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Optical and Photoemissive Properties of Palladium in the Vacuum Ultraviolet Spectral Region*

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Measurements of the optical properties of evaporated films of Pd for the spectral region from 2 to 24 eV are reported for films prepared and studied in a vacuum of 10^{-8} Torr. The results are correlated with the photoemissive properties of similarly prepared samples for photon energies of 10.2 to 22.4 eV. Interband transitions are identified from the optical data at 1.3, 3.6, 15.2, and 20.5 eV. Pronounced peaks appear in the energy-loss function $-\mathrm{Im}[1/(\epsilon+1)]$ at 7.3 eV and in $-\mathrm{Im}(1/\epsilon)$ at 7.6 eV. Structure in the photoelectron energy-distribution curves is identified, by correlation with the optical data, as being due to the effects of interband transitions and photoelectron excitation of collective electron oscillations. The temporal dependence of the photoelectron energy distribution curves is also studied.

I. INTRODUCTION

In a recent paper,[1] Yu and Spicer have calculated the optical density of states of Pd from photoemission and optical studies made on samples prepared and studied in a vacuum of approximately 5×10^{-9} Torr, but limited by the LiF cutoff at 11.8 eV. Photoelectron energy-distribution curves were also obtained for photon energies of 18.6 and 21.3 eV, but their interpretation is limited by the poor vacuum conditions of 2×10^{-5} Torr.

This paper presents optical data from 2 to 24 eV for evaporated films of Pd prepared and studied in a vacuum of 10^{-8} Torr. These data are correlated with previously published photoelectric data[2] from 10.2 to 22.4 eV obtained on similarly prepared samples. In addition, the variation of the photoelectric properties with time after film deposition is presented and discussed.

II. EXPERIMENTAL TECHNIQUES

The experimental procedures used in obtaining the optical constants and photoelectric yields and energy distributions for Pd were identical with those reported previously for Ni.[3] The Pd samples were obtained by vacuum evaporation of Pd wire of 99.9995% purity[4] in a vacuum of 10^{-8} Torr. The filaments used for the evaporation were of tungsten and the deposition rate was about 150 Å per sec. The thickness of the samples, measured by multiple-beam interferometry, ranged from 1600 to 2200 Å. Yu and Spicer[1] report that photoemission data for samples prepared in this way are not reproducible, apparently due to alloying of W with Pd. However, spectrochemical analysis of several samples prepared during the present investigation showed no detectable change in the purity of the Pd. The reflectance data were found to vary somewhat from sample to sample. Of the several samples prepared, those used to obtain the data presented in this paper were the ones with the highest reflectances measured immediately after film deposition. Also, time studies indicated deterioration of the samples with time after preparation even though measurements were made in a vacuum of 10^{-8} Torr. Thus, reflectance and photoelectron energy distributions had to be obtained within about an hour after film deposition.

III. RESULTS AND DISCUSSION

A. Optical Properties

The measured reflectance of Pd at near-normal incidence for photon energies from 2 to 24 eV is presented in Fig. 1. For the sake of clarity, the data are plotted for only seven of the nine samples measured, with no misrepresentation of the actual spread of the experimental values obtained. The number ascribed to a given sample represents the chronological location of a particular "run" in the course of the optical and photoemission studies performed on various elements. It is seen that there is a large scatter in the reflectance data from about 4 eV up to the region of the surface plasma resonance at 7.3 eV. This could result from surface differences between different films, as it is known that the quality of the surface has a pronounced effect on the

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[2] R. C. Vehse, J. L. Stanford, and E. T. Arakawa, Phys. Rev. Letters **19**, 1041 (1967).

[3] R. C. Vehse and E. T. Arakawa, Phys. Rev. **180**, 695 (1969).

[4] Leico Industries, Inc., New York, N. Y.

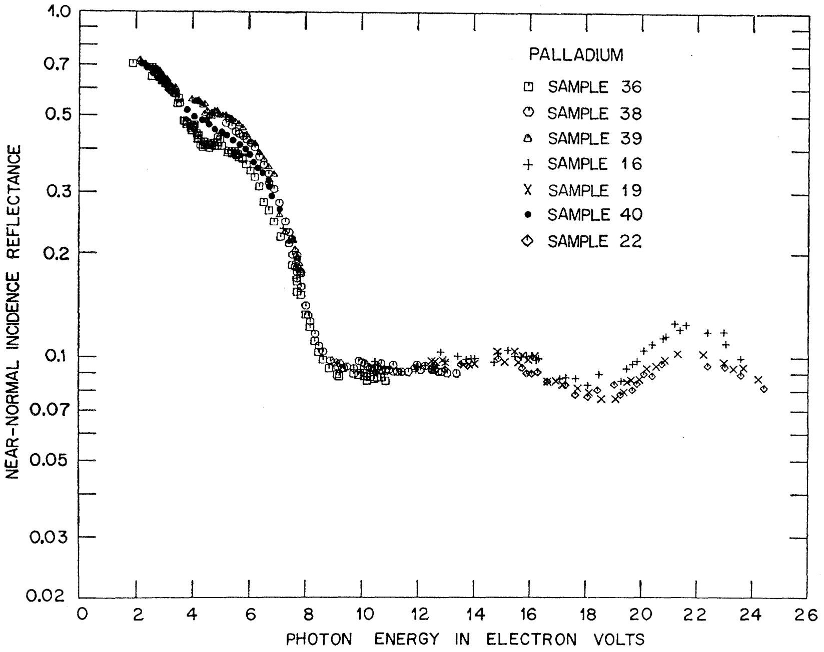

FIG. 1. Near-normal incidence reflectance data of palladium measured for photon energies of 2 to 24.5 eV.

measured optical properties in the vicinity of the surface plasma resonance.[5]

The present data are compared, in Fig. 2, with previously published reflectances at near-normal incidence for photon energies up to 25 eV. In general, the higher the reflectance for a given wavelength the better the surface. The highest reflectance values from Fig. 1 are replotted as Oak Ridge National Laboratory data in Fig. 2 and were used in subsequent calculations of the optical constants. For the measurements extending into the vacuum ultraviolet, Sabine,[6] Lostis,[7] Malé and Trompette,[8] Robin,[9] Yu and Spicer,[1] and Riedinger and Emerson[10] all used opaque films, evaporated on smooth substrates. The prevalent conditions during the evaporation and the history of the sample after its preparation must account for some of the disagreement in the reflectance values. Only in this work and that reported by Yu and Spicer[1] and Riedinger and Emerson[10] were the samples prepared *in situ*, thus reducing possible changes due to oxidation of the surface. However, even under these conditions discrepancies exist. Thus, correlation of optical and photoelectric data is valid only when the films used in the measurements have been evaporated and maintained under identical conditions.

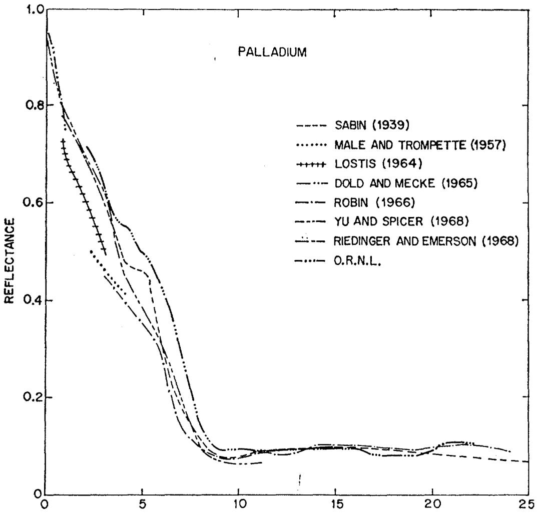

FIG. 2. Near-normal incidence reflectance data of palladium compiled from the literature.

In addition to the near-normal incidence reflectance from 2 to 24 eV, the reflectance was measured as a function of the angle of incidence for a few selected photon energies. The real and imaginary parts, n and k, of the complex refractive index were determined for these energies by means of a least-squares fit to Fresnel's equations. These values of n and k with their associated estimated errors are shown in Fig. 3. The optical constants of Pd from 2 to 24 eV were then determined by means of a Kramers-Kronig analysis as described for Ni.[3] These values of n and k, based on the highest re-

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[5] J. L. Stanford, H. E. Bennett, J. M. Bennett, E. J. Ashley, and E. T. Arakawa, Bull. Am. Phys. Soc. **13**, 989 (1968); S. E. Schnatterly, *ibid.* **13**, 989 (1968).

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[7] P. Lostis, J. Phys. Radium **25**, 118 (1964).

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flectance values from Fig. 1, are considered accurate to within ±5% and are also shown in Fig. 3. The real and imaginary parts, ϵ_1 and ϵ_2, of the complex dielectric constant ϵ where $\epsilon_1 = n^2 - k^2$ and $\epsilon_2 = 2nk$, are shown in Fig. 4, together with the energy-loss functions $-\mathrm{Im}[1/(\epsilon+1)]$ and $-\mathrm{Im}(1/\epsilon)$, and the conductivity $\sigma = \omega\epsilon_2/4\pi$, where ω is the angular frequency.

For Pd, ϵ_1 and ϵ_2 have roughly free-electron-like energy dependences at low photon energies; however, evidences of single-electron excitations appear throughout the energy range studied. Optical data in the far infrared[11,12] indicate that the true free-electron properties of the metal do not appear even in the limit of experimental measurements at about 0.06 eV. Thus it is not possible to perform a separation of the free- and bound-electron contributions to the dielectric functions,[13] because this separation requires sufficient data in the infrared to establish the free-electron behavior in terms of a constant intraband relaxation time. For single-electron interband transitions the energies are associated with maxima in the conductivity. For sufficiently low energies the free-electron contribution to ϵ_2 is proportional to ω^{-1}, and the energies of interband transitions can still be obtained directly from maxima in the conductivity. Similarly at sufficiently high energies where the free-electron contribution is negligible, the same result applies. It is seen in Fig. 4 that single-electron interband transitions occur at 1.3, 3.6, 15.2, and 20.5 eV.

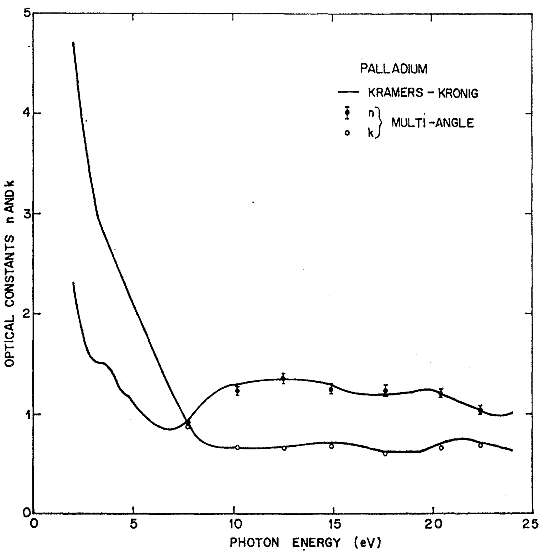

Fig. 3. The optical constants n and k of palladium as a function of incident photon energy.

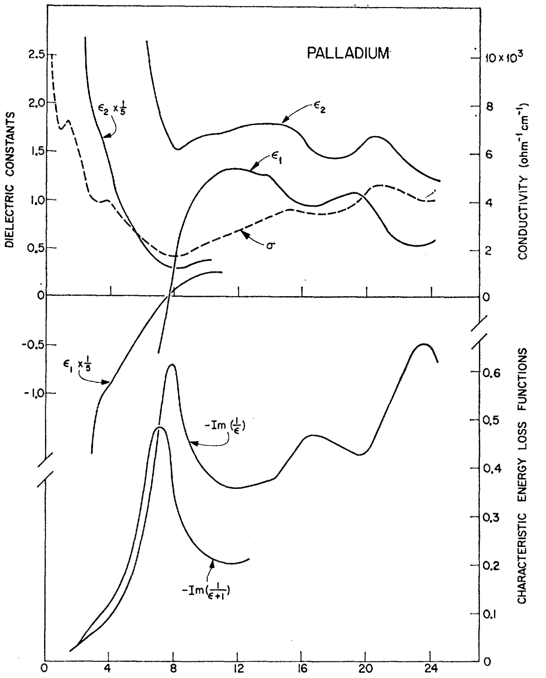

Fig. 4. Dielectric response functions (upper curves) and energy loss functions (lower curves) of palladium in the vacuum ultraviolet.

The energy-loss functions $-\mathrm{Im}[1/(\epsilon+1)]$ and $-\mathrm{Im}(1/\epsilon)$ are related to the probability that fast electrons will lose energy in traversing the surface and bulk, respectively, of the material.[14] In Fig. 4 it is seen that the sharpest maxima in the energy-loss functions $-\mathrm{Im}[1/(\epsilon+1)]$ and $-\mathrm{Im}(1/\epsilon)$ appear at 7.3 and 7.6 eV, respectively. These correspond to surface and volume plasma resonances, since all of the conditions for a plasma resonance are satisfied.[15] The presence of nearby interband transitions cause the two maxima to lie much closer together[16] than given by the free-electron theory. Structure is also seen to occur in $-\mathrm{Im}(1/\epsilon)$ at 17.0 and 23.5 eV.

Characteristic electron-energy losses have been observed in Pd at 6.8, 16.0, and 20.2 eV by Robins[17] and at 15.7 and 21.5 eV by Gauthé.[18] The peak reported by Robins at 6.8 eV is relatively strong and presumably results from the creation of both surface and volume plasma oscillations. The identification of the structure in $-\mathrm{Im}(1/\epsilon)$ and in the electron-energy loss spectra at higher energies cannot be made unambiguously. The structure in $-\mathrm{Im}(1/\epsilon)$ at 17.0 and 23.5 eV may be associated with structure in ϵ_2, and hence with interband transitions. Where ϵ_1 is nonzero and varying, the position of the peak in $-\mathrm{Im}(1/\epsilon) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$ associated with a peak in ϵ_2 may be shifted by a few eV.[16]

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[11] A. P. Lenham and D. M. Treherne, J. Opt. Soc. Am. **56**, 1137 (1966).

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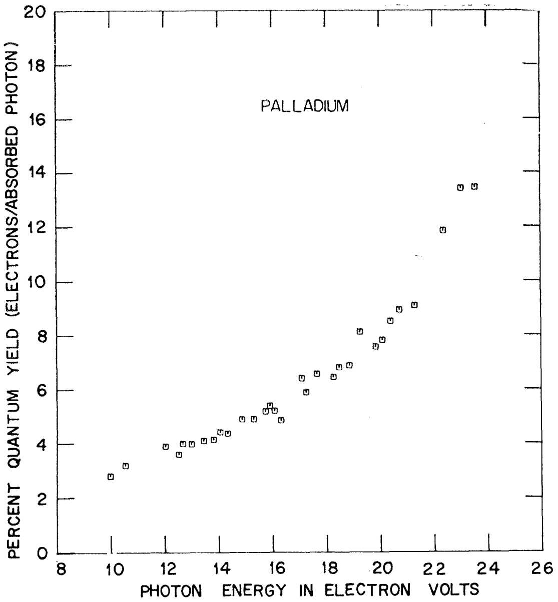

FIG. 5. Spectral distribution of the quantum yield of palladium for excitation energies 10 to 24 eV.

However, resonance effects cannot be ruled out entirely in the present case.

B. Photoemissive Properties

In a review article, Weissler[19] presented data showing the pronounced effect of sample treatment on the shape and magnitude of the photoelectron yield curves. The data of Walker *et al.*[20] for their cleanest samples show that the yield curves reach saturation at about 14 eV for Pd at roughly 0.02 electrons per incident photon. This corresponds to a yield of 0.022 electrons per absorbed photon if we assume a reflectance of 10% at 14 eV (Fig. 1). The variation of photoelectron yield per absorbed photon obtained in the present investigation, for Pd films prepared in the same way as for the optical measurements, is shown in Fig. 5. At 14 eV, the yield is twice that given by Walker *et al.* and continues to increase with increasing photon energy up to the highest photon energy used. It is difficult to offer a detailed explanation for this behavior of the spectral distribution of the total yield. For Pd, the width of the valence band is of the order of 4 eV,[21] so, allowing for a work function of 4.5 to 5.0 eV, the photon energy required to produce photoemission from all states in the conduction band is roughly 9 eV. At energies up to 9 eV, increasing photon energy allows photoexcitation from additional states toward the bottom of the conduction band. Above about 9 eV, electron-electron collisions may provide a means of exciting two or more electrons per incident photon. These effects could account for the monotonically increasing total yields observed in this work and possible specific electron-electron interactions are discussed later.

Photoelectron energy distribution curves for a Pd film measured for an incident photon energy $h\nu=10.2$ eV over a 24 h period at a pressure of 3×10^{-8} Torr are shown in Fig. 6. It is seen that the shape of the distribution curve is not distorted appreciably in the first 45 min after preparation; therefore, all of the optical and photoelectric data presented in this paper, with the exception of Fig. 6, were taken within an hour of film deposition.

The observed variation of photoelectron energy distribution with the age of the film appears to be due to photoemission from a surface layer. If energetic photoelectrons emerging from within the volume of the metal are scattered due to surface impurities, the peak that develops with time at the low-energy end of the distribution should grow at the expense of the high-energy electrons in the distribution. Examination of the data presented in Fig. 6 reveals that the number of electrons in the low-energy peak is not offset by a corresponding decrease in the number of high-energy electrons. Thus the development of the low-energy peak is probably due in part to photoemission from a surface layer. In addition, this surface layer introduces some inelastic scattering of the high-energy photoelectrons born within the volume of the sample and, at the same time, absorbs some of the incident photons. Both of these effects are responsible for the slight decrease in the number of high-energy electrons in the electron distribution. Ideally, the total width of the photoelectron distribution, including inelastic scatter-

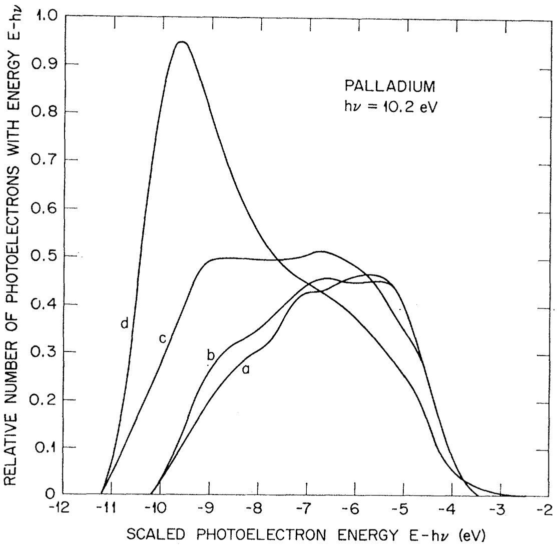

FIG. 6. Photoelectron energy distribution curves for palladium at $h\nu=10.2$ eV as a function of sample age. (a) $t=4$ min, (b) $t=45$ min, (c) $t=4$ h, and (d) $t=24$ h after evaporation.

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[19] G. L. Weissler, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1956), Vol. 21, pp. 342–382.

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ing of electrons on emission, should be $h\nu - \varphi$, where φ is the work function. In Fig. 6, the change in the distribution width between (b) and (c) is due to a 1 eV decrease in the work function occurring between 45 min and 4 h after film evaporation.

C. Correlation of Optical and Photoemissive Data

Photoelectron energy distribution curves for Pd films prepared in the same way as for the optical measurements have been presented previously.[2] In Fig. 7 these photoelectric data are compared with the optical data from Fig. 4. The curves are plotted so that the energy scale is relative to the Fermi level; that is, $E^* = E - h\nu + \varphi$, where E is the energy of the emitted electron. The work function assumed for Pd in this work was 4.8 eV, which is a weighted average of the available experimental values in the literature.[22] This is in agreement with the value determined in this work from the minimum retarding voltage necessary for emission-current cutoff. The optical data are plotted with $h\nu = 0$ coinciding with the Fermi level. With the data plotted in this way the energy distribution of the emitted electrons gives directly the distribution of occupied electronic states in the metal, modified by any structure present in the density of states above the vacuum level and by the effects of any scattering suffered by the photoelectrons on emission. Structure in ϵ_2 arises from structure in the joint density of states. Some correlation between the optical and the photoelectric data shown in Fig. 7 is thus possible.

At low photoexcitation energies, the electron energy distribution is characteristic of the density of the electronic states in the conduction band if no pronounced structure exists in the density of electronic states above the Fermi level. In Fig. 7 the peak in the electron-energy distribution curves lying just below the Fermi level, for all incident photon energies, corresponds to the peak in the density of states arising from the d-state electrons in the conduction band. This pronounced structure is evident in the soft x-ray emission data of Bonnelle and Mandé.[23] The d-state peak is 0.5 eV below the Fermi level, so energy losses, if they occur, must be taken with reference to this energy. The structures evident at about 1.5 and 3.5 eV below this peak for photon energies of 10.2 and 12.5 eV (see also Fig. 6) are also attributed to structure in the density of electronic states in the conduction band, the peaks being associated with the same structure in the optical transition probability function that gives rise to the peaks appearing in the conductivity (Fig. 4) at about the same energies.

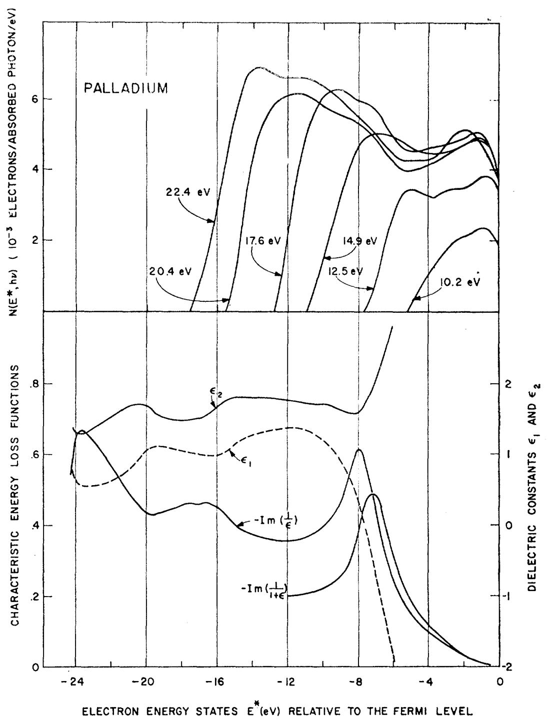

FIG. 7. Photoelectron energy distribution curves and optical data of palladium in the vacuum ultraviolet.

At higher excitation energies, a large fraction of the emitted electrons have undergone some form of inelastic scattering. The large peak appearing at the low-energy end of the distribution curves (for large negative values of E^*) arises from inelastic scattering of the excited electrons with other electrons in the conduction band and on emission across the surface of the film. Thus for higher excitation energies, structure that persists in the energy distribution curves $N(E^*,h\nu)$ at a constant value of E^* for varying photon energies may be attributed either to structure in the conduction band or to the discrete loss of energy suffered by the photoexcited electrons prior to emission. Such structure exists at $E^* = -7.5$ and -11.0 eV. Now, structure in the conduction band and also a discrete loss due to photoelectron excitation of an interband transition should be associated with structure in ϵ_2, whereas a discrete loss due to photoexcitation of a collective oscillation is not associated with structure in ϵ_2. The structure at $E^* = -7.5$ eV lies 7.0 eV below the d-state peak at -0.5 eV and can be associated with the peaks in the energy-loss functions $-\mathrm{Im}(1/\epsilon+1)$ and $-\mathrm{Im}(1/\epsilon)$ at 7.3 and 7.6 eV, since no structure appears in ϵ_2 at this energy to suggest interband effects. These data confirm the earlier suggestions[1,2] that this peak at $E^* = -7.5$ eV is due to photoelectron excitation of collective oscillations. The structure at $E^* = -11.0$ eV can be associated with structure in ϵ_2,[24] and may cor-

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[22] V. S. Fomenko, in *Handbook of Thermionic Properties*, edited by G. V. Samsonov (Plenum Press, Data Division, New York, 1966), pp. 1-63.

[23] C. Bonnelle and C. Mandé, Compt. Rend. **245**, 2253 (1957).

[24] Both ϵ_2 and the conductivity σ (Fig. 4) begin to rise at 8 eV, indicating the existence of interband transitions between 8 eV and the peak of the σ curve at 15.2 eV.

respond to discrete energy losses suffered by photoelectrons exciting interband transitions. Alternatively, the structure at $E^* = -11.0$ eV may be ascribed to energy losses suffered by the photoelectrons involving the excitation of both a 7-eV collective oscillation and a 3.5-eV interband transition.

Above an incident photon energy of 9 eV, electron-electron collisions may result in an increased total yield. In particular, for incident photon energies above 12 eV, the photoelectron excitation of 7-eV collective oscillations may give rise to an increased photoelectric yield, since the plasmon decay may result in a single-electron excitation.[25] For incident photon energies above 16 eV the yield may be further increased by the photoelectron excitation of the 11-eV transition. Such processes may explain the monotonic increase in photoelectric yield with increasing energy (Fig. 5) and are consistent with the predictions of very short electron-electron scattering lengths for these energies.[1]

ACKNOWLEDGMENT

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Slow-Electron Mean Free Paths in Aluminum, Silver, and Gold†

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Beam-attenuation measurements were made on free-standing polycrystalline films of various thicknesses at energies between the work function and several electron volts above. The electron-electron collision mean free paths l_e were determined by correction of the attenuation lengths for electron-phonon scattering lengths l_p deduced from the attenuation temperature dependence. Imperfection mean free paths were negligible. The following results were obtained: for aluminum, $l_e \sim 50$ Å and $l_p \sim 250$ Å near 5 eV above the Fermi level; for gold, $45\ \text{Å} > l_e > 15$ Å for energies between 5.5 and 10 eV; and for silver, $42\ \text{Å} > l_e > 20$ Å for energies between 5.5 and 8 eV. In the energy range between 5.5 and 7.5 eV, it was found that $l_p \sim 250$ Å for gold and $l_p \sim 400$ Å for silver. All measured l_p were only about two-thirds of the value near the Fermi level. Quinn's theory for l_e in a dense free-electron gas predicts that for aluminum $l_e \sim 60$ Å at 5 eV. Exchange corrections in Kleinman's dielectric screening function tend to bring the value closer to the observed one. In silver and gold, considerable interaction of the beam electrons with the d band occurred for which no theory is available as yet. The resulting data were compared with the energy dependence of l_e deduced semiempirically by Krolikowski and Spicer from the density of states obtained from photoemission experiments. Reasonable agreement with presently available data was observed.

I. INTRODUCTION

HOT-ELECTRON mean free paths (MFP) in metals for energies from several tenths of a volt to a few volts above the Fermi level have in the past primarily been measured with photoemission or tunnel-emission techniques. The former method[1] utilizes photoexcited electrons escaping from a metal film into an adjacent semiconductor or into a vacuum. Total yield is measured as a function of film thickness. The electron-attenuation length may be deduced from the data if the optical absorption in the metal film is known. Since this quantity depends critically on film quality and thickness, it must generally be determined separately. Furthermore, the energy is determined by the barrier height at the metal boundary. Variation of energy, thus, requires the use of different substrate materials with possible effects on the film structure. Hence, photoemission techniques are rather complex, and interpretation of the data is prone to error.

The tunnel-emission technique[2] produces hot electrons by field emission from a base metal, through a thin oxide layer, into a metal film deposited on top of the oxide. Variation of the number of electrons escaping through the top layer is measured as a function of thickness. Although in this geometry the electron source is confined to one boundary, the electron energy upon entering the metal film is not well defined because of considerable inelastic scattering in the oxide. Inelastic scattering may be avoided by tunneling through the forbidden gap of the oxide; this, however, restricts the applied potential. Measurement and interpretation of attenuation measurements as a function of energy is, thus, rendered difficult.

For a review of MFP measurements employing these older techniques, the reader is referred to a recent

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[2] C. A. Mead, Phys. Rev. Letters **8**, 56 (1962); **9**, 46 (1962); H. Kanter, J. Appl. Phys. **34**, 3629 (1963).