens, converted the film from n type to p type. On the assumption that the sensitizers diffuse inward, a p-type surface is developed on an n-type interior, thus producing an array of p-n junctions. From the similarity in the resistivity-temperature curves produced by the various sensitizers, we can argue that the junctions produced are all roughly of the same potential height. In general, impurities of any kind degrade minority carrier lifetime, whether they act as recombination centers or traps; therefore none of the sensitizers can be expected to improve the minority carrier lifetime. Consideration of these points along with Eq. (3) leads us to conclude that it is not possible to understand the dramatic difference in the role of oxygen as a sensitizing agent from that of sulfur, selenium, or the halogens, on the basis of the minority carrier model.

3. Majority Carrier Model

We now consider the possibility of the introduction of minority carrier traps by the various sensitizing agents. We assume that in the untreated material the time constant is controlled by the density of recombination centers [N_r, Fig. 1(a)]. Treatment with oxygen converts the film from n to p type, introducing acceptor impurity levels either in the interior of the crystallites [N_t, Fig. 1(b)] or on the surface [N_{ts}, Fig. 1(b)], which act as minority carrier traps. For the time constant for capture of an electron by the trap to be less than the time constant for subsequent capture of a hole, it is probable that the unoccupied traps are positively charged ions. Thus, the simple $O^{=}$ ion suggested by Harada and Minden[14] would not be effective. On the other hand, a $(PbO)^{++}$ ion could attract and trap an electron, becoming $(PbO)^{+}$. The $(PbO)^{+}$ would repel holes, thus producing trapping rather than recombination.

In the process of producing traps, the oxygen also lowers the Fermi level, thus achieving the condition of p-type material with most of the traps unoccupied by electrons. The majority carrier lifetime is increased by the lowering of the Fermi level, but the number of holes is also increased. Thus the optimum value of (τ_{maj}/n_{maj}) may be very dependent on the sensitization procedure; this is a possible explanation as to why there is so much technique involved in the production of highly sensitive evaporated films.

It is also possible that the trapping of electrons in the surface traps, N_{ts}, may result in secondary amplifi-

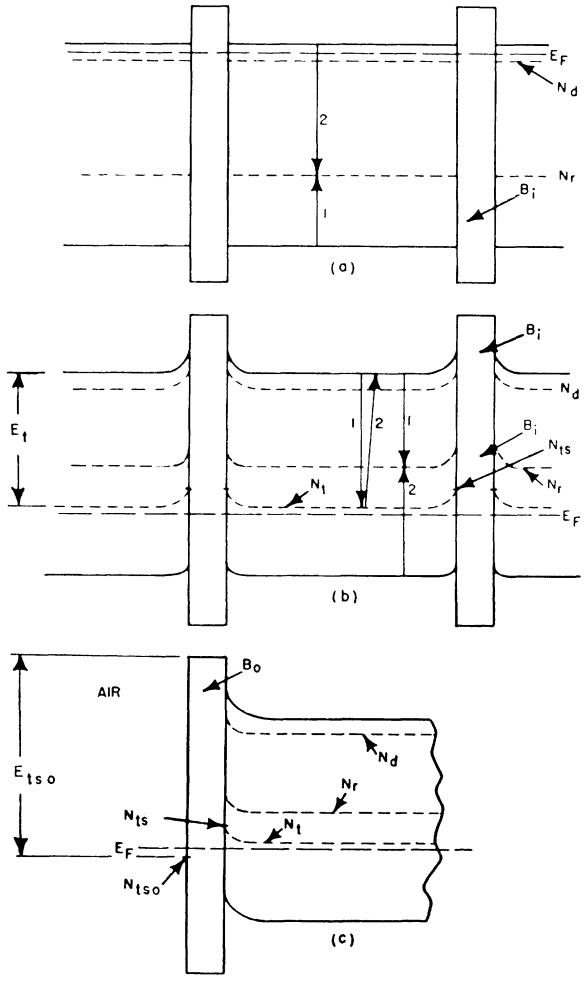

FIG. 1. (a) Energy levels for unsensitized PbSe. N_r is the density of recombination centers; N_d is the density of donor impurity levels; E_F is the Fermi level; B_i is an intercrystalline oxide layer. The steps in the recombination process take place in the order indicated. (b) Energy levels for PbSe sensitized with oxygen. N_t is the density of oxide ions in the crystallite interior; N_{ts} is the density of oxide ions on the intercrystallite surfaces. The order of steps in a trapping process is indicated. (c) Energy levels at the outer surface of a PbSe film sensitized with oxygen. B_o is the outer surface layer; N_{tso} are surface traps on the outside of B_o.

cation through a lowering of the intercrystalline barrier potential; no specific evidence on this question is obtained in this study. Woods[15] has recently reported a study of chemically deposited PbS films, in which he found no significant barrier modulation.

Because of the similarity of its chemical nature to that of oxygen, we suggest that sulfur also introduces traps. However, these traps are closer to the conduction band than those from oxygen, because the electronegativity of sulfur is less than that of oxygen. Therefore, according to Eqs. (4) and (5) the trapping time and responsivity are much less than for oxygen traps.

We suggest that because the halogens are monovalent the acceptor states they produce are not effective electron traps; thus while treatment with the halogens converts an n-type film to p type, no enhancement of the photoconductive time constant is obtained.

It therefore seems possible to account for the general differences in the sensitization behavior of oxygen, sulfur, selenium, and the halogens in terms of the majority carrier model: oxygen appears to be the only agent which produces effective minority carrier traps.

C. DETAILED EXAMINATION OF THE EXPERIMENTAL RESULTS

Consider first the effect of illumination on an unsensitized film at $-195°C$; the film is n type as shown in Fig. 1(a). A photon absorbed by the PbSe creates a hole-electron pair, thus lowering the resistance. Because of the presence of the recombination centers [N_r in Fig. 1(a)], the electron will rapidly recombine with a hole. The time constant (τ_r) associated with this is identified with the 20-microsecond time constant observed at $-195°C$. While the exact value of τ_r depends on the position of the Fermi-level relative to the recombination center, roughly the same behavior would exist whether the film were slightly n type, stoichiometric, or p type. Because of the lower value of carrier density, the responsivity will be highest for stoichiometric samples.

When the material is warmed to 25°C the responsivity is reduced to a level too low to be measured. This is because of an increase in carrier density and a decrease in time constant.

1. Oxygen Sensitization

Figure 1(b) shows the film after it has been exposed to oxygen and has become p type. We assume that the oxygen has diffused sufficiently far into the crystallites that we may consider them to be completely p type. The oxygen traps may occur on the interface between the PbSe and the intercrystalline oxide barrier B_i, and in the interior of the PbSe crystallites, with concentrations N_{ts} and N_t, respectively. We shall not try to distinguish between the two cases, but simply refer to them as oxygen traps. When a hole-electron pair is created the electron will be trapped and leave the hole free to conduct. The time constant (τ_t) for release of the electron from the trap is found to be long compared to the recombination center value τ_r. τ_t is identified as the majority carrier lifetime and as the 5-millisecond time constant observed at $-195°C$ in p-type materials.

The trap occupancy time τ_t decreases with increasing temperature [as given by Eq. (5)] and the density of majority carriers increases. Both effects reduce the responsivity [Eq. (4)] at room temperatures. However, the energy level of the oxygen traps is large enough that measurable responsivity can still exist in PbSe at room temperature; τ_t is identified as the observed 1-microsecond time constant.

We assume that outer surface traps of some type are present as shown in Fig. 1(c). These traps, designated N_{tso} will have a very long time constant τ_{tso} since the carrier must return over a barrier B_o of height $E_{tso} \gg E_t$. Similar barriers have been observed in Ge by Morrison[16] and in PbS by Zemel[17] by means of the slow field effect. The temperature dependence of the very long time constant, τ_{tso}, will also be of the form of Eq. (5), where E_{tso} is much greater than E_t. In PbSe, τ_{tso} is observed to be of the order of hours at $-195°C$, and one must warm the sample to empty the traps.

2. Sulfur and Selenium Sensitization

An initially n-type film is converted to p type by the treatment with sulfur or selenium, just as with oxygen. Thus these elements also introduce acceptor levels. In each case when the resistivity is high we observe photoconductivity at $-195°C$, with the short time constant (20 microseconds) attributed to recombination centers.

The experimental evidence indicates that sulfur also introduces traps. Because of the small value of E_t, τ_t is too short for appreciable enhancement of the photoresponse at room temperature; but at $-195°C$ it produces an increased responsivity, with τ_t of the order of milliseconds. The fact that selenium does not show any trapping effects is understandable; it should just enter the lattice to fill selenium vacancies.

3. Halogen Sensitization

Treatment with the halogens is found to control the Fermi level; at the condition of maximum resistivity we observe photoconductivity at $-195°C$ with the same constant observed with previous sensitizers. Trapping by outer surface states produced the very long

[15] J. F. Woods, Phys. Rev. (to be published); earlier reports published in the *Photoconductivity Conference, Atlantic City, 1954*, edited by Breckenridge, Russell, and Hahn (John Wiley and Sons, Inc., New York, 1956), p. 636, and Phys. Rev. **99**, 658(A) (1955).

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[17] J. N. Zemel, in *Semiconductor Surface Physics* edited by R. H. Kingston [University of Pennsylvania Press, Philadelphia (to be published)].

time constant τ_{ts_0}. No photoconductivity was observed at room temperature because of the short time constant in absence of traps.

4. Oxygen-Halogen Sensitization

In the case of pretreatment with oxygen followed by halogen treatment, the oxygen electron traps are produced by the oxygen treatment and not removed by baking in vacuum. Sufficient selenium atoms must evaporate from the lattice during the vacuum baking to produce *n*-type material. Then treatment with the halogen lowers the Fermi level and empties the oxygen traps so that they can effectively trap electrons. Appreciable sensitivity is observed at 25°C and −195°C, showing τ_t values of 1 microsecond and 5 milliseconds, respectively.

D. CONCLUSIONS

From an examination of the intrinsic, majority carrier, and minority carrier models of photoconductivity, in terms of an experimental study of the sensitization of PbSe films, we have concluded that oxygen serves the important function of introducing minority carrier traps which are effective at room temperature, and that the photoconductivity is due to a change in the density of majority carriers.

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Infrared-Absorption Studies on Barium Titanate and Related Materials*

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The infrared-absorption spectrum of $BaTiO_3$ has been measured for thin single crystals and for powder samples dispersed in pressed KBr disks. Absorption bands for single-crystal samples occur at 495 cm^{-1} and at *ca* 340 cm^{-1}, arising from normal vibrations of the TiO_3 group. A third vibration, a motion of Ba against the TiO_3 group, occurs below the experimentally accessible range. A frequency of about 225 cm^{-1} is expected for this vibration on the basis of a comparison of the specific heat contributions of the observed bands with the measured low-temperature specific heat. Measurements were made on the 495-cm^{-1} band over a wide temperature range. As the crystal changes from the cubic to the tetragonal, orthorhombic, and rhombohedral structures, there occurs band splitting which can be related to the change of crystal symmetry. The spectra of the perovskite titanates, $SrTiO_3$, $PbTiO_3$, and $CaTiO_3$, and the perovskite niobates, $KNbO_3$ and $NaNbO_3$, have been found to be similar, in general features, to that of $BaTiO_3$. The slight differences in band frequency and structure can be related to differences in unit-cell size and symmetry. Integrated band intensities have been found to be in reasonable agreement with measurements on other oxide systems that have vibrations in this spectral region.

INTRODUCTION

STUDIES of the spontaneous orientation of dipole moments in ferroelectrics and ferromagnetics have been carried out at the Laboratory for Insulation Research.[1,2] To investigate the phenomena taking place in such materials as the titanates or ferrites, tools of nondestructive analysis are needed which can give information on atomic arrangements and interatomic forces in the crystal lattice. One of these tools is infrared spectroscopy. A first infrared study of ferrites has recently been carried through in this laboratory[3] and has given promise of locating cations in their oxygen surroundings. The present investigation is a complementary study on ferroelectrics, to establish how the infrared vibrational frequencies, and thus the interatomic forces, are affected by the onset of the ferroelectric state and by the various low-temperature phase transitions. Measurements have been made of the absorption spectra of thin single crystals, the absorption spectra of powdered samples dispersed in pressed potassium bromide disks, and the reflection spectra of thick single crystals.

$BaTiO_3$, in the modification having unusual electrical properties, has a perovskite structure. Above the Curie temperature (~120°C) the lattice has cubic symmetry, with a Ti ion at the center of the unit cell, O ions centered on the six cube faces, and Ba ions on the cube corners (Fig. 1). The structure can be described as a system of TiO_6 octahedra joined at the corners with Ba ions placed in the interstitial positions between the octahedra.

As the cubic crystal is cooled through the Curie point, a polar axis develops along a [100] direction, and the elongation in this direction leads to a structure with tetragonal symmetry. In general, a ferroelectric

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