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Attenuation Length Measurements of Hot Electrons in Metal Films

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A study has been made of the photoemission from metal films evaporated on a freshly cleaved silicon surface, the silicon-metal junction acting as a collector. Plots of the photoemission as a function of photon energy yield values for the height of the potential barrier at this junction of 0.795±0.010 eV for Au, 0.655±0.010 eV for Ag, 0.55±0.03 eV for Cu, and 0.710±0.005 eV for Pd. The spectral dependence of the energy absorbed in reference films has been deduced from transmission and reflection measurements which permitted a calculation of the photoresponse per absorbed photon. Correlation of this photoresponse with film thickness yields a value for the electron attenuation length for electron energies slightly in excess of the barrier height. Photon energies were restricted to less than 1.1 eV to avoid the large photoresponse introduced by band-to-band transitions in the silicon. The electron attenuation lengths obtained are ≈740 Å for Au, ≈440 Å for Ag, ≈170 Å for Pd, and between 50 and 200 Å for Cu. These values have been compared with recent theoretical predictions of the electron mean free path. Qualitative agreement is found in the cases of Au and Ag, no calculation has been made for Pd, and the results in the case of Cu appear anomalous.

INTRODUCTION

In the present experiment a study has been made of photoemission from metal films evaporated on a semiconductor surface where the metal-semiconductor junction acts as a collector. Measurements of the photoelectric yield as a function of photon frequency and metal film thickness give the value of the attenuation length of low-energy (several tenths of an electron volt) hot electrons as well as the height of the potential barrier at the metal-semiconductor junction.

There has been considerable interest in the recent literature regarding the transport of hot electrons in metals. Much of the experimental information on this subject has been obtained from photoemission experiments. Some early evidence for a volume effect in photoemission from metals came from the interpretation of experiments on potassium by Mayer *et al.*[1] Strong evidence for a volume photoelectric effect comes from the recent work of Gobeli and Allen[2] in which the emission from atomically clean silicon surfaces has been interpreted in terms of direct and indirect (phonon assisted) optical excitations. Most of the vacuum photoemission experiments yield results compatible with the production of the photoemitted electrons being between 10 and 100 Å from the emitting surface (electron attenuation length $L \approx 10$ to 100 Å). In these experiments the excitation energy of the emitted electron must exceed the work function of the metal, which in most cases is of the order of 4 to 5 eV. In the case of potassium, however, where the work function is 2.2 eV, photoemission experiments by Thomas[3] indicate much larger values of L. His results showed the attenuation distance to be a function of the excitation energy: L decreasing with increasing excitation energy and being ≈1000 Å for photon energies slightly in excess of 2.2 eV. Thomas interpreted the decrease in L at higher photon energies as due to the excitation of plasma oscillations. The large values of L obtained by Thomas have been questioned by Katrich and Sarbei.[4] Their measurements on gold and chromium surfaces where the work functions had been lowered by an adsorbed BaO layer have been interpreted to yield an L value less than 70 Å for gold and less than 35 Å for chromium at a work function of ≈3.2 eV for Au and 2.8 eV for Cr. In both cases these energies are considerably below that necessary to excite plasma oscillations. These latter results are not consistent with Mead's[5] recent measurements of electron transport through thin gold films in which L values of 180 to 190 Å are reported for electrons spread in energy between 5 and 10 eV above the Fermi surface.

The theoretical work of Wolff[6] on secondary electron emission from metals points out the fact that for excitation energies less than the Fermi kinetic energy, a decrease in the mean free path for electron-electron interaction is to be expected for increasing excitation energy. On the basis of the exclusion principle an electron with an energy ξ above the Fermi energy E_0 can only interact with electrons in the energy range E_0 to $E_0-\xi$. Recently Quinn[7] has made an explicit calculation of the mean free path l of excited electrons as a function of the excitation energy. He considered the mechanism of energy loss as the interaction of the excited electron with the sea of conduction electrons. At excitation energies below those necessary to excite plasma oscillations and less than the Fermi energy, l varies approximately as the inverse square of the excitation energy.

On the basis of the above calculations large values of

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[1] H. Mayer, R. Nossek, and H. Thomas, J. phys. radium **17**, 204 (1956). H. Mayer and H. Thomas, Z. Physik **147**, 419 (1957). Earlier evidence for volume photoemission from alkali metalloids, particularly Cs_3Sb, is found in the work of Görlich and Burton [P. Görlich, Z. Physik **101**, 335 (1936); J. A. Burton, Phys. Rev. **72**, 531 (1947); V. K. Zworykin and E. G. Ramberg, *Photoelectricty and its Application* (John Wiley & Sons, Inc., New York, 1949), Chap. III].

[2] G. Gobeli and F. Allen, Phys. Rev. **127**, 141 (1962).

[3] H. Thomas, Z. Physik **147**, 395 (1957).

[4] G. A. Katrich and O. G. Sarbei, Soviet Phys.—Solid State **3**, 1181 (1961).

[5] C. A. Mead, Phys. Rev. Letters **8**, 56 (1962).

[6] P. A. Wolff, Phys. Rev. **95**, 56 (1954).

[7] J. J. Quinn, Bull. Am. Phys. Soc. **7**, 27 (1962).

l should be expected only for electrons with excitation energy much less than the Fermi energy. There has only been a small amount of experimental work in this energy range. Williams and Bube[8] investigated the photovoltaic response of electrochemically deposited gold and copper films on CdS. Their results are explained in terms of photoemission of electrons from the metal film into the CdS. The optically measured potential varrier at the interface was ≈ 1.1 eV. No quantitative value of L can however be deduced from their data. Similar though considerably less detailed measurements have been reported for tin films on germanium[9] and for Ag on AgCl, KBr, and NaCl.[10] In a recent paper, Spratt, Schwarz, and Kane[11] generated considerable interest in devices employing hot electron transport when they reported studies of the voltage-current characteristic of a triode structure composed of Au-Al_2O_3-Al on a germanium collector. They deduced an appreciable mean free path for hot electrons in Al. Hall,[12] however, has suggested that the reported characteristics can be explained by the existence of pinholes in the base layer.

It is apparent from the above discussion that very little quantitative information exists on the mean free path of electrons with small excitation energies. This paper reports a study of the photoemission from freshly evaporated metal films where the electrons are collected across an interface between the metal and a freshly cleaved silicon substrate. Au, Ag, Cu, and Pd films have been studied for film thicknesses ranging from ≈ 50 to 1000 Å and excitation energies from ≈ 0.7 to 1.1 eV. Analysis in terms of the photocurrent per absorbed photon yields values for both the metal-silicon barrier height and the electron attenuation length in the metal. A brief summary of some of these measurements for Au films has already been reported.[13]

METHOD OF ANALYSIS

When a metal film is deposited on a clean semiconductor surface, a potential energy barrier is formed at the interface. The height of this barrier depends primarily on the metal work function, the electron affinity of the semiconductor, and the distribution of surface states at the interface. The theory of these interfaces has been summarized in the literature.[14] If the contact is rectifying, a depletion layer is formed in the semiconductor. For an n-type semiconductor an electron injected into this region is subjected to a force directing it towards the body of the semiconductor. When photoexcited carriers are transferred from the metal to the semiconductor the situation is analogous to photoemission from a metal into a vacuum. Applying the conventional Fowler analysis,[15] the photoresponse is proportional to $(\nu-\nu_0)^2$ if $E_0 \gg h(\nu-\nu_0) \gg kT$, where $h\nu$ is the photon energy, $h\nu_0$ is the barrier height measured from the Fermi level, and E_0 is the Fermi kinetic energy. Recently Kane[16] has considered the forms of the photoresponse for indirect and direct optical excitations in metals. He found that the $(\nu-\nu_0)^2$ dependence should be observed for indirect transitions and for direct transitions followed by scattering of the photoelectrons.

The photoresponse per absorbed photon as a function of film thickness can be predicted in terms of an electron attenuation length from the following simple one-dimensional consideration. The photocurrent per absorbed photon, $\mathcal{R}$, is given by

$$\mathcal{R}=K\int_0^t Q_0\alpha\, e^{-\alpha x}\, e^{-(t-x)/L}dx \bigg/ \int_0^t Q_0\alpha\, e^{-\alpha x}dx, \quad (1)$$

which yields

$$\mathcal{R}=K\frac{\alpha L}{\alpha L-1}\frac{(e^{-t/L}-e^{-\alpha t})}{(1-e^{-\alpha t})}, \quad (2)$$

where Q_0 is the incident photon flux, α the optical absorption constant, t the film thickness, and K a constant of proportionality. It has been assumed that the radiation is attenuated in the metal according to $e^{-\alpha x}$, the optical reflection at the metal-semiconductor interface can be neglected, and the probability of collecting an electron originating a distance $t-x$ from the barrier is proportional to $e^{-(t-x)/L}$. Multiple reflections of the photoexcited electrons within the metal film have been neglected. If L is larger than the optical attenuation length, $\alpha L>1$, and $\alpha t>1$ then Eq. (2) approaches

$$\mathcal{R}=K[\alpha L/(\alpha L-1)]e^{-t/L}. \quad (3)$$

When $\alpha L \leqq 1$ and $\alpha t>1$, the response tends toward

$$\mathcal{R}=K\frac{\alpha L}{1-\alpha L}\left(\frac{1}{e^{\alpha t}-1}\right). \quad (4)$$

In this latter case it is difficult to determine L since the response is essentially proportional to the optical transmission of the metal film.

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[8] R. Williams and R. H. Bube, J. Appl. Phys. **31**, 968 (1960).

[9] G. W. Mahlman, Phys. Rev. Letters **7**, 408 (1961).

[10] M. A. Gilleo, Phys. Rev. **91**, 534 (1953).

[11] J. P. Spratt, R. F. Schwarz, and W. M. Kane, Phys. Rev. Letters **6**, 341 (1961).

[12] R. N. Hall, Solid State Electronics **3**, 320 (1961); also J. P. Spratt at a Philco Research Symposium, Blue Bell, Pennsylvania, February 28, 1962 stated that further investigation revealed that the characteristics of their structure cannot be explained on a hot electron basis.

[13] W. G. Spitzer, C. R. Crowell, and M. M. Atalla, Phys. Rev. Letters **8**, 57 (1962).

[14] H. K. Henisch, *Rectifying Semi-Conductor Contacts* (Clarendon Press, Oxford, 1957), Chap. VII.

[15] A. L. Hughes and L. A. DuBridge, *Photoelectric Phenomena* (McGraw-Hill Book Company, Inc., New York, 1932), p. 241.

[16] E. O. Kane (private communication).

EXPERIMENTAL PROCEDURE

Sample Preparation

Single crystals of *n*-type silicon of resistivity in the 1 to 10 Ω cm range were oriented along the [111] direction by using x rays and cut into rectangular bars. A slot along the (111) plane was cut into one side of the samples to facilitate cleavage (see Fig. 1). The samples were oxidized in steam at one atmosphere for 16 h at 1050°C which produced a vitreous silica layer $\approx 1\,\mu$ thick. The oxide was removed from one end to permit deposition and alloying of a gold antimony ohmic contact. The portion of the oxide near the cleavage plane was then covered with $\approx 1\,\mu$ thick chrome gold layer. The samples were mounted in a cleavage apparatus[17] and cleaved in a vacuum of 10^{-6} mm Hg. Immediately after cleavage a previously outgassed metal charge was evaporated on the exposed surface. A multiple source evaporator arrangement was used to ensure complete coverage of small irregularities in the cleaved surface. Three and four source schemes were used at distances of ≈ 10 cm from the cleaved sample. The cleaved surface area was 8 mm^2. All metals evaporated were of initial purity greater than 99.99%. A glass slide was placed 1 mm below the cleavage plane and adjacent to the sample. This made a reference film available for measurement of film thickness and the optical properties. It was assumed that the sticking probability on both the silicon and the glass slide was sufficiently large that the film thicknesses would not differ by more than a few monolayers. The chrome gold layer on the sides of the sample provided a reliable low resistance contact to the evaporated film. The leakage resistance across the vitreous silica layer was measured before cleavage and in all cases was much greater than the reverse impedance of the diodes. The diodes exhibited reverse saturation but a low voltage breakdown, ≈ 5 V. The diode impedance at a given voltage exhibited a marked increase with increasing barrier height.

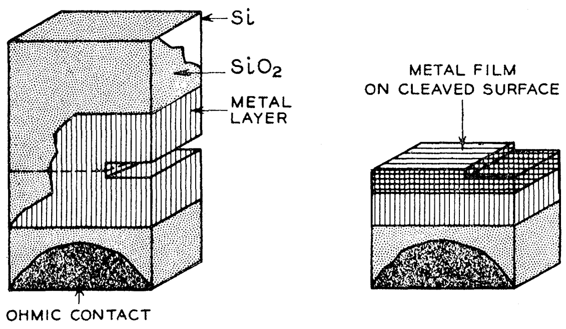

FIG. 1. The construction of a typical diode.

Method of Measurement

The diodes were placed at a focal point in the exit beam of a monochromator so that the radiation was incident on the metal film covering the cleaved surface. A Kipp and Zonen double monochromator with quartz prisms was used with a tungsten ribbon filament source. Since the area of the image was much smaller than that of the cleaved surface, the uniformity of the photoresponse was determined by scanning the surface. Within the edges of the cleaved area the response at all measured wavelengths was uniform within ±5% and linear with radiation intensity. The photoresponse was measured with a standard 13-cycle Perkin Elmer detection system and a modified PbS preamplifier. Provision was made for control of both the voltage and resistance of the bias source. This arrangement with the equivalent circuit of the diode is shown in Fig. 2. The photovoltage, V_{ph}, is given by

$$V_{\text{ph}}=i_{\text{ph}}\left(\frac{1}{r}+\frac{1}{r_l}+\frac{1}{r_c+R_b}\right)^{-1}\frac{R_b}{R_b+r_c}, \tag{5}$$

where r_c is the diode contact resistance, r_l the leakage resistance, r the dynamic junction resistance, and R_b the resistance of the bias source. In all cases the conditions $R_b \gg rr_l/(r+r_l) \gg r_c$ were satisfied which yields

$$V_{\text{ph}}=i_{\text{ph}}[rr_l/(r+r_l)]. \tag{6}$$

This relation was checked for the samples by measuring the response at a selection of bias voltages representing more than a decade variation in dynamic resistance of the diode.

Figure 3 shows a typical photoresponse curve. For $\lambda < 1.1\,\mu$ the response curve is dominated by a solar-cell type of action arising from band-to-band transitions in the silicon. As expected the response in this spectral region is proportional to the optical transmission of the metal film. For $\lambda > 1.2\,\mu$ the response is due to photoexcitation in the metal. Since this response is much smaller than that due to the silicon at shorter wavelengths, care must be exercised to exclude scattered radiation from the beam. The spectral purity of the exit beam from the double monochromator was demon-

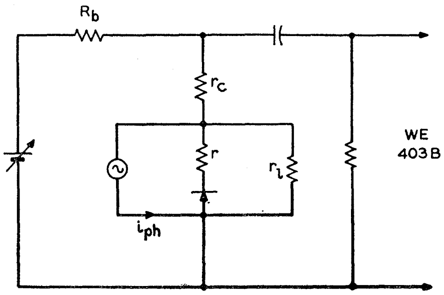

FIG. 2. Equivalent circuit of the photodiode with biassing source.

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[17] R. J. Archer and M. M. Atalla, Trans. N. Y. Acad. Sci. (to be published).

strated in two ways. The photoresponse for a silicon solar cell as shown by the long dashed curve in Fig. 3 does not yield a response for $\lambda > 1.3\ \mu$. The short dashes in Fig. 3 show the results of a more rigorous test in which the photoresponse of a diode is given with a thick (3/4 in.) Si filter placed in the spectrometer beam in front of the diode. The absence of response at the short wavelengths is expected since the filter is strongly absorbing in this region. The decrease in metal photoresponse by a factor of two is due to Fresnel losses in the Si filter.

For each of the metals studied a series of diodes of differing metal thicknesses was prepared. To minimize the error due to variations in source intensity, the samples were measured in immediate succession. In the course of the measurements the radiation intensity was frequently monitored with a radiation thermocouple. Intensity fluctuations were less than $\pm 5\%$. On removing and remounting the samples the measured responses agreed within $\pm 5\%$. Before and after each group of measurements the monochromator was calibrated with a mercury source. The calibration remained constant within the accuracy of the calibration ($\Delta\lambda = 0.004\ \mu$).

Since the response per absorbed photon in the metal film was desired, it was necessary to determine the energy absorbed in the metal films both as a function of thickness and wavelength. One could predict the energy absorbed from the standard thin-film transmission and reflection formulas by using the published values of the optical constants. It is well known, however, that this calculation of the energy absorbed can be seriously in error for thin metal films.[18] Accordingly the transmission and reflection of the films deposited on the glass slide adjacent to the sample were measured. The conventional film-in-film-out technique was used to measure transmission. The reflection was obtained by comparison with a freshly evaporated thick silver mirror where the published values for the reflectivity of silver were assumed.

The approximate thicknesses of the metal films were determined by control of the evaporator charge. Film thicknesses were measured by multiple beam inter-

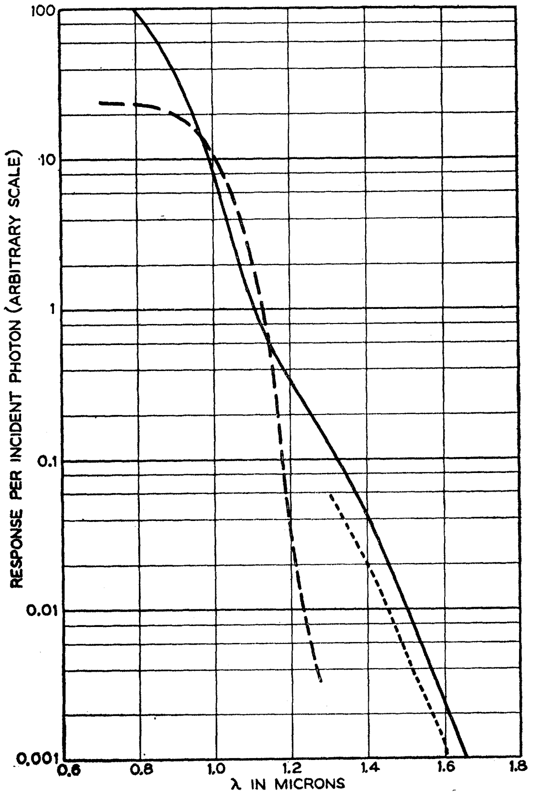

FIG. 3. Typical photoresponse curves: the solid line shows the response of a photodiode, the short dashes the photodiode response with a Si filter in the beam in front of the diode, and the long dashes the photoresponse of a silicon solar cell.

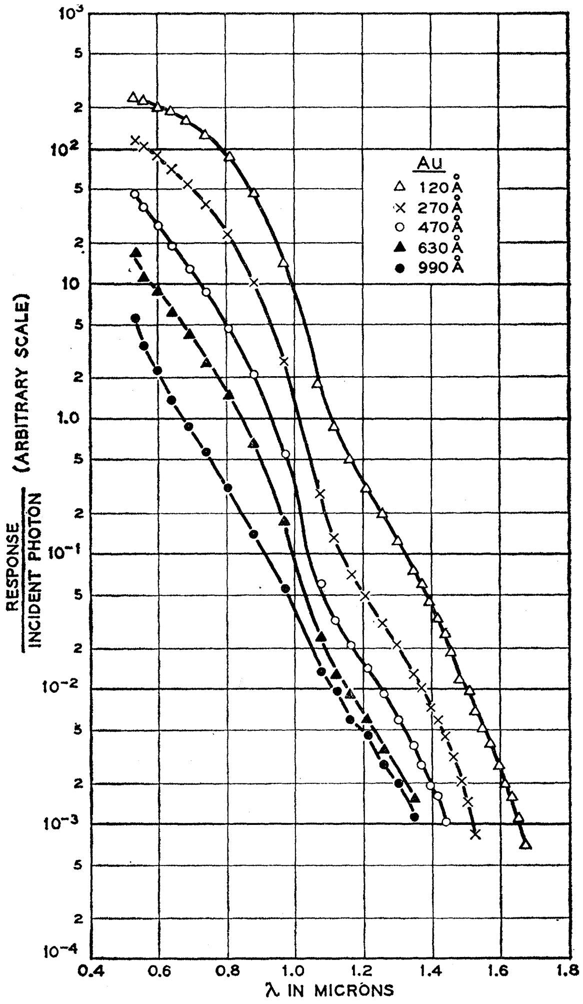

FIG. 4. Photoresponse per incident photon for five diodes with different Au film thicknesses.

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[18] S. Heavens, *Optical Properties of Thin Solid Films* (Butterworths Scientific Publications, London, 1955).

ferometry. These measurements were examined for consistency by comparison with the optical transmission and reflection data. In the cases of Au, Ag, and Cu the thicknesses were also estimated from the optical measurements by using the thin-film expressions with published values for the optical constants.[19,20] In almost all cases the agreement was within ±30 Å. Thus the optical attenuation length for these metals is also in good agreement with published values.[19] In the case of Pd, values of the optical constants are not available for the wavelength range of interest ($\lambda > 1.0\,\mu$). The correlation of transmission and measured thickness indicated a satisfactory fit to the data for an optical attenuation length of 100 Å.

EXPERIMENTAL MEASUREMENTS AND RESULTS

Gold Films

Figure 4 shows the response per incident photon for five diodes in the wavelength range from 0.5 μ to 1.7 μ. The metal and semiconductor photoresponse indicated in Fig. 3 are clearly seen. The square root of the response from the metal ($\lambda > 1.2\,\mu$) is plotted as a function of photon energy in Fig. 5. For a correct photothreshold

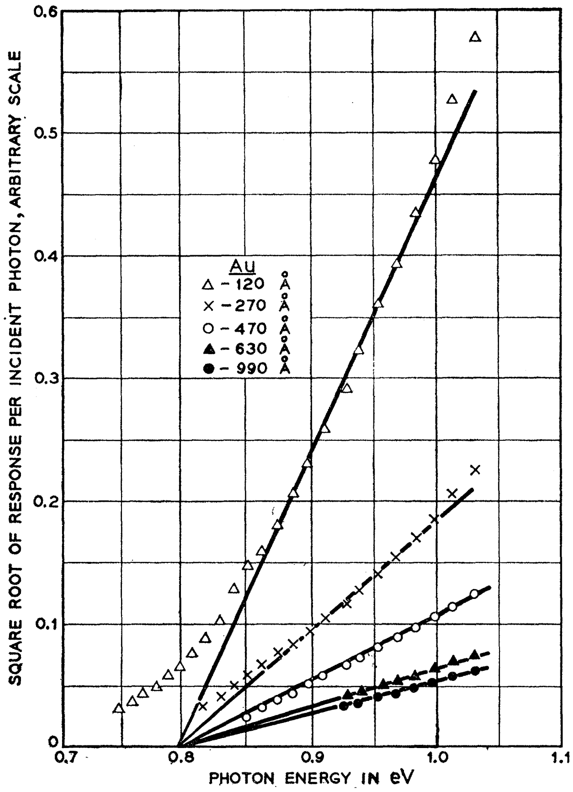

FIG. 5. The square root of the response per incident photon as a function of photon energy for the samples in Fig. 4.

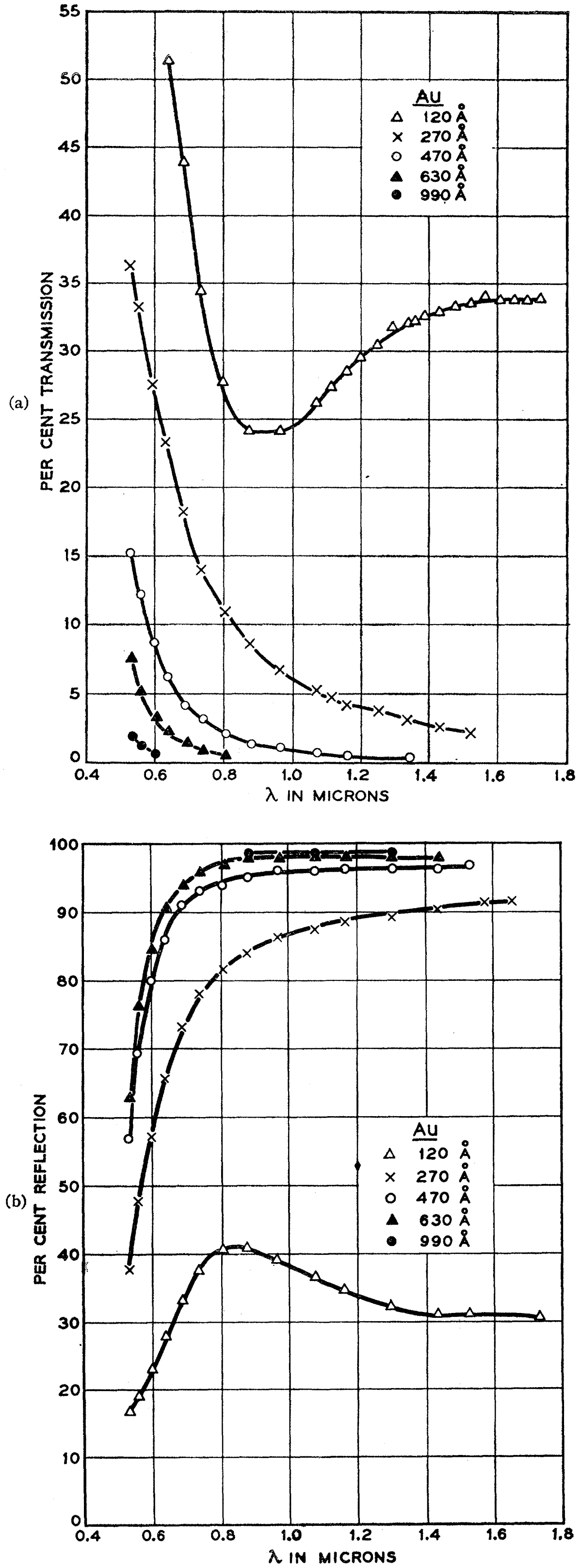

FIG. 6. The measured transmission and reflection of the five Au films are given in Figs. 6(a) and (b), respectively.

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[19] See reference 18, p. 167.

[20] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), p. 6–102.

plot the response per absorbed photon should be used; however, as will be shown, the energy absorbed for each of these films is very nearly constant in this range of photon energy. The prediction that the photoresponse varies as $(\nu-\nu_0)^2$ is well satisfied by the data. The diodes have a common threshold of 0.795±0.010 eV. The 120 Å sample exhibits considerable emission from the tail of the Fermi distribution in the metal. For this reason these data were analyzed by using a Fowler plot which also yielded a threshold of 0.795 eV.

The measured transmission T and reflection R of the gold films are shown in Figs. 6(a) and 6(b). The fraction of the incident photon flux which is absorbed is given by $A=1-(T+R)$. As previously indicated, for $\lambda>1.2\,\mu$, A is nearly independent of λ for each film. Using these data and the response curves of Fig. 4, the response per absorbed photon $\mathcal{R}$ was obtained as a function of photon energy. Figure 7 shows $\mathcal{R}$ as a function of film thickness for $E_{\text{ph}}=1.015$ and 0.952 eV. The slope of the curves indicates an attenuation length of 740 Å. The over-all estimated accuracy of the normalized response is ±20%. Since the optical attenuation length measured for gold is 120 Å, the curves of Fig. 7 correspond to the case for $L\gg1/\alpha$ [see Eq. (3)]. Therefore, the electron attenuation length $L=740$ Å with an estimated error of ±60 Å.

The surface of the 270 Å diode was directly examined by electron diffraction which revealed very little preferred orientation in the film and crystallite sizes of the order of 100 Å. A replica study showed a granular structure with no observable pinholes when the resolution was ≈100 Å.

Silver Films

Measurements of the photoresponse of diodes with an evaporated silver film gave results similar to those shown for gold in Fig. 4. The threshold plots obtained from the Ag measurements are shown in Fig. 8. In this case three of the four samples have a nearly common barrier height of 0.655±0.010 eV. The fourth sample has a barrier height of 0.615 eV. Since the photoresponse depends on the barrier height, to compare data for the different diodes it is essential that they all have a common threshold. Since the photoresponse has a $(\nu-\nu_0)^2$ dependence, according to the Fowler analysis

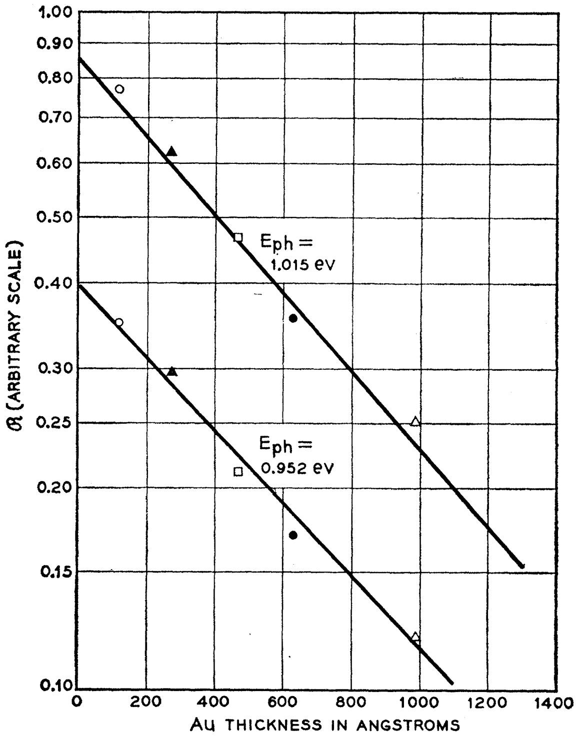

FIG. 7. The points give the response per absorbed photon $\mathcal{R}$ as a function of film thickness for photon energies $E_{\text{ph}}=1.015$ and 0.95$_2$ eV.

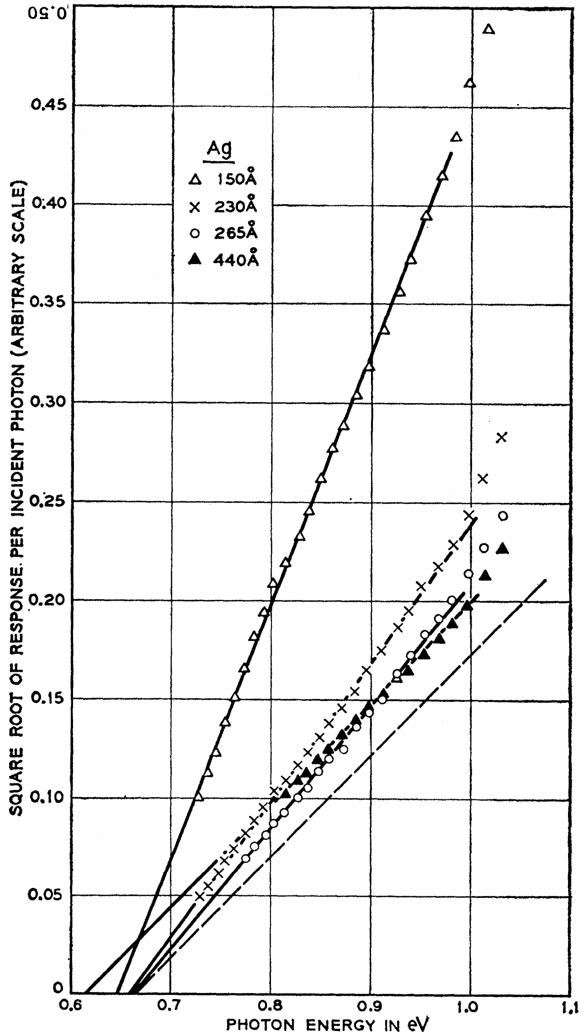

FIG. 8. A threshold plot similar to that of Fig. 5 for four Ag diodes. The dashed line shows the response of the thickest sample when adjusted to a barrier height of 0.65$_5$ eV.

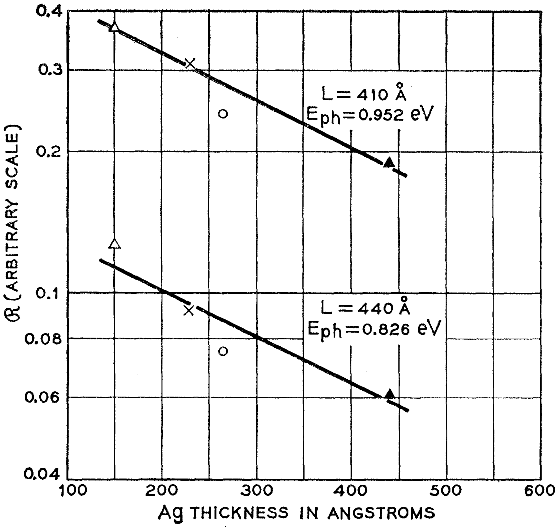

FIG. 9. The points give $\mathcal{R}$ as a function of Ag film thickness.

allowance for a small threshold change can be made by a translation of the curve along the energy scale. The corrected response for the 440 Å sample is indicated by the dashed line.

As in the case of Au, transmission and reflection measurements show the energy absorbed to be nearly independent of wavelength in the range of interest. $\mathcal{R}$ vs film thickness is given in Fig. 9. The value of L observed is 440±60 Å for the two indicated photon energies. It should be noted that this value is strongly dependent on the correction applied to the thickest sample. Without this correction the larger photoresponse observed for the thickest sample would imply a very large value for L. However, much of this photoresponse is due to the smaller value of $h\nu_0$. Further justification of this normalization is given in the section dealing with Pd.

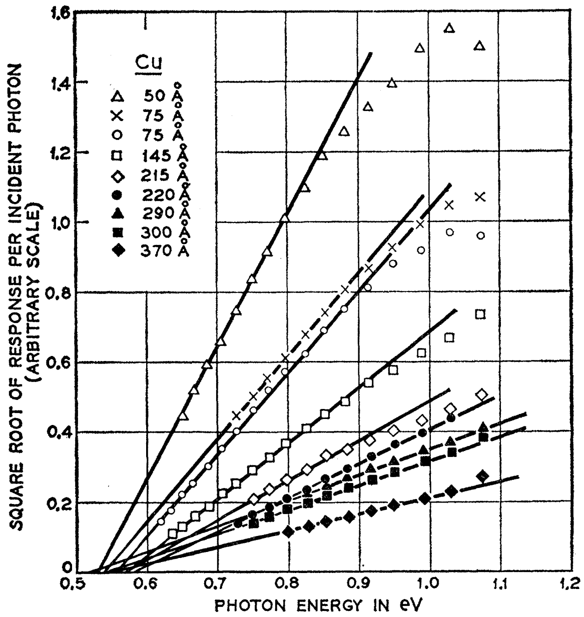

FIG. 10. The threshold plots for nine Cu diodes.

Copper Films

The threshold plots for the copper diodes are given in Fig. 10. The curves do not show a common barrier height. The values lie between 0.525 and 0.580 eV. The barrier heights do not show a systematic variation with any known variable. The film thicknesses measured by multiple beam interferometry are in very good agreement with those obtained from T and R measurements. Figure 11 shows $\mathcal{R}$ as a function of film thickness for the nine samples. The arrowheads indicate the value of $\mathcal{R}$ after normalizing to an average barrier height of 0.550 eV. The normalization procedure tends to reduce the scatter in these data. The slope of the solid curve gives an attenuation length of ≈145 Å. This is close to the optical attenuation length of 120 Å. The two dashed curves of Fig. 11 were calculated from Eq. (2) with values of $L=200$ and 50 Å where the constant of proportionality was chosen to make $\mathcal{R}=8.0$ at $t=100$ Å. A comparison of these curves and the data indicates that 50 Å $<L<$ 200 Å.

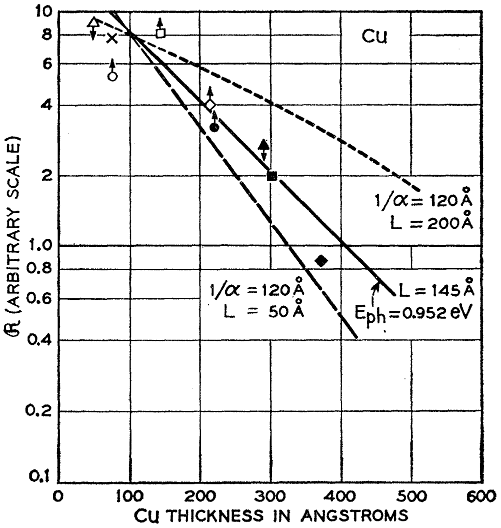

FIG. 11. The points give $\mathcal{R}$ as a function of Cu film thickness. The arrowheads indicate the position of the points when the photoresponse is normalized to a common barrier height of 0.55_0 eV. The dashed curves are calculated from Eq. (2), where the constant of proportionality is adjusted to give $\mathcal{R}=8.0$ at a film thickness of 100 Å.

Electron diffraction and replica studies were made of two of the Cu samples used in these measurements. The diffraction patterns indicated polycrystalline films with crystallite sizes of the order of 100 Å. Some preferred orientation was noted particularly in the thinner films. No holes were observed at a resolution of 100 Å.

Palladium Films

Figure 12 gives the threshold plots of five palladium diodes. Four of these have a threshold of 0.710±0.005 eV. The fifth sample, which was accidentally cleaved in air, has a threshold of 0.685 eV. Measurements of T and R for the Pd films were essential since values for the optical constants at relevant wavelengths were not available. The optical attenuation length given by the transmission data [Fig. 13(b)] is $1/\alpha\approx 100$ Å. $\mathcal{R}$ as a function of film thickness (see Fig. 14) yields an attenuation length of ≈170 Å which is substantially larger than $1/\alpha=100$ Å. Therefore $L=170\pm 30$ Å. It is of interest to note that when allowance is made for the difference in barrier height of the unit cleaved in air by the method of shifting the curve along the energy axis the response becomes consistent with the other data. This provides further justification for the procedure which was used to interpret the silver data.

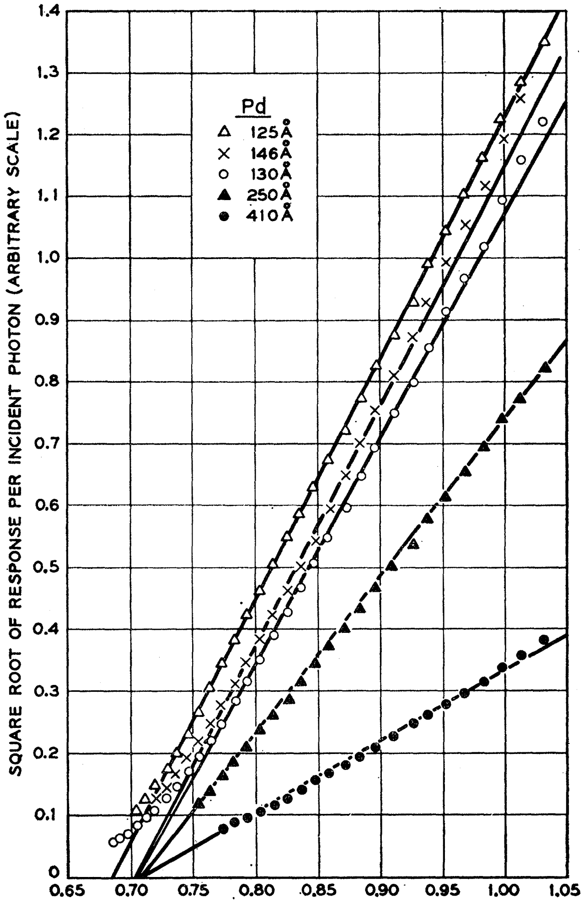

FIG. 12. The threshold plots for five Pd diodes.

DISCUSSION

These measurements have given experimental information concerning two quantities of physical interest: the electron attenuation length L, and the barrier height at the metal-silicon interface. It should be realized that the electron attenuation length measured in the present experiment for a given photon energy is an average value for electrons with excitation energies between $h\nu_0$ and $h\nu$. The Fowler theory, which predicts a response proportional to $(\nu-\nu_0)^2$ does not

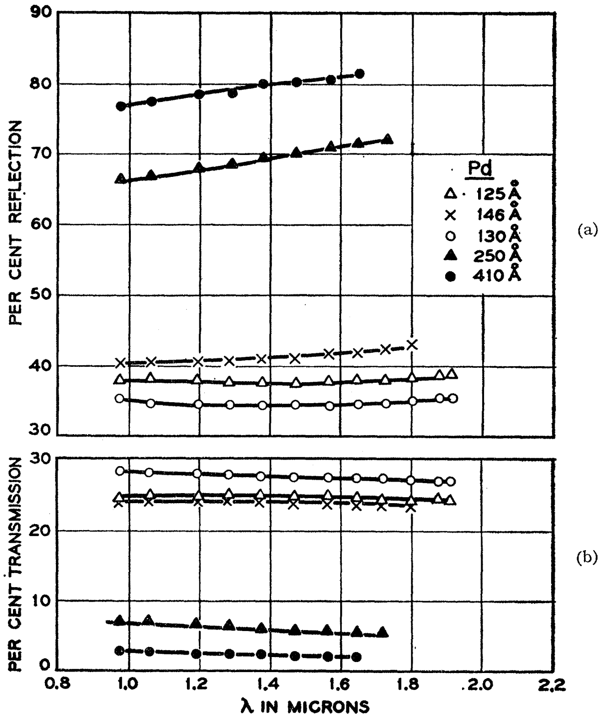

FIG. 13 (a) and (b). The reflection and transmission of five Pd films.

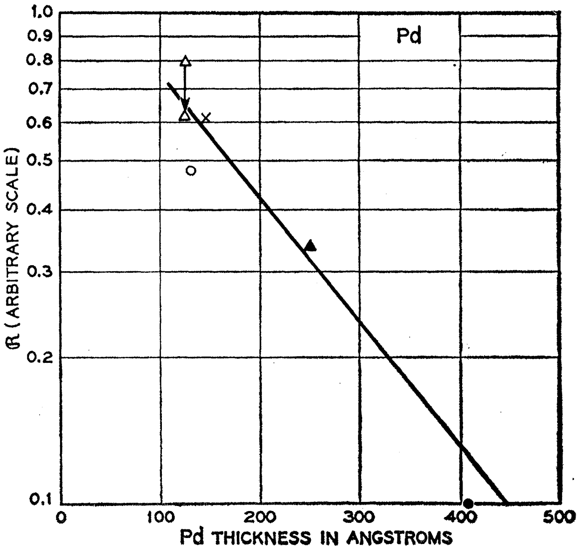

FIG. 14. The points give $\mathcal{R}$ as a function of film thickness for five Pd diodes.

Table I. The second and fourth columns give the measured barrier heights and electron attenuation distances. The third column gives the barrier heights obtained from reference 17. Where two values are indicated, the smaller value is characteristic of an interface exposed to oxygen. The mean free paths for electron-electron interaction calculated from Eq. (5) with $\xi = h\nu_0 + \frac{2}{3}h(\nu-\nu_0)$ are given in the fifth column. The last column gives the mean free path of the conduction electrons.

Metal	$h\nu_0$ (eV)	$h\nu_0$ (eV)[a]	L (Å)	l (Å)[b]	l_σ (Å)[c]
Au	0.79_5	0.81	740 ± 60	415	406
Ag	0.65_5	0.64–0.75	440 ± 60	560	570
Cu	0.55 ± 0.03	0.55–0.75	$50 < L < 200$	720	421
Pd	0.71_0	0.80	170 ± 30	···	110

[a] See reference 17.
[b] See reference 7.
[c] See reference 21.

take into account the variation in attenuation length with the electron energy. The appropriate modifications of both the threshold plot and the effective value of L are considered in Appendix I.

At the present time there is uncertainty concerning the contributions of different energy loss and scattering mechanisms to the measured L values. It is known from bulk electrical conductivity studies that the mean free path for phonon scattering[21] of electrons close to the Fermi level has the same order of magnitude as the film thicknesses used here (see l_σ in Table I). While the energy loss in phonon scattering is small, this mechanism can be expected to affect the path length of the electron in the film before being collected. Very little information is available on the possible roles of boundary scattering, impurity scattering, and radiative recombination.

Quinn[7] has recently considered the effect of electron-electron scattering and has deduced expressions for the mean free path and the range as a function of initial and final electron energies. This treatment leads to the following expression for the mean free path l:

$$l(\text{Å}) = \frac{14.5}{\sqrt{m^*}} \frac{E_0{}^{5/2}\beta^{3/2}}{[\tan^{-1}(\beta^{-1/2}) + \beta^{1/2}/(1+\beta)]} \frac{(1+\xi/E_0)}{\xi^2}, \qquad (7)$$

where E_0 is the Fermi energy in volts, m^* is the electron effective mass in units of the free electron mass, and ξ is the electron energy in the excited state measured with respect to the Fermi energy. The quantity β is given by

$$\beta = (4/9\pi)^{1/3}(r_s/\pi), \qquad (8)$$

where r_s is the radius, measured in units of the Bohr radius of a sphere equal in volume to the volume per electron. The values of l for Au, Ag, and Cu calculated from Eq. (7) for ξ equal to $h\nu_0 + \frac{2}{3}h(\nu-\nu_0)$ [see Appendix I] and $m^* = 1$ are listed in Table I. Better than order of magnitude agreement between L and l is observed for Au and Ag. It should be pointed out, however, that the roles of l_σ and other scattering mechanisms have not been considered. For Cu the experimental L is much less than the predicted l and l_σ. Copper is, however, the most chemically active of the materials investigated and therefore is the most likely to be contaminated by the ambient during the evaporation. This is supported by the variation in barrier heights observed for the different Cu samples. The barrier heights for Cu are all close to that given by Archer and Atalla[17] for an oxygen contaminated interface. Although the barrier height of the Ag samples was somewhat more reproducible, nevertheless the values obtained here also agree with that reported for an oxygen contaminated interface.[17] In the case of Au the observed barrier height agrees very well with previous measurements where no effect was observed due to exposure of the cleaved surface to oxygen. Similar to the case of Au, oxygen exposure had little effect on the barrier height for Pd in the work reported here as well as in previous work. The discrepancy, however, between the Pd barrier height obtained here and by Archer and Atalla is not understood at present.

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APPENDIX I

The Fowler theory does not take into account the origin of the photoemitted electrons. Under the assumption that $E_0 \gg h(\nu-\nu_0) \gg kT$ and that L is energy dependent, the response per absorbed photon can be written as

$$\mathcal{R} = C\int_0^{h(\nu-\nu_0)} \Delta E \int_0^t \alpha\, e^{-\alpha x}\, e^{-(t-x)/L} dx\, d\Delta E \bigg/ \int_0^t \alpha\, e^{-\alpha x} dx,$$

which yields

$$\mathcal{R} = \frac{C\alpha}{1-e^{-\alpha t}} \int_0^{h(\nu-\nu_0)} \frac{\Delta E(e^{-\alpha t} - e^{-t/L})}{-\alpha + 1/L} d\Delta E.$$

If, in the range of ΔE considered, L varies only slightly, then the form of the threshold plot will not be appreciably altered. If $\alpha L \gg 1$ and $L \gg t$, then the form of the threshold plot will not be altered even if L varies appreciably. The effective L measured in this work may

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[21] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958), p. 268.

be defined as

$$\frac{1}{L_{\rm eff}} \equiv \frac{1}{\mathcal{R}}\frac{d\mathcal{R}}{dt} = \frac{\alpha}{e^{\alpha t}-1} - \frac{\displaystyle\int_0^{h(\nu-\nu_0)} \Delta E \frac{[-\alpha e^{-\alpha t}+(1/L)e^{-t/L}]}{-\alpha+1/L}\, d\Delta E}{\displaystyle\int_0^{h(\nu-\nu_0)} \Delta E \frac{(e^{-\alpha t}-e^{-t/L})}{-\alpha+1/L}\, d\Delta E}$$

When $\alpha L \gg 1$ and $\alpha t > 1$,

$$\frac{1}{L_{\rm eff}} \approx \int_0^{h(\nu-\nu_0)} \frac{\Delta E}{L} e^{-t/L} d\Delta E \bigg/ \int_0^{h(\nu-\nu_0)} \Delta E\, e^{-t/L} d\Delta E.$$

If $1/L$ is expanded in a Taylor series in ΔE and if quadratic and higher order terms in ΔE can be neglected, then $L_{\rm eff}$ is the electron attenuation length of an electron with an energy $h\nu_0 + \frac{2}{3}h(\nu-\nu_0)$ above the Fermi energy.

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Irradiation-Produced Paramagnetic Oxides of Nitrogen in Single-Crystal Potassium Azide

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A magnetic resonance absorption centered about $g=2$ and showing no evidence of fine structure is reported in x-irradiated single crystals of potassium azide. Six absorption lines are detected which appear to exhibit axial symmetry about the crystal C direction. These lines are shown to be a composition of two distinct spectra each consisting of three nuclear hyperfine components. For one set of lines, an anisotropic hyperfine splitting varying from 38 to 3 Oe is observed as the magnetic field is rotated from the crystal C axis to a direction perpendicular to this axis. The other set similarly exhibits splittings between 62 and 31 Oe. The inner and outer sets of lines are believed to be due to NO and NO_2 molecules, respectively, with both molecules located at crystal sites having axial symmetry. These molecular species are formed during the irradiation process, perhaps from nitrate and/or nitrite impurities known to be contained in the lattice. Each of the three components of the outer set of lines exhibits a partially resolved seven-line multiplet structure which is interpreted to be the result of an interaction between the paramagnetic electron and the nuclei of two crystallographically equivalent nearest-neighbor potassium ions.

I. INTRODUCTION

IN the past several years, the effects of radiation on single crystals of potassium azide (KN_3) have become the source of some considerable interest.[1–4] From the optical work reported by Tompkins and Young[2] and Cunningham and Tompkins,[3] it is clear that the irradiation of potassium azide presents a manifold of problems related to defects whose properties are to some extent dependent on the radiation energy, on the total irradiation dosage, and on the temperature at which these defects are generated. Since it has been shown that some of these defects are paramagnetic,[5–7] a magnetic resonance absorption study was undertaken in ultraviolet- and x-irradiated potassium azide single crystals containing trace amounts of oxides of nitrogen to determine the nature of these defects. This work as well as that of others has demonstrated the existence of a number of distinct paramagnetic defects, some being stable only at temperatures considerably below 0°C and some produced only after specific irradiation and thermal treatment.

As a consequence of the over-all complexity of the problem, this report concerns itself with only those defects which are responsible for a spectrum consisting of six strong absorption lines observed in crystals which are permitted to thermally bleach at room temperature after irradiation at temperatures below 50°C.

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