

One might expect such a potential to occur as the result of a thin oxide layer between the surfaces of the metal and the semiconductor. One could reasonably expect  $V_1$ , in such a case, to be a monotonic function of  $V$ . The actual relationship would of course depend on the electronic processes which occur in the oxide. It should be noted, however, that extensive scattering of electrons in the oxide might limit the validity of the derivation, in particular the assumption about  $k'(E_1, E_2)$  used in obtaining Eqs. (9) and (10). In such a case, our equations would be merely an indication of what to expect.

Finally, we would like to discuss briefly some formal implications of the generalized emission equations for a barrier. In the general case, the equations would have the following form:

$$I_p = qvA \{ p_1 \exp[-q(V_2 - V_1)/kT] - p_2 \}, \quad (28)$$

where the subscripts refer to the two sides of the barrier. (The situation for electrons is exactly analogous, and will not be discussed.) It is assumed, without loss of generality, the region 1 is more  $p$  type than region 2.

On substituting Eqs. (4) and (5), one obtains

$$I_p = qvA p_{20} \exp(E_{f2}/kT) \times [\exp(-E_{p2}/kT) - \exp(-E_{p1}/kT)], \quad (29)$$

where  $p_{20}$  is the equilibrium hole concentration in region two. The interesting aspect of this result is that the flow is proportional to the difference in the Boltzmann factors for the quasi-Fermi levels. This is analogous to the expression for the diffusion flow:<sup>3</sup>

$$I_p = qD_p A p \nabla (E_f - E_p)/kT. \quad (30)$$

Indeed, one can derive Eq. (30) in a crude way from Eq. (29) by considering the diffusion process to be the result of emission between successive regions separated by a distance equal to the mean free path for carriers  $\lambda$ . One obtains the above result on assuming that  $(E_{p2} - E_{p1})/kT \ll 1$ , and identifying the product  $v\lambda$  with  $D_p$ .

The author would like to gratefully acknowledge the aid of his associates, particularly H. Winston who, through discussions and criticism, have helped to carry out this work.

## Effect of Oxygen on the Electrical Properties of Lead Telluride Films\*

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The effect of oxygen on the electrical properties of PbTe films has been investigated. Oxygen, which presumably is adsorbed on the surface of the film, causes an increase in film resistance, followed by a decrease in resistance with increasing exposure to oxygen. The film which is originally "n" type changes to "p" type in the vicinity of the resistance maximum. The magnitude of the photoresistive and photovoltaic effect varies with the amount of oxygen adsorbed by the film. A model has been presented whereby oxygen removes electrons first from the conduction band, then from trapping states, and finally from the valence band, thereby producing the observed effects.

### I. INTRODUCTION

IN the study of the electrical properties of thin films adsorbed oxygen is generally undesirable since it obscures the true properties of the film. Sometimes, however, films must be exposed to oxygen to bring out properties which cannot be observed otherwise. PbS, PbSe, and PbTe films exhibit photoconductivity after the films have been treated with oxygen. Sensitization techniques require certain recipes whereby maximum sensitivity is obtained if well-tested empirical rules are followed. Lead telluride cells, as described in the literature,<sup>1-3</sup> have been used in recent

years as detectors of infrared radiation. They have a rapid response time (time constants of the order of 10 microseconds), high sensitivity, and a long wavelength threshold at about 5.5 microns with peak sensitivity at about 4.5 microns. PbTe cells show this sensitivity only if they are cooled below 100°K. Figure 1 shows a conventional PbTe cell. The Dewar construction is necessary to permit cooling of the sensitive layer. A sapphire window whose transmission remains satisfactory to 6 microns is sealed to the Pyrex by means of a graded seal.

The cell is prepared by placing powdered PbTe, formed by the fusion of stoichiometric amounts of Pb and Te, into a cell blank and subliming it in a high vacuum. The PbTe vapor is condensed onto the region between previously ruled conducting electrodes by cooling this region with an air jet. Sensitization consists of oxygen treatments until optimum sensitivity is

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<sup>1</sup> O. Simpson, Trans. Roy. Soc. (London) A243, 547-584 (1951).

<sup>2</sup> R. A. Smith, Advances in Physics 2, 321-369 (1953).

<sup>3</sup> R. A. Smith, *Semiconducting Materials* edited by H. K. Henisch (Butterworth Publications Ltd., London, 1951), p. 205.

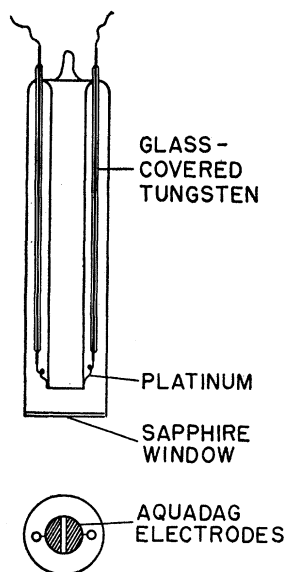


FIG. 1. Conventional cell blank used for the study of spectral sensitivity of films.

obtained. Such a completed cell, however useful, does not provide an insight into the effects of oxygen on the film properties. This study was undertaken to determine the effects of oxygen on various film parameters (such as: resistance, thermoelectric power, and sensitivity to both monochromatic and white radiation) with the aim of correlating these effects and understanding the various phenomena involved. No emphasis has been placed in this study on obtaining films with optimum sensitivity.

## II. EXPERIMENTAL ARRANGEMENT

The apparatus used may be placed into four categories: vacuum system, specially constructed PbTe cell blanks for various types of measurements, electrical system, and optical system. The vacuum system consists of a three-stage water-cooled oil

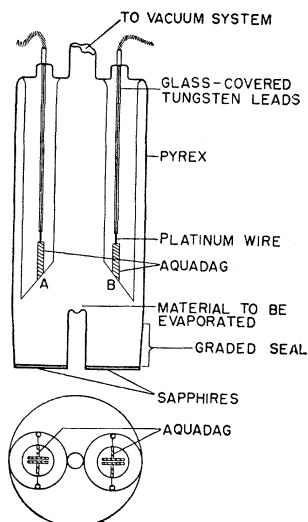


FIG. 2. Dual cell blank used for the determination of the effect of substrate temperature on film properties.

diffusion pump backed by a Welch forepump. A high vacuum stopcock and liquid air trap are provided between the diffusion pump and the cell assembly. Pressures lower than  $10^{-7}$  mm of Hg may be obtained with this system. Oxygen can be admitted to the system in the form of pressure pulses from a liter flask containing oxygen. The flask is attached to the vacuum system by means of a capillary tube containing two stopcocks 3 centimeters apart. By opening and then closing the stopcock nearest the flask, oxygen is admitted into the region between the stopcocks. By opening the other stopcock a known amount of oxygen may then be admitted into the cell. Calibrated pulses of oxygen are thus obtained and controlled by varying the pressure in the flask.

Before each cell blank is used, it is evacuated for several hours and the blank, manifold and contents are baked for about 2 hours at about  $550^{\circ}\text{C}$ . Films may

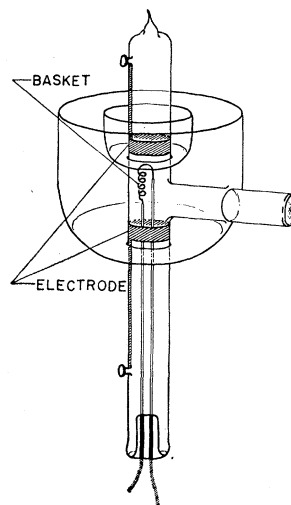


FIG. 3. Cell used for the determination of thermoelectric power and film resistance as a function of oxygen content of the film.

then be deposited by either subliming the material from a tungsten basket or by placing the entire cell blank into an oven at about  $525^{\circ}\text{C}$  and cooling the region where the material is to condense.

Several experimental cells were used for the measurements. The cell shown in Fig. 1 was used for routine measurements of cell resistance as a function of film temperature. In order to compare films formed under different conditions of substrate temperature, the cell shown in Fig. 2 was constructed. It is similar to that shown in Fig. 1, but since it contains 2 elements controlled experiments were made possible. For the study of thermoelectric power measurements, a tube similar to that used by Hintenberger<sup>4</sup> was constructed. (See Fig. 3.) The material was evaporated from a tungsten basket and condensed between the ring electrodes. The thermoelectric power of the film was then measured while holding liquids in the upper and lower cups at different temperatures. Film resistance at

<sup>4</sup> H. Hintenberger, Z. Physik 119, 1 (1942).

various temperatures could be measured by filling the lower cup with a liquid at the desired temperature and connecting an ohmmeter to the ring electrodes.

Electrical measurements consisted of resistance measurements most conveniently made with an RCA voltohmmyst and of thermoelectric voltage made with a conventional dc amplifier. For measurement of film response to radiation an ac method was used. Radiation from a globar or a galvanometer lamp was interrupted by a chopper before it fell onto the film. The film was connected in series with a resistor and several dry cells. Voltage variations across the resistor were amplified and measured by means of a VTVM or a calibrated oscilloscope.

In order to determine the response to monochromatic radiation, a Perkin-Elmer infrared monochromator was introduced between the globar and the film.

### III. PROCEDURE AND RESULTS

#### A. The Effect of Oxygen on Film Resistance and on the Temperature Coefficient of Resistance

The cell blank shown in Fig. 1 was attached to the vacuum system and evacuated. PbTe was deposited on the glass substrate between graphite electrodes which were 1.0 cm long and 0.1 cm apart. The temperature of the substrate was maintained at 40°C during the deposition by a water-cooled bath. After a deposition time of one hour the film was about 0.5 micron thick and had a resistance of 160 ohms. Mercury was then inserted into the coolant chamber of the cell and a heater element and thermocouple were dipped into this mercury bath. A liquid oxygen bath was then placed around the cell to shield the sensitive area from room temperature radiation. Figure 4 shows a diagram of the experimental setup. The mercury was frozen and cooled to about 80°K by slowly pouring liquid nitrogen into the coolant chamber. The temperature of the mercury slug was then permitted to rise slowly to room temperature by passing a small current through the heater. During this process resistance and temperature measurements were made. As the film temperature approached 295°K a pulse of oxygen was admitted dynamically into the system causing the pressure to increase to about 5 microns. An immediate rise in film resistance was observed. The resistance decreased only slightly to an equilibrium value as the original high vacuum was restored. The film was then cooled and measurements of resistance were again made as it warmed to room temperature. The procedure was repeated until the film had been exposed to 12 oxygen pulses. In order to obtain significant resistance changes the size of the pressure pulses was gradually increased over the last three pulses. Figure 5 shows the results of the entire experiment. Each curve was nearly reversible as long as the film temperature was not raised above about 600°K. When an oxygenated film was heated above about

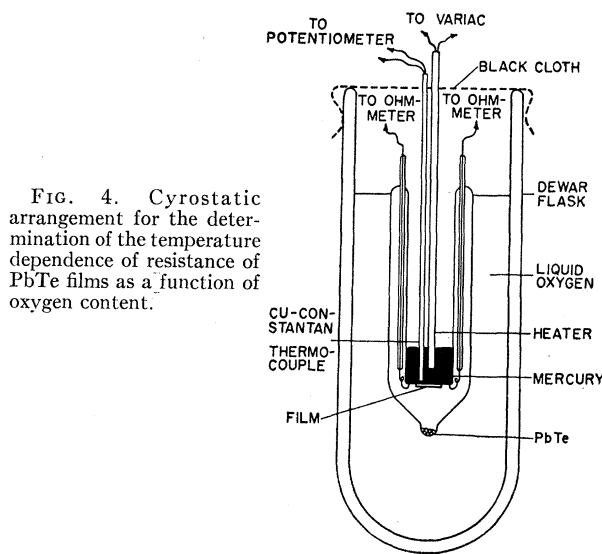


FIG. 4. Cyrostatic arrangement for the determination of the temperature dependence of resistance of PbTe films as a function of oxygen content.

650°K it was returned to its original condition as shown by curve 0 in Fig. 5. This indicates that oxygen is driven from the film by excessive heating in a high vacuum.

Figure 6 is a plot of resistance isotherms of the PbTe film just described obtained by sectioning Fig. 5. It is to be noted that with the addition of oxygen the resistance of a film rises to a maximum and then falls.

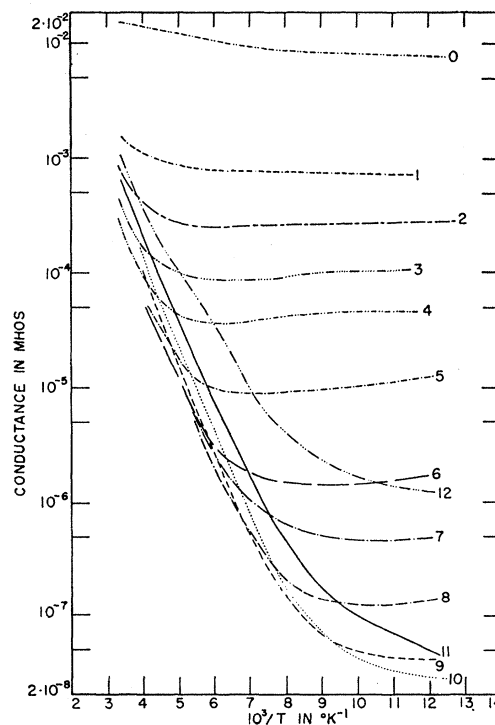


FIG. 5. Conductance of films as a function of film temperature for increasing exposure to oxygen at room temperature.

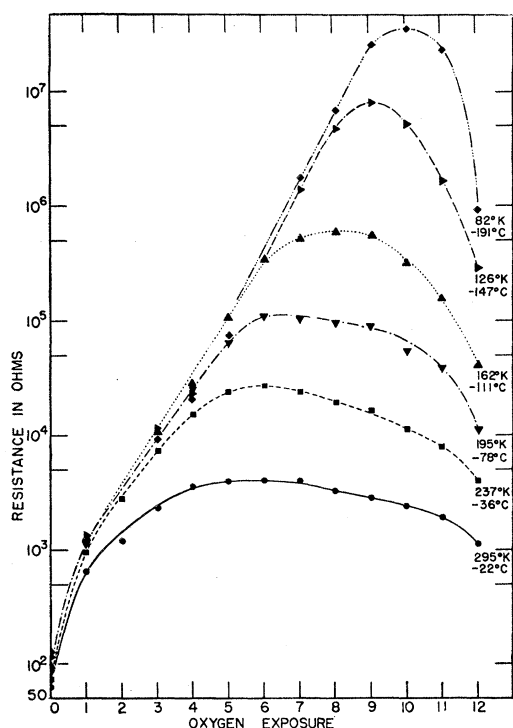


FIG. 6. Conductance of films for various temperatures as a function of oxygen exposures.

### B. The Effect of Oxygen on the Thermoelectric Power of the Film

The thermoelectric power of the film as a function of oxygen content was measured. The tube shown in Fig. 3 was used for this experiment. By using an ice water mixture in one cup and a hot bath (50°C) in the other cup a thermal gradient was produced across the film and the thermoelectric emf was measured. Figure 7 shows a curve of thermoelectric power plotted against oxygen content. The addition of oxygen changes the film from "n" to "p" type. By simultaneously measuring the resistance it was found that the change in sign of the thermoelectric power occurred near the resistance maximum.

### C. The Effect of Oxygen on the Photoconductive Sensitivity of a PbTe Film

In order to observe the sensitivity to light, the film temperature was reduced to about 90°K after each pulse of oxygen had been admitted at room temperature. A global was placed at 100 cm from the film and the radiation was chopped at about 200 cycles/second. The film sensitivity is defined as  $(I_1 - I_d)/I_d$ , where  $I_d$  is the current flowing through the film in the dark and  $I_1$  is the current through the film when the film is illuminated. This ratio was determined by measuring the ac voltage across, and the dc current through the load resistor. Figure 8 shows the results of these

measurements for a typical case. A peak in sensitivity occurred at a degree of oxygenation somewhat larger than is required to produce the room temperature resistance maximum.

### D. The Effect of Oxygen on the Spectral Response of PbTe

In order to determine the effect of oxygen on spectral sensitivity of a PbTe film, chopped radiation from the global was passed through a Perkin-Elmer infrared monochromator. The spectral sensitivity was then determined with the cell at about 90°K. Oxygen was admitted as in earlier experiments. There seemed to be no variation in the shape of the spectral response until the 90°K-resistance isotherm had passed its maximum. Curve A of Fig. 9 shows a characteristic curve. After the film had been oxygenated beyond its resistance maximum a new sensitivity peak occurred at about 1.5 microns as shown by curve B of Fig. 9. Additional oxygenation lead to the spectral response shown by curve C. The time constant associated with the new peak at about 1.5 microns was generally between  $10^{-2}$  and  $10^{-3}$  second while that associated with the original photoeffect shown in curve A generally varied between  $10^{-4}$  and  $10^{-6}$  second. Continued oxygenation gradually increased the time constant associated with the 4.5 micron effect. In addition, it was observed that if the cell was cooled with dry ice instead of liquid oxygen while the spectral response was measured the peak originally at about 4.5 microns shifted slightly toward the visible (to about 4.0 microns) and the 1.5 micron peak disappeared completely. The over-all signal at 195°K was generally less than 1 percent of the signal at 90°K.

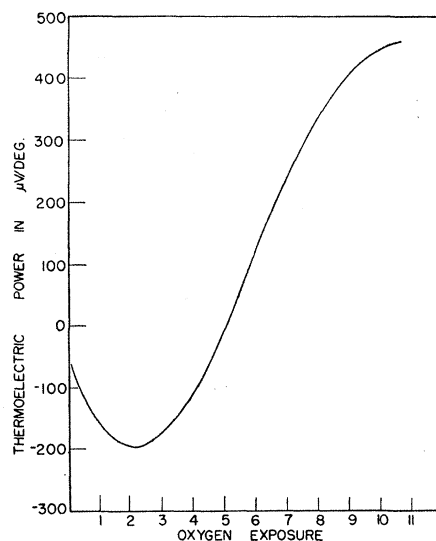


FIG. 7. Variation of thermoelectric power of a film as a function of exposure to oxygen.

### E. The Photovoltaic Effect in PbTe Films

All films of PbTe exhibited some degree of photovoltaic sensitivity upon oxygenation. The peak photovoltaic sensitivity at 90°K occurred at the transition from "n" to "p" type. The upper limit of the photovoltaic effect in films is in approximate agreement with that observed by Gibson<sup>5</sup> for point contact single crystal PbTe photocells.

### F. Factors Affecting the Reproducibility of the Experiment

#### 1. Substrate Temperature

During preliminary experiments it was observed that under certain conditions, oxygen had a much greater effect on film properties than has been described. This variation was traced to variations in substrate temperature between different evaporations. An experiment was, therefore, designed to study the effect of substrate temperature during evaporation on the ultimate oxygen susceptibility and properties of the resulting film. The tube shown in Fig. 2 was used for the experiment. Substrate A was held at 40°C and substrate B at 200°C. The PbTe to be sublimed was pulverized and placed midway between the two substrate surfaces. Thus all parameters except the substrate temperature were the same during film formation. After the films were formed, oxygen was admitted in the conventional fashion with both films at room temperature. The resistance was measured as a function of oxygen content, both at room temperature

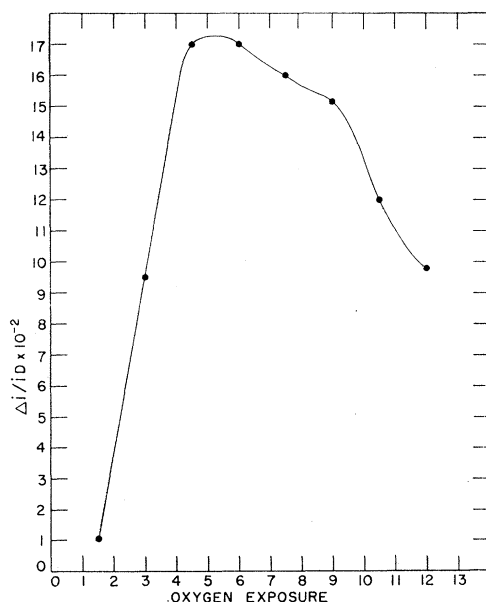


FIG. 8. Variation of film sensitivity as a function of exposure to oxygen.

<sup>5</sup> A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 196 (1952).

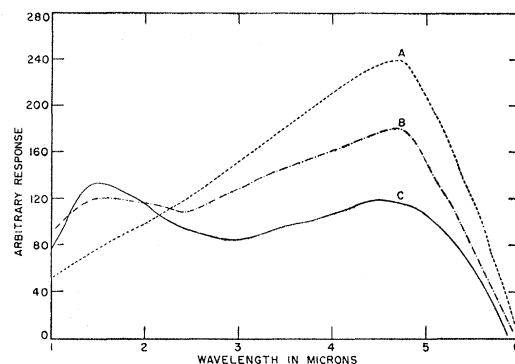


FIG. 9. Spectral response of several typical PbTe films. A: After exposure to small amounts of oxygen (layer is "n" type). B: Exposure to moderate amounts of oxygen. C: Heavily oxygenated film (layer is "p" type).

and liquid oxygen temperature. Figure 10 shows the results of these measurements. It is to be noted that the film deposited on the lower temperature substrate was much more susceptible to oxygen than the one deposited onto the higher temperature surface. Considerably less oxygen was required to transform the film deposited on the 40°C substrate from "n" to "p" type than that on the 200°C substrate. It is also of interest to note that the magnitudes of the resistance maximum for both film A and film B were approximately the same.

#### 2. The Effect of Strong Illumination

In the early stages of this investigation fairly intense white light shining onto the cell for several minutes was used to determine white light sensitivity. It was found, however, that this produced a secondary effect which obscured the measurements on the primary effect. As white light first fell onto some of the films, the resistance dropped sharply as was expected. However, with prolonged illumination, the resistance began to rise again in a nearly exponential manner reaching an equilibrium value after several minutes. After the light was turned off the resistance was considerably higher than the original dark resistance. The original resistance could only be obtained after the cell had been warmed to room temperature and recooled in the dark. Figure 11A shows this type of behavior. For other films it was observed that after light was permitted to fall onto the cell the film resistance dropped at first rapidly, and then more slowly as indicated by curve B in Fig. 11. After removal of the light the dark resistance was lower than before exposure to light, but again it could be returned to its original value by warming and recooling the cell. The long period characteristics of 11A were exhibited by films which did not have sufficient oxygen and were "n" type at liquid air temperatures; those exhibited by 11B were "p" type at low temperatures. The magnitude shown by curve B increased greatly with the amount of overoxygenation. In

addition, it was found that in the presence of oxygen (at  $10^{-4}$  mm pressure) the long period effect in a particular film was much more severe than it was at pressures below  $10^{-7}$  mm of Hg.

#### IV. DISCUSSION OF RESULTS

The explanation of the effects of oxygen on the electrical properties of films is complicated by the very nature of films. A film is composed of microcrystals of various sizes, ranging from about 10 Å to 1000 Å. These crystallites contain all types of known imperfections in addition to impurities. Large scale inhomogeneities may also be produced by differential expansion of substrate and film, by substrate contamination and in general by variations of film growth in different regions of the film. Since the electrical properties are not only dependent on the crystallite structure, but also on contacts between crystallites, additional complications are introduced. At least two models have been proposed to explain photoconductivity in PbTe films. Smith<sup>3</sup> and his collaborators suggest that photoconductivity in PbTe is due to the effects produced by radiation falling on the barriers between crystallites. Simpson,<sup>1</sup> on the other hand, proposes excitation from a modified valence band to the conduction band of PbTe to explain his results. Neither of these models

can be used entirely to explain the observed results, although there is considerable merit in each.

A model for photoconductivity in PbTe must first of all explain the long wavelength threshold of about 5.5 microns when the film is cooled to 90°K. Measurements of thermal activation energy have yielded a value of 0.62 ev.<sup>6</sup> Such a value would indicate a long wavelength threshold occurring at about 2 microns, if one assumes that photoconductivity is due to excitation of electrons from the valence to the conduction bands. One can perhaps overcome this difficulty by postulating that the long wavelength cutoff be due to excitation of electrons from the valence band to impurity levels. Such a picture could not, however, explain the high absorption coefficient extending to about 5 microns as reported by Gibson.<sup>7</sup> Scanlon<sup>8</sup> in a recent study of thermal activation energy has shown that for PbS crystals the previously measured thermal activation energy of 1.1 ev is reduced to 0.38 ev when purer crystals are used such that the activation energy may be measured in the vicinity of room temperature instead of at 700°K. It is thus entirely probable that when techniques for producing purer PbTe crystals are found, the thermal activation energy will be considerably smaller than first reported by Chasmar and Putley.<sup>6</sup> It seems thus entirely proper to disregard measurements of thermal activation energy in the formulation of a mechanism and assume the forbidden gap width to be about 0.22 ev as determined from absorption and photoeffect data.

The film when freshly deposited is "n" type due to an effective excess of Pb atoms. The free electron density in the conduction band of the film has been found to be about  $10^{18}$  per cc.<sup>9</sup> The electrons are supplied by excess Pb atoms lying just below the conduction band. In addition to these Pb centers just below the conduction band and Te centers or Pb vacancies just above the valence band, the film contains many traps which may be represented symbolically as potential wells, somewhere between the valence and conduction bands. Initially these traps are all filled, because of the high concentration of electrons in the conduction band. The film thus behaves like a metal with an electron mobility between 5 and 500 cm<sup>2</sup>/volt-sec, depending on the effect of grain boundaries. When oxygen is permitted to enter the cell, some of the oxygen atoms are adsorbed on the crystallite surface. Electrons from the film attach themselves to the adsorbed atoms of oxygen, forming negative ions. It is this process which, according to Smith<sup>3</sup> produces barriers between crystallites. As oxygenation proceeds the density of electrons in the conduction band is diminished and films gradually take on properties of a

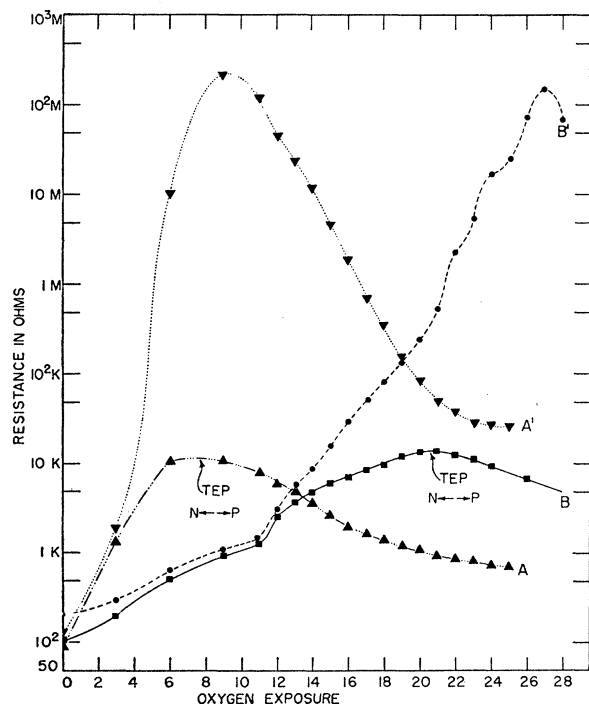


FIG. 10. Variation of film properties as a function of substrate temperature. A. Film deposited on a 40°C substrate—measurements while film is at room temperature. A'. Film deposited on a 40°C substrate—measurements while film is at 90°K. B. Film deposited on 200°C substrate—measurements while film is at room temperature. B'. Film deposited on 200°C substrate—measurements while film is at 90°K.

<sup>6</sup> R. P. Chasmar and E. H. Putley, *Semiconducting Materials* edited by H. K. Henisch (Butterworth Publications Ltd., London, 1951), p. 208.

<sup>7</sup> A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952).

<sup>8</sup> W. W. Scanlon, Phys. Rev. **92**, 573 (1953).

<sup>9</sup> S. J. Silverman and H. Levinstein, Phys. Rev. **94**, 871 (1954).

semiconductor as shown in Fig. 5. Such a model is further substantiated on examination of Fig. 10, the effect of substrate temperature on the resistance-oxygen dependence of films. When the substrate temperature is low, porous films are formed, where the ratio of film surface to crystallite volume is considerably larger than for less porous films formed at higher substrate temperatures. As the films become less porous, the decreased availability of oxygen sites will produce smaller variations in film resistance when the film is exposed to oxygen. If one assumes photoconductivity to be due to excitation of electrons from valence to conduction bands such a model explains the variations of sensitivity with the addition of oxygen as shown in Fig. 8. The relationship  $(I_1 - I_d)/I_d$  increases as oxygen is added since  $I_d$  is at first decreased. Then, as holes are created in the valence band by the continuous addition of oxygen, increasing dark conductivity decreases the sensitivity. Films require cooling for optimum sensitivity to reduce thermal excitation of electrons across the relatively narrow energy gap of 0.22 ev. The change in the sign of the thermoelectric power as shown in Fig. 7, occurs near the point where the conduction band is emptied of electrons. The exact location of the changeover with oxygen depends, of course, on the relative mobility of electrons and holes, and thus varies somewhat from film to film and with film temperature. The lengthening of the time constant with increasing oxygenation may also be understood from this model. As oxygen is added to the film, more and more traps between the conduction and valence bands will be emptied. They will then act as traps for excited electrons and increase the lifetime of holes.

Up to this point, no attention has been paid to the manner in which the entire film changes from "n" to "p" by the addition of oxygen. It is quite clear that the process is not a slow, uniform change. In all probability the surface layer will become "p" type first. This is followed by the diffusion of oxygen along grain boundaries, producing certain "p" type regions within the film while the remaining film may still be "n" type. These regions may cover areas from one microcrystal to many thousands of microcrystals. Photovoltaic effects, as have been described, are due to *p-n* junctions thus created. These junctions will also account for large deviations from Ohm's law observed in many films. Large "p" and "n" regions within a film have been observed by scanning the film with a small spot

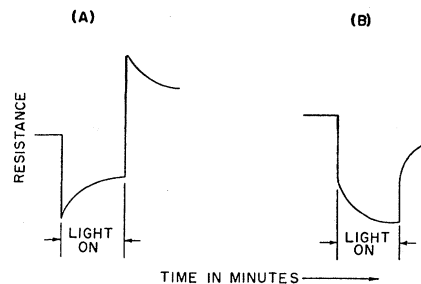


FIG. 11. Effect of strong radiation on film resistance (long period effect). A. "n" type film. B. "p" type film.

of light. These regions have been altered by the addition of small pulses of oxygen. The peak in spectral response in the vicinity of 1.5 microns and its long time constant could be attributed to the formation of surface layers of energy gaps larger than those of the remaining film as more and more oxygen is permitted to interact with the film.

Long period photoeffects which make dc measurements impossible are evidently caused by deep surface oxygen traps. White light would excite electrons into these traps from the interior of the crystallites. When a film is predominately "n" type at low temperature, this trapping will result in a decrease of electrons in the conduction band with an increase in resistance. When the film is predominately "p" type any trapping will increase the hole concentration with a resulting decrease in resistance. Warming to room temperature frees the deeply trapped electrons and returns the film to its original condition.

## V. CONCLUSIONS

The phenomena described here represent a small phase of rather detailed investigation into the nature of photoconducting layers. The model presented here was adopted only after many other models did not qualitatively stand the test of experiment. While it is desirable to develop a more quantitative picture, the nature of thin films makes this quite impractical. It is hoped that this study will provide an insight into the processes which take place on the surface of crystals, where measurements such as those performed on film would not be possible.

We wish to acknowledge the assistance of Mr. Werner Beyen, Mr. Channing Dichter, and Mr. Dean Mitchell, who have aided in making many of the measurements reported here.