Theory of Photoconductivity in Semiconductor Films

RICHARD L. PETRITZ
United States Naval Ordnance Laboratory, White Oak, Maryland
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Photoconductive films of the lead salt family are composed of a system of crystallites separated by intercrystalline barriers. The crystallites are lead salts while the intercrystalline barriers are an oxide of lead or of the lead salt. Space charge regions are present at the surface of the crystallites. The lifetime of hole-electron pairs is determined in part by surface states while the resistivity is strongly affected by intercrystalline barriers.

We analyze a model which incorporates the above characteristics of a photoconductive film, except for the space charge effects. It is assumed that the primary photoeffect is absorption of light and production of hole-electron pairs in the crystallites. The change in conductivity results from a change in majority carrier density in the crystallites, and from reduction of intercrystalline barrier potentials.

Equations are developed for the response to radiation, for the noise, and for the limit of sensitivity of the detector. These expressions contain familiar semiconductor parameters, and a new parameter which characterizes the relative importance of the change in carrier density as compared to the change in barrier potential. No attempt is made to calculate the parameters, but measurements necessary for their evaluation are briefly discussed. This permits a prediction of numerical values for responsivity, noise, and sensitivity which can be compared with experiment.

I. INTRODUCTION

PHOTOCONDUCTIVE films of the lead salt family (PbS, PbSe, PbTe) are composed of a system of crystallites separated by intercrystalline barriers. The crystallites are lead salts while the intercrystalline barriers are oxides of lead or lead salts. The crystallites are about 0.1 to 1 micron on a side [l_c, Fig. 1(a)] and the width of the intercrystalline barrier is about 5 to 20 angstroms [l_b, Fig. 1(a)].[1] Space charge regions are present at the surface of the crystallites.[2,3] The lifetime of hole-electron pairs is determined in part by surface states, while the resistivity is strongly affected by intercrystalline barriers.

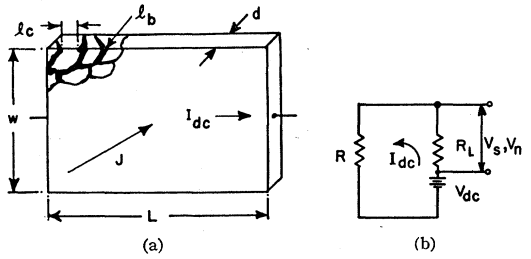

FIG. 1. (a) Pictorial representation of a polycrystalline film. (b) Circuit for measuring the specific responsivity as given by Eq. (27) and the specific noise as given by Eq. (61).

Previous theories[4] of photoconductivity in films of PbS and related semiconductors can be grouped into three classes, differing in the aspect of the film considered most important. The simplest model focuses attention on the crystallites and assumes the change in conductivity to arise from a change in the density of carriers in the crystallites.[5] The role of intercrystalline barriers and space charge regions is neglected.

In a second class, emphasis is placed on the space charge regions in the crystallites[2]; the oxide intercrystalline barriers are neglected. Evaporated lead salt films are initially *n*-type and exposure to oxygen converts them to *p*-type. It is postulated that this produces a series of *p-n* junctions, to which properties of the film are ascribed. The most complete analyses of this model are that recently reported by Slater[2] and that of Rittner.[2] The latter also considers the limiting case of heavy oxidation. This results in a large quasi-intrinsic region in the crystallites and the photoconductive behavior is then characteristic of an intrinsic semiconductor.[5] In both of the above classes the fundamental absorption process is assumed to be an intrinsic electron transition in the crystallites.

A third model focuses attention on the oxide-intercrystalline barriers, where the absorption is assumed to take place.[6] The change in resistance is related to the change in barrier potential, which depends on the charge density at the barriers. However, agreement now exists between the long wavelength photoconductive

[1] H. Pick, Z. Physik **126**, 12 (1949); Doughty, Lark-Horovitz, Roth, and Shapiro, Phys. Rev. **79**, 203(A) (1950); H. T. Minden, J. Chem. Phys. **23**, 1948 (1955); R. H. Harada, J. Chem. Phys. (to be published).

[2] Sosnowski, Starkiewicz, and Simpson, Nature **159**, 818 (1947); H. M. James, Science **110**, 254 (1949); E. S. Rittner, Science **111**, 685 (1950); Mahlman, Nottingham, and Slater in *Photoconductivity Conference*, edited by Breckenridge, Russell and Hahn (John Wiley and Sons, New York, 1956), p. 489; G. W. Mahlman, Phys. Rev. **103**, 1619 (1956); J. C. Slater, Phys. Rev. **103**, 1631 (1956). Also see reference 4 for additional references.

[3] E. S. Rittner in *Photoconductivity Conference*, p. 215; H. T. Minden, J. Chem. Phys. **25**, 241 (1956); Petritz, Lummis, Sorrows, and Woods in *Semiconductor Surface Physics*, edited by R. H. Kingston (University of Pennsylvania Press, Philadelphia, to be published).

[4] For a review of photoconductivity and extensive bibliographies see: T. S. Moss, Proc. Inst. Radio Engrs. **43**, 1869 (1955); R. A. Smith, Advances in Physics **2**, 321 (1953); and T. S. Moss, *Photoconductivity* (Butterworths Scientific Publications, London, 1952).

[5] 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). Also see reference 4 for additional references.

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

edge in PbS films and the intrinsic energy gap of PbS crystals as shown by Scanlon's Hall data[7] and Smith's reinterpretation of optical absorption data.[8] This indicates that the absorption takes place in the crystallites, rather than in the barriers; thus ruling out this model.

In this paper we develop a model which combines features of the first and third classes. We assume that the primary photoeffect is absorption of light and production of hole-electron pairs in the lead salt crystallites. Amplification effects due to possible changes in the oxide-intercrystalline barrier potentials are included in the formulation, but space charge regions within the crystallites are neglected.

The current is assumed to be carried by majority carriers. This does not mean that the minority carrier is unimportant in the basic mechanism of photoconductivity; on the contrary, recent experimental and theoretical work indicates that it is a trapping of minority carriers that increases the lifetime of the majority carriers.[9] But the direct contribution of the minority carrier to the current is assumed negligible.

We develop equations for the response to low level radiation and for the noise. These results are combined into an expression for the limit of sensitivity of the detector. Our resulting expressions contain familiar semiconductor parameters, and a new parameter which characterizes the relative importance of the change in carrier density as compared to changes in barrier potential. No attempt is made to calculate the parameters, but measurements necessary for their evaluation are briefly discussed.

The model was developed with the lead salt family of photoconductors in mind, but may well be applicable to a wider class of semiconducting films. PbS has received more attention than any other photoconductive film and therefore is referred to for data and examples throughout.

II. DEFINITION OF THE MACROSCOPIC CONDUCTIVITY AND HALL COEFFICIENT OF A FILM

The observable properties of a photoconductive film are a result of the average properties of many crystallites; there being some 10^8 crystallites per square centimeter of film area. It would be cumbersome to indicate by symbols an average over the many crystallites because we later need to denote time averages as well. Thus we shall not specifically denote averages over the crystallites but wish to emphasize that all quantities are to be considered as the average of many crystallites.

The total resistivity of a barrier in series with a crystallite is

$$\rho=\rho_b+\rho_c,$$

where the subscripts b and c mean barrier and crystallite, respectively. A comparison of resistivity data in films[4,10] with that in crystals[11] of PbS shows that $\rho_b \gg \rho_c$. To develop an expression for the macroscopic conductivity we neglect ρ_c compared to ρ_b and write the current-voltage relation of the barrier[12]:

$$j=Mpe^{-q\phi/kT}(e^{q\Delta V_b/kT}-1), \tag{1}$$

where j is the current density, q is the charge of an electron, p is the mean density of majority carriers (assumed to be holes) in the crystallites, ϕ is the potential height of the barriers referred to the valence band edge, k is Boltzman's constant, T is the absolute temperature, ΔV_b is the voltage drop across the barrier, and M is a parameter which is independent of ϕ but depends on the specific nature of the barrier. For a barrier of thickness of 5 to 20 A the shot theory should apply, for which $M=qv_{\text{thermal}}$, where v_{thermal} is the mean thermal velocity of the holes. Because of the many barriers in the film the voltage drop across any one is small compared to kT/q; thus

$$j=Mpe^{-q\phi/kT}q\Delta V_b/kT. \tag{2}$$

Considering that there are N_1 crystallites in series, ΔV_b is related to the total voltage V across the film by

$$\Delta V_b=V/N_1=V/n_1L, \tag{3}$$

where n_1 is the number of crystallites per cm of length of film and L is the length of the film in the direction of current flow [Fig. 1(a)]. For crystallites 10^{-4} cm on a side, $n_1\cong 10^4$ cm^{-1} since the space occupied by intercrystalline barriers is negligible. Using Eqs. (2) and (3), we have for the total current:

$$I=jwd=Mpe^{-q\phi/kT}qVwd/Ln_1kT, \tag{4}$$

where w and d are the width and thickness of the film, respectively [Fig. 1(a)]. The macroscopic electric field, conductivity, and resistance are defined as:

$$\mathcal{E}=V/L, \tag{5}$$

$$\sigma=j/\mathcal{E}, \tag{6}$$

$$R=L/\sigma wd. \tag{7}$$

[7] W. W. Scanlon, Phys. Rev. **92**, 1573 (1953).

[8] R. A. Smith, Physica **20**, 910 (1954); A. F. Gibson, Proc. Phys. Soc. (London) **B65**, 378 (1952); M. A. Clark and R. J. Cashman, Phys. Rev. **85**, 1043 (1952); D. G. Avery, Proc. Phys. Soc. (London) **B67**, 2 (1954).

[9] D. E. Bode and H. Levinstein, Phys. Rev. **96**, 259 (1954); R. A. Smith, Physica **20**, 910 (1954); J. N. Humphrey, Phys. Rev. **99**, 625(A) (1955); E. S. Rittner and S. Fine, Phys. Rev. **98**, 545 (1955); R. L. Petritz, Bull. Am. Phys. Soc. Ser. II, **1**, 177 (1956); R. H. Harada and H. T. Minden, Phys. Rev. **102**, 1258 (1956); J. N. Humphrey and R. L. Petritz (submitted to Phys. Rev.).

[10] E. W. Lothrup, Jr., thesis, Northwestern University, Evanston, Illinois, 1949 (unpublished); J. L. Levy, Phys. Rev. **92**, 215 (1953); J. F. Woods in *Photoconductivity Conference* (John Wiley and Sons, New York, 1956), p. 636; Phys. Rev. **99**, 658(A) (1955). Also see Petritz, et al., reference 3.

[11] R. F. Brebrick and W. W. Scanlon, Phys. Rev. **96**, 598 (1954); R. P. Chasmar, in *Photoconductivity Conference* (John Wiley and Sons, New York, 1956), p. 463; R. L. Petritz and W. W. Scanlon, Phys. Rev. **97**, 1620 (1955); E. H. Putley, Proc. Phys. Soc. (London) **B68**, 22 (1955).

[12] H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948), pp. 77–82.

Substituting Eqs. (4) and (5) into Eq. (6), we find

$$\sigma = q\mu p e^{-q\phi/kT}, \tag{8}$$

where

$$\mu = M/n_1 kT.$$

The term $e^{-q\phi/kT}$ in σ provides the essential characterization of a barrier. One can write Eq. (8) either as

$$\sigma = qp\mu^*, \quad \text{where} \quad \mu^* = \mu e^{-q\phi/kT}; \tag{9}$$

or as

$$\sigma = qp^*\mu, \quad \text{where} \quad p^* = pe^{-q\phi/kT}. \tag{10}$$

In Eq. (9) one implies that all of the holes in the crystallite take part in the conduction process but with a reduced mobility μ^*. In Eq. (10) one implies that only p^*/p of the crystallite carriers take part in the conduction process, but with the mobility μ. We use Eq. (9) since the macroscopic Hall coefficient, R_H, gives the total carrier density in the crystallites. This is because the crystallites are of much lower resistivity than the intercrystalline barriers.[13] Thus

$$R_H = \tfrac{3}{8}\pi/qp. \tag{11}$$

Defining the Hall mobility as

$$\mu_H = R_H\sigma, \tag{12}$$

and substituting Eq. (9) for σ and Eq. (11) for R_H, we have:

$$\mu_H = \tfrac{3}{8}\pi\mu^*. \tag{13}$$

Therefore, the Hall mobility is a direct measure of μ^* and includes the effects of barriers.

The macroscopic parameters are useful because they are directly measurable. However, they imply that the electric field is V/L and that it is uniform over the entire film. Actually, the electric field is stronger in the regions of the barriers and is reduced in the crystallites. Conductivities and electric fields that apply locally to the barriers and crystallites are developed in the Appendix.

III. PHOTOCONDUCTIVE RESPONSE TO RADIATION

A. Derivation

The change in conductivity that occurs when radiation falls on a film can result from a change in the density of carriers and from a change in the effective mobility. From Eq. (9) we have for small changes,

$$\Delta\sigma = q\mu^*\Delta p + qp\Delta\mu^*, \tag{14}$$

where

$$\Delta\mu^* = -\mu e^{-q\phi/kT} q\Delta\phi/kT. \tag{15}$$

Since light is absorbed by a main-band transition, the primary photoeffect in PbS is a change in the number of hole-electron pairs in the crystallites. Any increase in mobility resulting from barrier modulation is thus a secondary process. However, the latter's influence on the change in conductivity could overshadow that of the primary effect. A possible mechanism of barrier modulation is trapping of minority carriers in the region of the barrier.

We define a parameter B to characterize the relative effect of barrier modulation on the conductivity as compared to the change in density of carriers:

$$B = (\Delta\mu^*/\mu^*)/(\Delta p/p). \tag{16}$$

Substituting Eq. (16) into Eq. (14), we have

$$\Delta\sigma = q\mu^*(1+B)\Delta p. \tag{17}$$

$B=0$ means no barrier modulation, while $B \gg 0$ means that the change in conductivity is mainly a result of barrier modulation. In the small-signal range of photoconductivity, B should be independent of the amplitude of the signal.

In writing Eq. (14) we have implicitly assumed that the total change in majority carriers in each crystallite contributes to the change in conductivity. This is true if the diffusion length of minority carriers, L_n, is large compared to the crystallite size. Using mobility data from PbS crystals[11] one can show that $L_n \geqslant d$ for minority carrier lifetimes as short as 10^{-9} sec and $d=1$ micron.

The majority carrier lifetime is assumed to be equal to the photoconductive response time. Thus we write as the equation of the primary photoresponse,

$$\frac{d\Delta p}{dt} + \frac{\Delta p}{\tau} = g, \tag{18}$$

where

$$g = \eta_s J/h\nu_s d, \tag{19}$$

Δp is the increase in majority carrier density over the mean value, τ is the majority carrier lifetime, g is the rate of absorption of the incident photons, J is the incident signal flux (watts/cm^2) and $h\nu_s$ is the energy per photon. η_s is the probability that an incident photon will be absorbed, producing a hole-electron pair. Moss has shown[14] that

$$\eta_s = (1-r)(1-e^{-\alpha d})/(1-re^{-\alpha d}) \leqslant 1, \tag{20}$$

where α is the absorption coefficient at the wavelength of the signal, and r is the reflection coefficient of the film. We call η_s the quantum efficiency.

Rittner[3] has shown that the carriers can be assumed to be produced uniformly throughout the crystallites as described by Eqs. (18) and (19) so long as the diffusion distance of minority carriers is large compared to the crystallite size. This condition was discussed above. Then effects of the surface on the lifetime are incorporated into τ as

$$1/\tau = (1/\tau_b) + (1/\tau_s), \tag{21}$$

[13] G. R. Wait, Phys. Rev. **19**, 615 (1922); J. Vogler, Phys. Rev. **79**, 1023 (1950).

[14] T. S. Moss in *Photoconductivity Conference* (John Wiley and Sons, Inc., New York, 1956), p. 427.

where τ_b and τ_s are the bulk and surface lifetimes respectively. τ_s can be expressed in terms of the surface recombination velocity s, by

$$\tau_s = d/2s. \tag{22}$$

Considering the radiation to be turned on at time $t=0$, we find the transient response from Eq. (18):

$$\Delta p = g\tau(1-e^{-t/\tau}). \tag{23}$$

Substituting Eq. (23) into Eq. (17), we have

$$\Delta\sigma = (1+B)q\mu^* g\tau(1-e^{-t/\tau}). \tag{24}$$

The corresponding response to a radiation signal chopped at an angular frequency ω is

$$\Delta\sigma = (1+B)q\mu^* g\tau/[1+(\omega\tau)^2]^{\frac{1}{2}}. \tag{25}$$

B. Normalization of Photoresponse

In order to compare one film with another, it is useful to normalize the response. Mundie[15] has suggested the form $\Delta\sigma/4\sigma J$ and has called this the specific sensitivity. We shall use this definition but prefer to call it the specific responsivity, since the use of sensitivity has been largely restricted to signal-to-noise concepts. We therefore define

$$R_s = \Delta\sigma/4\sigma J \quad \text{(specific responsivity)}. \tag{26}$$

A convenient method of measuring R_s is shown in Fig. 1(b). The signal voltage, V_s, across the load resistance, R_L, is a measure of R_s according to the equation

$$R_s = \left(\frac{V_s}{V_{dc}J}\right)\left(\frac{(R+R_L)^2}{4RR_L}\right), \tag{27}$$

where V_{dc} is the battery voltage.

This definition normalizes the response to unit biasing voltage and unit incident radiation flux. Equation (27) shows that R_s is a measure of the effectiveness by which a detector converts radiation flux to signal voltage.

Substituting Eqs. (9), (19), and (25) into Eq. (26) we find a theoretical expression for R_s,

$$R_s = \frac{(1+B)\eta_s\tau}{4pdh\nu_s[1+(\omega\tau)^2]^{\frac{1}{2}}}. \tag{28}$$

We now call attention to another definition that has been used to characterize the signal response. This is the electrical signal current produced per current of incident photons,[16] sometimes called an apparent quantum efficiency, η^*. One finds for this model:

$$\eta^* = \frac{\Delta I_{\text{electron current}}}{\Delta I_{\text{photon current}}} = \frac{\mathcal{E}\Delta\sigma wd/q}{JwL/h\nu_s} = (1+B)\eta_s\frac{\tau}{\tau_t}, \tag{29}$$

$$\tau_t = L/\mathcal{E}\mu^*.$$

τ_t is the macroscopic transit time of a hole across the film. η^* can be greater than one if large barrier amplification is present or if τ is greater than τ_t. The latter is possible in a photoconductor where charge can flow in and out at the contacts, as is the case in infrared detectors.

We prefer the specific responsivity [Eq. (28)] for characterizing the signal response rather than η^* [Eq. (29)] because the latter definition involves the applied electric field and therefore is not a specific function of the detector. We shall restrict the term quantum efficiency to the definition in Eq. (20).

In summary, we have the specific responsivity given by Eq. (28) and see that to study this our measurements should include ways of finding B, η_s, τ, and pd. In particular, it is necessary to separate $(1+B)$ and η_s in order to determine if barrier modulation is occurring.

IV. PHOTOCONDUCTOR NOISE

Noise mechanisms in a semiconductor type photodetector can be grouped into two general classes: electronic and modulation noise.[17,18] The electronic noise includes all fluctuations inherent in the electronic system of a semiconductor. Modulation noise includes fluctuations in quantities which exert a control over the average current. Most theories of $1/f$ noise are of the latter variety,[19,20] although some recent theories[21] have attempted to explain it as an electronic noise.

A. Electronic Noise

The kinetic mechanism of the noise associated directly with the barriers depends on the specific model of barrier, but in general can be described as a fluctuation in the rate at which carriers cross the barrier. This leads to the Nyquist[22] and shot noise discussed below.

A second source of noise results from fluctuations in the number of holes in the crystallites. This causes a fluctuation in the conductivity as can be seen from Eq. (17). Since radiation is detected by measuring a change in conductivity, this noise sets a fundamental limit to the sensitivity of the detector.

The relation of fluctuations in the number of holes[23]

[15] L. G. Mundie (private communication).

[16] A. Rose, RCA Review **12**, 362 (1951); Phys. Rev. **97**, 322 (1955); and Proc. Inst. Radio Engrs. **43**, 1850 (1955).

[17] R. L. Petritz, Proc. Inst. Radio Engrs. **40**, 1440 (1952).

[18] K. M. Van Vliet and J. Blok, Physica **22**, 231 (1956).

[19] G. G. Macfarlane, Proc. Phys. Soc. (London) **B63**, 807 (1950); J. M. Richardson, Bell System Tech. J. **29**, 117 (1950); A. van der Ziel, Physica **16**, 359 (1950); R. L. Petritz, Phys. Rev. **87**, 189(A) and 535 (1952); R. L. Petritz in *Semiconductor Surface Physics*, 1956 (University of Pennsylvania Press, Philadelphia, to be published). Also see references given in references 17 and 20.

[20] A. van der Ziel, *Noise* (Prentice-Hall Inc., New York, 1955).

[21] A. L. McWhorter, Phys. Rev. **98**, 1191(A) (1955); also thesis, Massachusetts Institute of Technology, 1955 (unpublished) and *Semiconductor Surface Physics*, 1956 (University of Pennsylvania Press, Philadelphia, to be published); S. R. Morrison, Phys. Rev. **99**, 1655(A) and 1704 (1955).

[22] H. Nyquist, Phys. Rev. **32**, 110 (1928).

[23] B. I. Davydov and G. Gurevich, J. Phys. (U.S.S.R.) **7**, 138 (1943). J. H. Gisolf, Physica **15**, 825 (1949); R. L. Petritz, in *Summary of Doctoral Theses* (Northwestern University Press,

to fluctuations in the rate at which photons are incident on the detector[24] was recently clarified for the intrinsic model of a semiconductor.[25] It was shown that the fluctuations in the number of holes and electrons are in part caused by fluctuations in the rate of absorption and emission of background radiation, and in part by absorption and emission of lattice phonons. Following the terminology of Van Vliet and Blok,[18] we call this generation-recombination noise.

1. *Nyquist and Shot Noise*

If the barriers are thin compared to a mean-free-path in the crystallites, the shot theory of barriers will apply.[12] Weisskopf has examined the noise of such a barrier and finds for the spectrum of the short-circuit noise current generator,[26]

$$G(I^2)=2q(I_b+2I_s)=4qI_s+2qI_b$$
$$=(4kT/R_b)+2qI_b, \tag{30}$$

where, from Eq. (1),

$$I_b=I_s(e^{q\Delta V_b/kT}-1),$$
$$I_s=A_bMpe^{-q\phi/kT},$$
$$1/R_b=\partial I_b/\partial\Delta V_b|_{\Delta V_b=0,\ I_b=0}=I_sq/kT,$$

and A_b is the area of a single barrier.

At zero bias this reduces to the usual Nyquist formula,

$$G(I^2)=4kT/R_b.$$

When the voltage drop across individual barriers is finite but small compared to kT/q, Eq. (30) can be written to first order in $q\Delta V_b/kT$ as

$$G(I^2)=(4kT/R_b)(1+\tfrac{1}{2}q\Delta V_b/kT),$$
$$I_b=I_sq\Delta V_b/kT.$$

Therefore in the ohmic region, $q\Delta V_b/kT\ll 1$, the Nyquist equation is a good approximation for each barrier.

At large forward or reverse bias Eq. (30) reduces to

$$G(I^2)=2qI_b.$$

This is the shot-noise formula, which is to be expected since the kinetic basis is the random passage of electrons across the barrier.

The only other type of barrier whose noise characteristics have been studied in detail is the *p-n* junction.[17,27] Its short-circuit noise current generator is described by an equation similar to Eq. (30); it is linear in the current and reduces to the Nyquist value when $\Delta V_b<kT/q$.

To derive the expression for the total noise due to barriers, we first add the current generators in parallel, considering that there are approximately

$$N_2=wd/A_b$$

barriers in parallel all with the voltage, ΔV_b, across them. Then, from Eq. (30) and assuming $q\Delta V_b/kT<1$, we have

$$G(I^2,\text{ parallel})=N_2[(4kT/R_b)(1+q\Delta V_b/2kT)].$$

To add the noise of barriers which are in series in the direction of the length of the film, we convert this to a voltage generator,

$$G(V^2,\text{ parallel})=G(I^2,\text{ parallel})(R_b/N_2)^2,$$

where R_b/N_2 is the resistance of N_2 barriers in parallel. Then, adding $N_1=n_1L$ of these voltage generators in series, we have

$$G(V^2)=N_1G(I^2)(R_b/N_2)^2$$
$$=R4kT(1+q\Delta V_b/2kT),$$

where $R=N_1R_b/N_2$ is the macroscopic resistance defined in Eq. (7). The macroscopic short-circuit current generator then is,

$$G(I^2)=(4kT/R)(1+q\Delta V_b/2kT),$$
$$=(4kT/R)+(2qI_{dc}/n_1L), \tag{31}$$

where we have used Eqs. (3) and (4). Equation (31) shows that the contribution of the barriers is in first approximation a Nyquist term; and in second approximation includes a term of order $q\Delta V_b/kT$, linear in the bias current, I_{dc}, and called a shot component; it neglects terms of order $(q\Delta V_b/kT)^2$.

In addition to these barrier contributions, the usual Nyquist noise occurs in each crystallite resistance. Its kinetic basis is fluctuations in the velocities of majority carriers. It remains independent of current throughout the ohmic range of current in the crystallites. The Nyquist noise of the crystallites is in effect incorporated into Eq. (31) if R is interpreted to include crystallite as well as barrier resistance.

2. *Generation-Recombination Noise*

(*a*) *Derivation.*—Extension of the theory of generation-recombination noise to a film with barriers will only be sketched here, since the procedure is quite similar to that of Appendix A of reference 25.

We use Eq. (18) to describe the response of Δp to fluctuations in the generation-recombination rates and Eq. (17) to describe the corresponding fluctuations in

Evaston, Illinois, 1950); H. Muser, Z. Physik **129**, 504 (1951). For additional references see references 17 and 20.

[24] W. B. Lewis, Proc. Phys. Soc. (London) **59**, 34 (1947); R. Clark Jones, J. Opt. Soc. Am. **37**, 879 (1947); P. Fellgett, J. Opt. Soc. Am. **39**, 970 (1949); T. S. Moss, J. Opt. Soc. Am. **40**, 603 (1950). For an extensive list of references on this subject see R. Clark Jones, in *Advances in Electronics* (Academic Press, New York, 1953), Vol. V, p. 2.

[25] R. L. Petritz in *Photoconductivity Conference* (John Wiley and Sons, Inc., New York, 1956), p. 49.

[26] V. F. Weisskopf, National Defense Research Committee Report NDRC 14–133, May 15, 1943 (unpublished). See Chap. 6 of reference 12 for an outline of Weisskopf's paper.

[27] R. L. Petritz, Phys. Rev. **91**, 231(A) and 204 (1953); A. van der Ziel, Proc. Inst. Radio Engrs. **43**, 1639 (1955).

conductivity. In the language of the theory of random processes, we are using the Langevin formulism, but we do not assume anything concerning the spectra of the random forces. Defining $N=Apd$ as the instantaneous total number of holes in the detector, we have

$$d\Delta N/dt+\Delta N/\tau=F_r(t)-R_r(t)+F_l(t)-R_l(t), \quad (32)$$

where $F_r(t)$ is the instantaneous rate of generation of holes by absorption of radiation, $R_r(t)$ is the instantaneous rate of recombination with emission of radiation, $F_l(t)$ and $R_l(t)$ are the corresponding rates of generation and recombination by lattice processes. These are the random forces of the theory.

The spectrum of N is found following the procedure of Eqs. (A-17) to (A-22) in reference 25. One finds

$$G(\Delta N^2)=2\tau^2(\bar{F}_r+\bar{F}_l+\bar{R}_r+\bar{R}_l)/[1+(\omega\tau)^2]. \quad (33)$$

In the derivation we will use bars to denote mean rates for the quantities which appear explicitly as both instantaneous and mean values. In the final expressions [Eq. (51) and beyond] it will be possible to drop the bars, reverting to the notation of Sec. II. From Eq. (17) the spectrum of the conductivity fluctuations is related to Eq. (33) by

$$G(\Delta\sigma^2)=[q\mu^*(1+B)]^2G(\Delta N^2)/(Ad)^2. \quad (34)$$

When a dc current is flowing the conductivity fluctuations give rise to a noise current. With the aid of Eqs. (4)–(9), (33), and (34) the spectrum of the short-circuit noise current generator is:

$$G(I^2)=\frac{I_{dc}^2(1+B)^2\tau^2(\bar{F}_r+\bar{F}_l+\bar{R}_r+\bar{R}_l)}{A^2(\bar{p}d)^2[1+(\omega\tau)^2]}. \quad (35)$$

It is useful to express the noise in terms of background radiation and lattice vibrations, and also directly in terms of characteristic semiconductor parameters. A first step for doing this is to use the condition of dynamic equilibrium,

$$\bar{F}_r+\bar{F}_l=\bar{R}_r+\bar{R}_l, \quad (36)$$

which allows us to express Eq. (35) entirely in terms of generation rates or recombination rates.

(*b*) *Expression of the generation-recombination noise in terms of background radiation and lattice vibrations.*—$\bar{F}_r$ can be expressed in terms of the background radiation incident on the detector by

$$\bar{F}_r=\tfrac{1}{4}cA\int_0^\infty \eta(\nu)n_r d\nu, \quad (37)$$

$$n_r(\nu)=8\pi(\nu/c)^2/(e^{h\nu/kT_r}-1), \quad (38)$$

where $\eta(\nu)$ is the quantum efficiency at a spectral frequency ν, [Eq. (20)], $n_r(\nu)$ is the mean density of photons in the background radiation field per $d\nu$, and T_r is the temperature of the background radiation field. $\eta(\nu)$ goes to zero for wavelengths longer than $\lambda_i=hc/E_i$, where E_i is the intrinsic energy gap of the semiconductor. Thus $\bar{F}_r$ can be expressed as

$$\bar{F}_r=\eta_r J_r A, \quad (39)$$

where

$$J_r=\frac{c}{4}\int_{E_i/h}^\infty n_r(\nu)d\nu \text{ photons/cm}^2\text{-sec}. \quad (40)$$

J_r is the mean background photon flux incident on the detector with energy $\geqslant E_i$. η_r is defined by Eqs. (37), (39), and (40). An approximation to η_r is the value of the quantum efficiency in the region of maximum photoconductive response.

An approximate expression for J_r, obtained from Eq. (40) by neglecting -1 in the denominator of $n_r(\nu)$, is

$$J_r=B_r(T_r)e^{-E_i/kT_r},$$

where

$$B_r(T_r)=2\pi c\left(\frac{kT_r}{hc}\right)^3\left[\left(\frac{E_i}{kT_r}\right)^2+\frac{2E_i}{kT_r}+2\right]. \quad (41)$$

The mean lattice generation rate $\bar{F}_l$ can also be expressed formally as an integral similar to Eq. (37), with n_r replaced by n_l, the density of lattice phonons. Lacking detailed information on the lattice vibrational spectrum, we write

$$\begin{aligned} J_l&=B_l(T_l)e^{-E_i/kT_l} \text{ phonons/cm}^2\text{-sec},\\ \bar{F}_l&=\eta_l J_l A, \end{aligned} \quad (42)$$

where T_l is the temperature of the lattice and η_l is a quantum efficiency for absorption of phonons.

Substituting Eqs. (39) and (42) into Eq. (35) and using Eq. (36) we write the noise in terms of background radiation and lattice vibrations,

$$G(I^2)=\frac{I_{dc}^2(1+B)^2 4\tau^2(\eta_r J_r+\eta_l J_l)}{A(\bar{p}d)^2[1+(\omega\tau)^2]}. \quad (43)$$

This equation can be used to discuss the effects of cooling the background radiation and/or the lattice, since J_r and J_l are functions of T_r and T_l, respectively, [Eqs. (41) and (42)].

When the detector exchanges radiation with several objects at different temperatures, Eq. (37) will have one term for each object with the appropriate solid angles as weighting terms (Lewis[24]). As a result Eq. (43) will have a flux component from each object.

(*c*) *Expression of generation-recombination noise in terms of parameters of the photoconductor.*—This can be done with the aid of detailed balance and time constant realtions. For this model the mean rate of hole-electron recombination by emission of a photon is related to the radiative lifetime, τ_r, by

$$\bar{R}_r=\bar{N}/\tau_r. \quad (44)$$

Similarly, for recombination through phonon emission

we have

$$\bar{R}_l=\bar{N}/\tau_l, \tag{44b}$$

where τ_l is the lattice lifetime. The total rate of recombination defines the majority carrier lifetime, τ, by

$$\bar{R}_r+\bar{R}_l=\bar{N}/\tau, \tag{45}$$

where

$$1/\tau=(1/\tau_r)+(1/\tau_l). \tag{46}$$

Substituting Eq. (45) into Eq. (36), we have

$$\bar{F}_r+\bar{F}_l=\bar{N}/\tau. \tag{47}$$

Using Eqs. (39) and (42), we can express this on a unit sensitive area basis,

$$\eta_r J_r+\eta_l J_l=\bar{p}d/\tau. \tag{48}$$

Substituting Eq. (48) into Eq. (43), we find

$$G(I^2)=\frac{I_{dc}^2 4\tau(1+B)^2}{A\bar{p}d[1+(\omega\tau)^2]}. \tag{49}$$

This equation contains only parameters of the photoconductor.

Equations (49) and (43) together with Eq. (48) allow for a complete discussion of the limiting noise of the photoconductive detector under conditions of nonthermal equilibrium as well as thermal equilibrium. Equation (48) assumes only the condition of dynamic equilibrium, and does not assume thermal equilibrium. At thermal equilibrium we have in addition to Eq. (48),

$$\begin{aligned}\eta_r J_r&=\bar{p}d/\tau_r,\\ \eta_l J_l&=\bar{p}d/\tau_l,\end{aligned} \tag{50}$$

which are the conditions of detailed balance for the radiative and lattice processes, respectively.

(*d*) *Normalization.*—As suggested by Mundie,[15] it is useful to express the noise in a normalized manner to eliminate the dc bias current, the cell area, and the bandwidth. We define the specific generation-recombination noise as

$$N_s(G\text{-}R)=[G(I^2)A]^{\frac{1}{2}}/4I_{dc}, \tag{51}$$

which differs from that of Mundie in that a $1/f$ spectrum is not assumed for the noise. Substituting Eqs. (49) and (43) into (51) and dropping the bars for denoting averages, we find, respectively,

$$N_s(G\text{-}R)=\tfrac{1}{2}(1+B)(\tau/pd)^{\frac{1}{2}}/[1+(\omega\tau)^2]^{\frac{1}{4}}, \tag{52}$$

$$N_s(G\text{-}R)=\tfrac{1}{2}(1+B)(\tau/pd)(\eta_r J_r+\eta_l J_l)^{\frac{1}{2}}/\times[1+(\omega\tau)^2]^{\frac{1}{2}}. \tag{53}$$

Equation (53) can be written as $N_s^2(G\text{-}R)=N_{sr}^2(G\text{-}R)+N_{sl}^2(G\text{-}R)$, so we can identify the specific noise caused by fluctuations in the rate of radiative processes as

$$N_{sr}(G\text{-}R)=\tfrac{1}{2}(1+B)(\tau/pd)(\eta_r J_r)^{\frac{1}{2}}/[1+(\omega\tau)^2]^{\frac{1}{4}}, \tag{54}$$

and the corresponding noise resulting from lattice processes as

$$N_{sl}(G\text{-}R)=\tfrac{1}{2}(1+B)(\tau/pd)(\eta_l J_l)^{\frac{1}{2}}/[1+(\omega\tau)^2]^{\frac{1}{4}}. \tag{55}$$

$N_{sr}(G\text{-}R)$ is the noise limit set by the fluctuations in the absorption and emission of background radiation and establishes the ultimate limit of sensitivity.[24,25]

B. Modulation Noise

Experiment shows that there is a component of noise characterized by a $1/f$ spectrum. Its physical origin is not completely understood but recent experiments[21] indicate that the surface is an important source of this noise. Theories of $1/f$ noise will be found in references 19, 20, and 21. Since the photodetector shows an exponential time response with a single time constant, the theory[17,28] of irreversible processes indicates that $1/f$ noise is not fundamental to the detection process. Thus one can hope to minimize it by improved manufacturing techniques.

The spectrum of the $1/f$ noise can be empirically characterized by the short-circuit noise current generator,

$$G(I^2)=CI_{dc}^2/fAd, \tag{56}$$

where C is found by experiment. The specific $1/f$ noise is defined analogously to Eq. (51):

$$N_s(1/f)=[G(I^2)A]^{\frac{1}{2}}/4I_{dc}=\tfrac{1}{4}(C/fd)^{\frac{1}{2}}. \tag{57}$$

C. Total Photoconductor Noise

From Eqs. (31), (49), and (56) we have for the spectrum of the total short-circuit noise current generator of a photodetector

$$G(I^2)=(4kT/R)+G[I_c^2(G\text{-}R,\ 1/f,\ \text{shot})], \tag{58}$$

$$G[I_c^2(G\text{-}R,\ 1/f,\ \text{shot})]=\frac{4\tau I_{dc}^2(1+B)^2}{Apd[1+(\omega\tau)^2]}+\frac{CI_{dc}^2}{fAd}+\frac{2qI_{dc}}{nL}. \tag{59}$$

Under normal biasing conditions the first term in Eq. (58) is negligible compared to the second and the shot term is also negligible in Eq. (59). It is then useful to define the total specific noise of the detector analogously to Eq. (51):

$$\begin{aligned}N_s^2&=G[I_c^2(G\text{-}R,\ 1/f)]A/16I_{dc}^2\\&=N_s^2(G\text{-}R)+N_s^2(1/f),\end{aligned} \tag{60}$$

where $N_s(G\text{-}R)$ and $N_s(1/f)$ are given by Eqs. (52) [or (53)] and (57), respectively.

[28] H. B. G. Casimir, Revs. Modern Phys. **17**, 343 (1945); S. R. de Groot, *Thermodynamics of Irreversible Processes* (Interscience Publishers, Inc., New York, 1951), pp. 17–18.

We have defined the specific noise in terms of short-circuit noise current generators because the noise sources are in parallel. The definition of specific noise in terms of a noise voltage, V_n, appearing across a load resistor R_L in the circuit shown in Fig. 1(b) is

$$N_s=V_n(A/\Delta f)^{\frac{1}{2}}(R+R_L)^2/4RR_LV_{\rm dc}. \tag{61}$$

Circuit analysis shows that Eq. (60) and Eq. (61) are equivalent.

V. LIMIT OF SENSITIVITY

The limit of sensitivity of a photoconductor is defined as the radiation signal power necessary to produce a signal-to-noise ratio equal to unity. The specific sensitivity, S_s, removes the area and bandwidth dependence from the definition:

$$S_s=J(A/\Delta f)^{\frac{1}{2}}V_n/V_s. \tag{62}$$

S_s is the noise-equivalent-power of a cell of 1 cm^2 sensitive area when a band width of 1 cps is used. S_s is closely related to Jones' S which is defined[29] as

$$\mathrm{S}=J(f_0A/\Delta f)^{\frac{1}{2}}V_n/V_s, \tag{63}$$

where f_0 is the center frequency at which the noise is measured. The f_0 factor was introduced by Jones to account for the $1/f$ noise spectrum commonly observed at that time. However, detectors are now available[30] in which $1/f$ noise is less important than generation-recombination noise and the insertion of f_0 into the equation has significance only for $1/f$ noise. We therefore shall use Eq. (62) instead of Eq. (63) because it does not assume any particular spectrum for the noise.

Substituting Eqs. (27) and (61) into Eq. (62) we find

$$S_s=N_s/R_s. \tag{64}$$

When the noise is generation-recombination noise, we have

$$S_s(G\text{-}R)=N_s(G\text{-}R)/R_s. \tag{65}$$

Substituting Eqs. (28), (52), and (53) into this, we find as theoretical expressions:

$$S_s(G\text{-}R)=2h\nu_s(pd/\tau)^{\frac{1}{2}}/\eta_s, \tag{66}$$

$$S_s(G\text{-}R)=2h\nu_s(\eta_rJ_r+\eta_lJ_l)^{\frac{1}{2}}/\eta_s. \tag{67}$$

As pointed out in reference 25, barrier amplification does not affect $S_s(G\text{-}R)$ because both signal and noise are amplified.

The ultimate limit of sensitivity is set by fluctuations in radiative processes[24,25] and is obtained when $\eta_lJ_l\ll\eta_rJ_r$ in Eq. (67):

$$S_{sr}(G\text{-}R)=2h\nu_s(\eta_rJ_r)^{\frac{1}{2}}/\eta_s. \tag{68}$$

[29] R. Clark Jones, Rev. Sci. Instr. **24**, 1035 (1953).
[30] F. L. Lummis and R. L. Petritz, Phys. Rev. **86**, 660(A) (1952); B. Wolfe, Rev. Sci. Instr. **27**, 60 (1956).

VI. CONCLUSION

The above theory relates the specific responsivity, Eq. (28), the specific generation-recombination noise [Eqs. (52) and (53)], and the specific sensitivity [Eqs. (66), (67)] to basic semiconductor parameters and to radiation and lattice fluxes. The semiconductor parameters, pd, τ, and B, can be measured directly: pd by the Hall-coefficient [Eq. (11)], τ by the transient response to a square wave [Eq. (24)], and B by measuring the fractional change in resistance $\Delta R/R$ and Hall-coefficient, $\Delta R_H/R_H$, under illumination,

$$B=\frac{\Delta R/R}{\Delta R_H/R_H}-1. \tag{69}$$

The quantum efficiency, η_s, can be estimated from Eq. (20) using known values of α and r. Therefore theoretical values of R_s, N_s, and S_s can be predicted by using measured values of pd, τ, B, and η_s in Eqs. (28), (52), and (66). Thus the theory can be checked by comparing theoretical with experimental values of R_s, $N_s(G\text{-}R)$, and $S_s(G\text{-}R)$. Such measurements have been made and will be reported in forthcoming papers. Theory and experiment are found to be in good agreement.

APPENDIX. MICROSCOPIC CONDUCTIVITIES AND ELECTRIC FIELDS

(a) Parameters of the Barriers

A barrier conductivity σ_b can be defined from Eq. (2) by writing

$$\begin{aligned} j&=(M/kT)pe^{-q\phi/kT}q\mathcal{E}_bl_b,\\ \mathcal{E}_b&=\Delta V_b/l_b=j/\sigma_b,\end{aligned} \tag{A-1}$$

where $\mathcal{E}_b$ is the electric field across the barrier and l_b is the width of the barrier [Fig. 1(a)]. Then using Eqs. (3), (5), and (8):

$$\sigma_b=(M/kT)pe^{-q\phi/kT}ql_b=n_1l_b\sigma, \tag{A-2}$$

$$\mathcal{E}_b=\mathcal{E}/n_1l_b=\mathcal{E}\sigma/\sigma_b. \tag{A-3}$$

To show that $\mathcal{E}_b$ is normally higher than $\mathcal{E}$, and σ_b lower than σ, we put some representative numbers in Eqs. (A-2) and (A-3). For $n_1=10^4$/cm and $l_b=10^{-7}$ cm, we obtain $\mathcal{E}_b=10^3\mathcal{E}$ and $\sigma_b=10^{-3}\sigma$.

(b) Parameters of the Crystallites

The voltage drop across a crystallite is

$$\Delta V_c=jl_c/\sigma_c, \tag{A-4}$$

where the conductivity of a crystallite is

$$\sigma_c=qp\mu_c, \tag{A-5}$$

and we assume the current density in the crystallites to be the same as in the barriers. μ_c is the mobility of carriers in the crystallites and should be somewhat less than that in single crystals because of surface

scattering. The electric field in the crystallites is

$$\mathcal{E}_c = \Delta V_c / l_c = j/\sigma_c. \quad \text{(A-6)}$$

Substituting Eqs. (6), (9), and (A-5) in Eq. (A-6) we obtain

$$\mathcal{E}_c = \mathcal{E}\sigma/\sigma_c = \mathcal{E}\mu^*/\mu_c. \quad \text{(A-7)}$$

$\mathcal{E}_c$ will normally be less than $\mathcal{E}$ because μ^* is less than μ_c, as shown by comparing the Hall mobility of films[10] with that of single crystals.[11] At room temperature in PbS, $\mu^* \cong 5$ while $\mu_c \cong 400$ cm²/volt-sec.

From the above and the results of Sec. II we see that a precise characterization of a film involves three conductivities, mobilities, and electric fields. The macroscopic definitions are most useful for this paper, but when microscopic properties are discussed care must be taken to insure that the correct electric field is used.

It is also possible that the current density in the barriers is greater than in the crystallites, as when the effective cross-sectional area of a barrier, A_b, is small compared to that of the adjacent crystallites. We do not attempt to discuss this effect quantitatively here.

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Effect of Monolayer Adsorption on the Ejection of Electrons from Metals by Ions

HOMER D. HAGSTRUM
Bell Telephone Laboratories, Murray Hill, New Jersey

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Electron ejection from metals by ions is shown in this work to be a surface-sensitive phenomenon which is profoundly affected by the adsorption of a monolayer of foreign gas on an atomically clean metal surface. Monolayer adsorption is shown to decrease the total electron yield, γ_i, primarily at the expense of the faster electrons ejected from the metal. Measurements of γ_i show it to decrease steadily as the monolayer forms and to level off at a value characteristic of the covered surface when the monolayer is completed. Measurements have been made for the adsorption of N_2, H_2, and CO on tungsten. Electron ejection by all the singly-charged ions of the noble gases has been studied. It was possible to clean the tungsten surface in the presence of N_2 and CO but not in H_2. In H_2 the tungsten surface, as judged from γ_i measurement, was found to be covered with about 75% of a monolayer immediately upon cooling from 2000°K. It is shown that the effect of monolayer adsorption cannot possibly be simply the result of change in work function. There is also evidence that electrons are ejected in non-Auger processes at higher ion energies when the surface is covered.

I. INTRODUCTION

As might be expected, the ejection of electrons from metals by slowly moving positive ions is a surface-sensitive phenomenon. For this reason one would like to study it not only with atomically clean surfaces[1,2] but also with surfaces having known amounts of known gases adsorbed upon them.

If foreign atoms adsorbed on a metal surface change the work function, the probability of escape of electrons excited inside the metal is also changed. For secondary emission by a beam of primary electrons this is the only effect of surface coverage since the surface film has negligible effect upon the production of internal secondary electrons in the body of the metal.[3] It seems clear that one is not justified in drawing any such conclusion *a priori* for the Auger ejection of electrons by slowly moving positive ions. Here the primary process of excitation of the internal secondary electron takes place with the ion just *outside* the metal surface and proceeds with a probability which depends upon whether the excited electron may escape from the metal or not.[4] Thus it is certainly possible that the interposition of a layer of foreign atoms between the metal lattice and the incoming ion will affect not only the probability of electron escape but also other aspects of the phenomenon (Sec. VII). It is also possible that non-Auger processes of electron ejection become important for the gas-covered surface.

The results reported in this paper concern the effect of adsorption of the common gases H_2, N_2, and CO on the electron ejection from tungsten by singly-charged ions of the noble gases. Experimental apparatus is discussed in Sec. II and experimental conditions prevailing when measurements were made are discussed in Sec. III. It is shown that experimental conditions can be established in which it is possible to produce a monolayer of adsorbed gas of a high degree of purity. The effects of the presence of this monolayer on the total yield of electrons for incident ion (Sec. IV) and on

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