Concerning the Theory of Photoconductivity in Infrared-sensitive Semiconducting Films[1]

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THE PROPERTIES of Tl_2S, PbS, PbSe, PbTe, and other infrared-sensitive photoconductive cells are so strikingly similar as to suggest that a single explanation should apply to this class of materials. At present three different pictures to account for the properties of specific systems are in use: 1) The photosensitivity is characteristic of a uniform "intrinsic" semiconductor produced by detailed balancing of *n*- and *p*-type impurities. 2) The photosensitivity arises from the presence of a large number of *n-p* barriers, distributed at random. 3) The photosensitivity is characteristic of an impurity semiconductor. The first picture has been proposed by von Hippel and Rittner (*10*) for Tl_2S and has been further considered by the writer (*5*) in connection with the behavior of PbS; the second has been advanced also for PbS by Sosnowski, Starkiewicz, and Simpson (*7*) and has been further developed by James (*3*); the third has been proposed recently by Genzel and Muser (*2*) for PbS and also by Simpson (*6*) for unoxidized PbSe and PbTe.

We believe that the third picture may be ruled out on the basis of existing absorption data (*4, 6, 9*) which correspond to large absorption coefficients, of the order of 10^4 to 10^5 cm^{-1}, over most of the spectral range of Tl_2S, PbS, PbSe, and PbTe photocells, thus implying fundamental rather than impurity absorption. The two remaining pictures appear to be mutually exclusive, and as a general explanation of photoconductivity in semiconductors, each is subject to difficulties. The first one fails to explain a-c resistance data (*1, 5*) on PbS cells and carries the extremely stringent requirement that the *n*- and *p*-type impurities balance each other so exactly that the maximum net impurity concentration anywhere in the layer be less than the intrinsic concentration of charge carriers ($10^{16}/cm^3$ in PbS or $10^{11}/cm^3$ in Tl_2S at $T = 300°$ K). The second picture fails to account for the bimolecular recombination law that has been observed in Tl_2S (*10*), PbS (*5*) and PbTe (*6*) photocells. It is the purpose of this note to present a more general explanation of the phenomena observed in infrared semiconductors, an explanation which follows naturally from one method of preparing the photocells and which reduces in limiting cases to essentially pictures (*10*) or (*5*), while avoiding the difficulty of the exact balancing of impurities.

It is perhaps not unreasonable to assume that the following events occur in the course of fabricating photocells by vacuum evaporation and subsequent sensitization. During vacuum evaporation of the material to form a thin layer, a slight loss of the electronegative constituent occurs, giving rise to an *n*-type semiconductor in which the photosensitivity may be extremely small, owing to the rapid recombination of the electrons and holes created optically with the thermally produced ionized donors and free electrons respectively. Subsequent heat treatment in the presence of the electronegative constituent or oxygen converts portions of the surfaces of the grains into *p*-type material, thus calling into existence randomly distributed local *n-p* transition regions. As the "oxidation" proceeds further, the *n*-type conducting paths become more and more disrupted by the *p*-type regions, until a point is reached where all charge carriers traveling between electrodes have to pass through some of the *n-p* transition regions. With still further "oxidation," continuous threads of *p*-type material of negligible photosensitivity are formed, and these grow progressively thicker, until in the limit the layer may become completely *p*-type. With sufficient exposure to oxygen, new phases such as Tl_2SO_2 or $PbO \cdot PbSO_4$ may make their appearance, but the role of these oxidation products will usually be that of an inert surface layer.

The properties of the photocell layer are determined mainly by those of the transition region, which in turn depend upon the details of the impurity distribution. Fig. 1 illustrates the sort of impurity distribution to be anticipated in the sensitization process outlined above, i.e., the interpenetration of an *n*-type region of relatively constant donor concentration with a *p*-type region in which the acceptor concentration tails off with distance. To the left of line 1 in Fig. 1 some of the electrons from the donors fall spontane-

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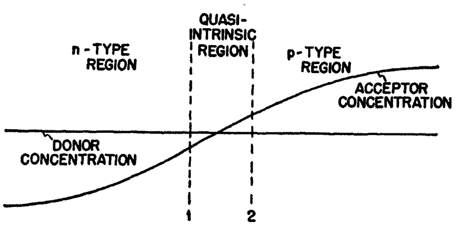

FIG. 1. Impurity distribution in *n-p* transition region.

ously into the acceptors, completely filling them.[3] Since the net donor concentration remains high, the material is *n*-type. To the right of line 2, all of the donors are emptied of electrons by spontaneous transitions to the acceptors, but since the net acceptor concentration is high, the material is *p*-type.[3] Between lines 1 and 2, the net impurity concentration is either zero or extremely small, and this transition region behaves essentially as an intrinsic semiconductor. The thickness of this quasi-intrinsic region increases with temperature because of the tendency of the Fermi level to merge with the intrinsic line[4] at high temperatures. It is also larger the more gradually the concentration of *p*-type impurity varies with distance in the transition region. Thus, in general, a quasi-intrinsic region is to be expected, the thickness of which may vary widely, depending upon the chemical and heat treatments employed and upon the operating temperature of the photocell. Moreover, the equilibrium condition that the Fermi level be everywhere the same requires transfer of electrons from the *n*-type region to the intrinsic region and from the intrinsic region to the *p*-type region. Thus, space charges are set up which correspond to potential barriers for the passage of charge carriers. The situation is illustrated by the energy level diagrams of Fig. 2 which show two limiting cases, one where the thickness of the quasi-intrinsic region is zero (left) and one where it is large (right) as compared to the thickness of the space charge region. Although intermediate cases are of great interest, we shall for simplicity discuss only these limiting ones.

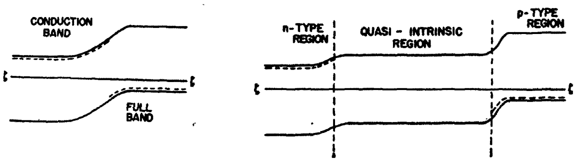

FIG. 2. *Left*, energy level diagram for sharp *n-p* transition. *Right*, energy level diagram for gradual *n-p* transition.

Case a—Sharp n-p *Transition.* (*Fig. 2, left*). In a perfectly sharp contact between *n*- and *p*-type regions, the establishment of equilibrium requires that electrons be transferred from the *n*- to the *p*-type material in the neighborhood of the contact. This creates a positive space charge in the *n*-type region and a negative space charge in the *p*-type region, corresponding to a variation of potential which, in the present instance, is continuous across the plane of contact and which obeys Poisson's equation in both regions. The height of the (rectifying) potential barrier so created is equal to the difference in the Fermi level positions that would obtain if the *n*- and *p*-type regions were separated. This height can vary from zero (high temperatures, low impurity content) to about the energy separation between the bands (low temperatures, high impurity content), as may be seen from the calculated values of the Fermi level for PbS (see Fig. 3). With reasonable impurity content (about 10^{17}–10^{19}/cm^3) the resistance of such a potential barrier can greatly exceed the resistance of an impurity semiconductor of comparable thickness.

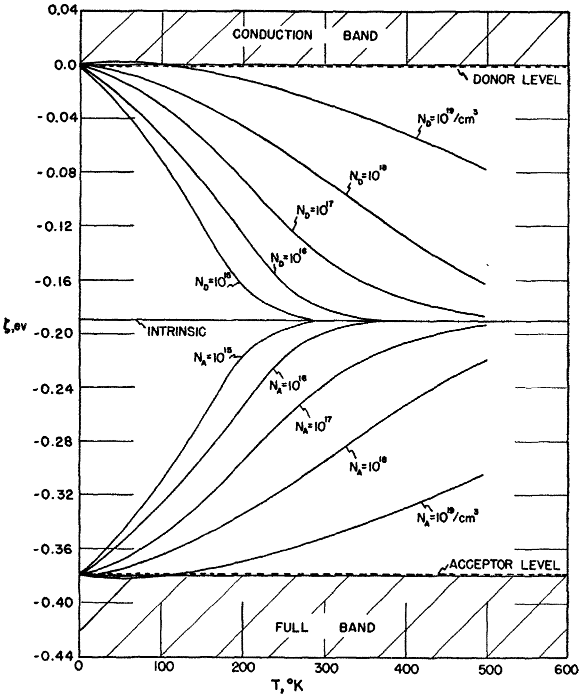

FIG. 3. Variation of Fermi level with temperature and impurity content in lead sulfide. Separation between full and conduction bands, 0.38 ev. Each impurity level is taken to be 0.001 ev from the nearest band and the effective masses of electrons and holes are taken as equal. The curves in the upper portion of the figure represent the behavior in *n*-type material of varying donor concentrations; the curves in the lower portion of the figure are the corresponding ones for *p*-type material.

On exposure to steady illumination, electrons are excited from the full band to the conduction band

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[3] An alternative possibility, having essentially the same consequences, is the mutual annihilation of donors and acceptors by recombination.

[4] By the intrinsic line is meant the line showing the variation of the Fermi level with temperature in a model comprising only a full band and a conduction band.

everywhere throughout the material. In both the *n*- and *p*-type regions far from the plane of contact, the electrons and positive holes created optically disappear so rapidly by recombination with the thermally produced fixed positive charges and electrons that the net increase in charge carrier density is extremely small. However, electrons and holes produced in the space charge region are rapidly separated by the strong electric field; electrons are drawn into the *n*-type region and partially neutralize the positive space charge, whereas the holes are drawn into the *p*-type region and partially neutralize the negative space charge. Consequently, the height of the space charge barrier and the corresponding d-c resistance are lowered. It will be noted that for each pair of charge carriers created optically and separated in the space charge region (photovoltaic effect) many charge carrier pairs can pass over the barrier (photoconductive effect). On removing the illumination, the system will spontaneously return to its equilibrium state in the dark with great rapidity by thermionic emission over the barrier of the excess charge.

The following behavior is expected of a photocell which may be approximated by a large number of sharp barriers of the type just described, shunted by thin well-conducting threads of *n*- or *p*-type material. The d-c resistance will appear to be ohmic and will be determined at high temperatures by the barriers and at low temperatures by the thin conducting threads. The d-c resistance will be considerably higher than the a-c resistance at high frequencies; the former will be appreciably lowered by radiation but not the latter. The photoconductivity can be shown to be a linear function of the intensity of radiation up to very high levels. The response time will probably be determined by the product of resistance and capacitance of the photocell.

Case b—Gradual n-p *Transition.* (*Fig. 2, right*). If the quasi-intrinsic region is much thicker than the space charge region, the potential barrier becomes split into two halves. Electrons and holes need only surmount the smaller barriers in order to recombine with each other. Under these circumstances the barrier resistances will nearly always be negligible with respect to the resistance of the quasi-intrinsic region and the properties of the latter will dominate.

Under steady illumination electrons and holes created optically in the quasi-intrinsic region recombine with each other and with the thermally released carriers until the rates of formation and recombination of charge carriers are equal. In the steady state a net increase in the charge carrier density and a corresponding decrease in resistance result. If the density of thermally released carriers is sufficiently small (large band separation, low temperature), the recombination rate will be low and the average lifetime of the "extra" carriers will be long. For sufficiently long lifetime, the number of charges flowing through the layer may greatly exceed the number created optically.

The following behavior is expected of a photocell which may be approximated by a large number of diffuse barriers of this type, shunted by thin threads of well-conducting material. The d-c resistance and the a-c resistance at high frequencies will be the same and both will be equally affected by radiation. The resistance-temperature behavior will be similar to that of a homogeneous intrinsic semiconductor containing impurities. The photoconductivity will be a nonlinear function of the intensity of radiation, following the bimolecular recombination law. The response time will be determined by either the recombination relaxation time or by the *RC* time constant, whichever is the longer.

The preceding discussion has stressed the extreme differences in properties resulting in two limiting cases. Obviously all shades of intermediate behavior are possible in actual photocells—for example, appreciable barrier contribution to the d-c resistance and nonlinearity with radiation intensity. There is evidence (*5, 1*) that some of the PbS cells which have been studied may approximate the sharp transition case. On the other hand, the nonlinear response to radiation which has been observed (*5, 6, 10*) in Tl_2S and in other PbS and PbTe cells indicates more gradual *n-p* transitions in these layers. The a-c resistance-temperature-illumination data of Chasmar (*1*) may perhaps be understood on the basis of barriers in which a relatively thin quasi-intrinsic region at low temperatures becomes thicker at higher temperatures.

Independently of the thickness of the quasi-intrinsic region, the general picture outlined here is capable of explaining a number of additional observations (*5–9*), e.g. the sensitizing role of oxygen or of the electronegative constituent, the requirement for high photosensitivity that both *n*- and *p*-type impurities be present simultaneously, the change in sign of the thermal emf coefficient with "oxidation," the correlation of maximum photosensitivity (expressed as $\frac{\Delta I}{I_d}$) with minimum conductivity, increase in photosensitivity with a decrease in temperature, quantum yields exceeding unity, and the occurrence of photo-emf's varying in magnitude and sign from point to point in the layer.

A detailed account will be published at the completion of an experimental program which has been in progress in this laboratory for some time.

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Technical Papers

Hemolytic Activity of Some Nonionic Surface-active Agents

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For a long time it has been known that surface-active agents, as exemplified by the soaps, possess marked hemolytic activity. Recent studies using synthetic anionic surface-active agents have confirmed these observations and demonstrated that the cytolytic efficiency of a homologous series of these compounds is dependent upon their carbon chain length. In discussion of these observations, emphasis has been placed upon correlation of the cytolytic power of these compounds to their surface activity (*3*) and upon complex formation, based upon electrostatic interaction, between the anionic surface-active agents and lipid, lipoprotein, and protein components of the red blood cell ultrastructure (*6*).

It is desirable to report upon the hemolytic activity of certain nonionic surface-active compounds at this time, both because of its pertinence to any consideration of the mechanism of these cytolytic effects and because of the practical importance of having available surface-active agents with desirable physical properties but largely devoid of such deleterious biological effects as hemolysis and toxicity.

This report will be confined primarily to a series of nonionic polymeric surface-active agents[1] based upon alkyl phenols made water-soluble by interaction with an alkylene oxide.[2] The alkyl-substituted phenol represents the hydrophobic portion of the molecule, while the ether-alcohol groups are the hydrophilic portion. The hemolysis studies utilized a 5% suspension of washed sheep red cells made up in 0.16M NaCl + 0.015M phosphate, buffered at pH 7.4. Hemolysis was studied by mixing 0.2 ml of the 5% sheep red cell suspension with 4.5 ml of buffered NaCl to which the desired amount of the surface-active agent had been added. This mixture is translucent, due to the scattering of light by the intact erythrocytes, but upon hemolysis it becomes transparent. The time required to achieve hemolysis of 75% of the cells has been used as an end point and was determined by visual comparison with a standard (*4*). Twofold dilutions of the surface-active agents were used and the time for hemolysis was plotted against the concentration of these compounds. From these plots the concentration per ml of surface active agent necessary for an hemolysis time of 100 min was estimated and used as a basis of comparison. Surface tensions at 25° C were determined with the duNouy tensiometer, previously standardized against H_2O and benzene.

It will be seen (Table 1) that two of the nonionic compounds, Tritons WR-1352 and A-20, are distinguished from the other surface-active agents listed in being nonhemolytic. This is evident at concentration levels approximately 1,000-fold greater than is necessary to produce hemolysis with the other surface-active compounds. These two compounds, which in high concentration are nonhemolytic to sheep cells, evidence this innocuousness at concentration levels at which they depress the surface tension of H_2O from a control value of 72 to 33 or 42 dynes per cm. In contrast, the other nonionic and ionic surface-active agents in Table 1 are hemolytic at concentration levels which depress the surface tension of their aqueous solutions to 37 dynes per cm for the least hemolytic and to 68 dynes per cm for the most hemolytic compound. Thus, alteration of the physical properties of the solution as exemplified by measurements of surface tension can in no way suffice to explain the presence or lack of hemolytic activity of surface-active agents. Both anionic and cationic surface-active agents have been shown to form saltlike, stoichiometric complexes with proteins and to cause their denaturation (*2*, *7*). Nonionic compounds, on the other hand, do not possess strong polar groups and are thus unable to enter into electrostatic interaction with proteins, as is evident from studies of electrophoresis (*5*), precipitation (*1*, *2*), and alteration of biological activity (*1*, *2*). This means that the hemolytic activity of those nonionic compounds which evidence this property must be based upon nonelectro-

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[1] The Triton compounds, as listed in Table 1, were made available through the courtesy of the Rohm and Haas Company.

[2] Bock, L. H. and Rainey, J. L. 1948 U. S. Patent 2,454,541.