Attenuation Length for Photoelectrons Excited in Aluminum by 21.2-eV Photons*

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(Received 10 November 1970)

The attenuation length l for photoelectrons excited in aluminum by 584-Å photons has been determined and found to lie in the range $4 \leq l \leq 12.8$ Å. The determination was made by analyzing the relative photoemissive yield as a function of angle. The method also provides an accurate means of obtaining the film thickness and index of refraction of aluminum from photoemission measurements alone.

Previous attempts to extract electron attenuation lengths from photoemission data have been based upon (a) the dependence of the quantum yield on the thickness of the photoemitter,[1-4] (b) the dependence of normalized photoelectron energy distributions upon the thickness of a photoemitter evaporated upon a dissimilar substrate,[3-5] (c) the fitting of electron-energy distribution curves to a Monte Carlo model for scattering,[6] or (d) the fitting of the attenuation length to the absolute yield.[7] We present here a new approach in which the electron attenuation length is extracted from the angular dependence of the quantum yield.

Recently Pepper[8] calculated the yield of an arbitrary photoemissive material as a function of the optical constants of the photoemitter and the substrate, the thickness of the photoemitter, the wavelength, the polarization and angle of incidence of the exciting light, and the attenuation length of the electrons. He suggested that measurements of the photoelectric yield as a function of angle might be used to determine the attenuation length of the photoelectrons. We have made these measurements and have determined the attenuation length of photoelectrons excited in aluminum by 21.2-eV photons.

The most important result of this study is the addition of decisive independent experimental evidence for the existence of very short electron attenuation lengths in aluminum. Several conflicting results exist in the recent literature.[4,6,9-11] The essential conclusion of this work is that the average attenuation length for all electrons photoemitted by 21.2-eV photons lies in the range $4 \text{ Å} \leq l \leq 12.8$ Å. The implication of this range of values is discussed.

The basic apparatus consisted of a gas-discharge light source, a Seya vacuum ultraviolet monochromator, and a stainless-steel high-vacuum chamber ($\sim 8 \times 10^{-9}$ Torr) optically coupled to the monochromator with an ~1000-Å–thick tin window. This window allowed us to operate the chamber in the 10^{-9}-Torr region and the monochromator in the 10^{-5}-Torr region without differential pumping. The window also acted as a bandpass filter in the region 500-800 Å[12] and transmitted ~20% of the 584-Å He resonance line while excluding all other lines in the He discharge. Consequently, the normal grating was replaced with a gold mirror which afforded an order of magnitude increase in intensity and allowed us to calculate readily the polarization of the light.

The essential features of the experimental chamber were a sample holder which rotated through 360°, a combination electron collector and liquid-nitrogen cold trap which surrounded the sample, a quartz-crystal film-thickness monitor, and equipment for evaporating materials onto the substrate. The chamber was pumped with a liquid-nitrogen–trapped diffusion pump.

Measurements were made as follows. Aluminum of 99.9% purity was evaporated from a helical W filament onto a carefully cleaned glass microscope slide using the quartz-crystal thickness monitor to estimate the rate of deposition as well as the final thickness of the film. Within one minute, measurements of the photoelectric current as a function of angle were begun. Every 20° or so, the photoelectric current at 0° was remeasured. We found that the photoelectric current at 0° increased slowly in time, consistent with the findings of other investigators.[4] The first set of measurements or "run" was completed in approximately six minutes and subsequent runs were taken as desired. Upon completion of the measurements, the thickness of the film was measured interferometrically. The data were then tabulated as the fractional increase in yield as a function of angle.

Pepper[8] rigorously calculated the absorption of the radiant energy throughout the photoemissive material and then treated the diffusion and escape aspects of the photoemission process with a simple model attributable to Spicer.[13] According to this model, the probability that an electron excit-

ed at a depth y in the photoemissive medium escapes into the collecting medium is given by $C \times \exp(-y/l)$. The electron attenuation length is l which depends upon the different physical mechanisms which de-excite the electron such as e^--e^- scattering and e^--phonon scattering. The factor C takes into account the excitation probability and the probability of penetrating the surface barrier.

If the absorption of the radiant energy is given by $\eta(y)$, then the quantum yield for a photoemitter of thickness d may be written as

$$Y = C\int_0^d e^{-y/l}\eta(y)dy = CF(l),$$

where $F(l)$ is a function of the optical constants of the photoemissive material and substrate, the thickness of the photoemitter, the wavelength, the polarization and angle of incidence of the light, and the attenuation length. The expressions for $\eta(y)$ and $F(l)$ are quite complicated, and the reader is referred to Pepper's work[8] for them. In the absence of vectorial effects, the quantity C is independent of the angle of incidence of the exciting light; and so one has a direct comparison of theory with experiment by simply comparing measured values of the $Y(\theta)$ with the calculated values.

All the parameters in the theory are independently measurable except for the attenuation length l. In practice, however, we have found that the equations are quite sensitive to two other parameters: the thickness of the film d and the index of refraction of the aluminum n. The sensitivity to d is such that the method provides an accurate means of obtaining film thickness from photoemission measurements alone. Because of this sensitivity to d and n the data were compared with the theory using two- (d and l) or three- (d, l, and n) parameter least-squares fits. A fit was considered valid only if the values for d and/or n that gave the best fit fell within reasonable limits of their independently measured values. Two fitting criteria were employed: absolute least squares, for which the quantity

$$\sum_{\theta=0}^{\theta=\theta_{\max}} \{[Y(\theta)/Y(0)]_{\text{exp}} - [Y(\theta)/Y(0)]_{\text{theor}}\}^2$$

was minimized, and relative least squares, for which the quantity

$$\sum_{\theta=0}^{\theta=\theta_{\max}} \left\{\frac{[Y(\theta)/Y(0)]_{\text{exp}} - [Y(\theta)/Y(0)]_{\text{theor}}}{[Y(\theta)/Y(0)]_{\text{exp}}}\right\}^2$$

was minimized.

Altogether, measurements were made on five films. Data from the last two films, which were measured reliably to larger angles than the first three, will be presented here. Figure 1 shows the data for the first run of the two films, the best three-parameter fit obtained for each, and calculated results for attenuation lengths of 1 and 20 Å. It can be easily seen that the fit is very good, and that it is possible using this method to distinguish between different escape lengths.

The sensitivity of the angular dependence of the yield to the attenuation length is a function of the film thickness. If we define the sensitivity as the change in the relative yield per unit change in the attenuation length, $\Delta[Y(\theta)/Y(0)]/\Delta l$, then this sensitivity goes through several maxima and minima as the film thickness is increased. The thickness of film a was near that for a minimum in sensitivity, while the thickness for film b was near that for a maximum in sensitivity.

Table I summarizes the results of the fitting calculations. Except in the three-parameter fit,

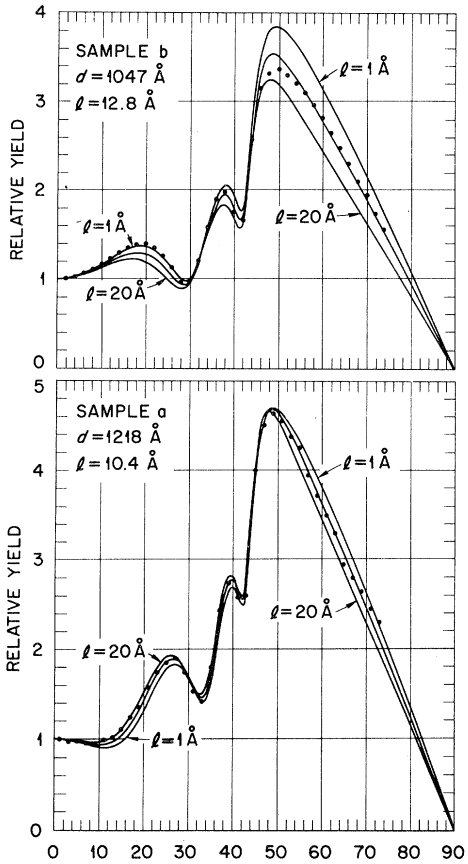

FIG. 1. $Y(\theta)/Y(0)$ for the first run of two samples, together with the best three-parameter absolute least-squares fit to each, plus a calculated curve for $l = 1$ Å and $l = 20$ Å for comparison.

Table I. Results of fitting theory to data.

Fitting parameters	Attenuation length l (Å)	Film thickness d (Å)	Index of refraction n	Sum of squares
		Film a		
l, d, n, abs.[a]	10.4	1218	0.716	0.157
l, d, n, rel.[a]	11.4	1216	0.716	0.033
l, d, abs.	5.4	1230	0.71[b]	0.245
l, d, rel.	7.8	1227	0.71[b]	0.049
		Measured thickness 1250 ± 50 Å		
		Film b		
l, d, n, abs.	9.8	1047	0.720	0.203
l, d, n, rel.	12.8	1056	0.722	0.042
l, d, abs.	4.0	1051	0.71[b]	0.382
l, d, rel.	7.2	1064	0.71[b]	0.100
		Measured thickness 1050 ± 50 Å		

[a]The abbreviations abs. and rel. refer to the fitting criteria, either absolute least squares or relative least squares.

[b]Taken from Ref. 9.

where n for aluminum was allowed to vary, the optical constants used were those of Madden, Canfield, and Hass.[14] The main result is that the best fit for the electron attenuation length lies in the region $4 \text{ Å} \leq l \leq 12.8 \text{ Å}$.

Berglund and Spicer[15] have given a model for the diffusion and escape process which accounts for the fact that the escaping electrons do not all travel normally to the surface. By comparing this model with the one used by Pepper, we have estimated that attenuation lengths calculated from the more sophisticated model would be ~15% larger than those reported here. This is not a large correction in view of the spread in l values.

The theoretical calculations of Quinn[9] and Ritchie et al.[10] as well as the experiments of Kanter,[11] who directly measured the attenuation of an electron beam, indicate that the attenuation length for electrons in aluminum is less than 50 Å for electron energies greater than ~5 eV above the Fermi level. On the other hand, the experiments and analysis of Stuart and Wooten[6] indicate that electrons which are about 9 eV above the Fermi level have a mean free path for electron-electron scattering of ~510 Å and a mean free path for phonon scattering of 130 Å. In support of Stuart and Wooten is the recent work of Pong[4] who finds an attenuation length of ~230 Å for photoelectrons excited by 7.5- to 11-eV photons. Pong shows that his attenuation length, which includes all types of scattering, is equivalent to the separate e^--e^- and e^--phonon mean free paths of Stuart and Wooten.

Our results can be shown to be in substantial agreement with the calculations of Ritchie et al.[10] if we average their values for the attenuation length over the energy distribution of initially excited electrons. For a free electronlike metal such as aluminum, the initial density of states is nearly parabolic. If we assume indirect transitions[15] to final states whose density is independent of energy, the average attenuation length $\bar{l}$ takes the form

$$\bar{l} = \left[\int_0^{E_F} E^{1/2} l(E + h\nu - E_F) dE\right] / \int_0^{E_F} E^{1/2} dE,$$

where E_F is the Fermi energy. The result of this calculation is $\bar{l} = 12.7$ Å. If, on the other hand, a simple, direct transition theory is used, the density of initial excited states is rectangular,[16] and for this case the result is $\bar{l} = 14.5$ Å. The result of Kanter[11] is that the attenuation length for electrons in the energy range $4.5 \text{ eV} \leq E \leq 5.5 \text{ eV}$ is ~50 Å. Thus, our results qualitatively agree with those of Kanter since mean free paths are known in general to decrease with increasing energy. We substantially disagree with the results of Stu-

art and Wooten[6] and those of Pong.[4] A possible reason for this disagreement has been given by Endriz[17] who suggested that the results of Stuart and Wooten may be substantially in error because of surface-plasmon–one-electron transitions that were not considered by the authors. Pong's results may have been similarly influenced.

In conclusion, we have demonstrated the applicability of Pepper's calculations to the determination of experimental attenuation lengths and determined the attenuation length for photoemitted electrons in an energy range heretofore unmeasured. We suggest that future measurements might be refined by including energy analysis of the photoelectrons as well as variation of the photon energy.

The authors wish to thank B. L. McGill and R. N. Hamm for coding the equations and T. A. Callcott and R. H. Ritchie for a critical reading of the manuscript.

*Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

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New Value for Work Function of Sodium and the Observation of Surface-Plasmon Effects

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Clean vacuum-deposited films of sodium were found to exhibit a work function of approximately 2.75 eV. Modification of the surface-plasmon frequency due to sulfur surface contamination was observed. The new value of the work function was shown to be due to a lack of surface contamination.

The properties of the alkali metals in the optical region have become the subject of considerable interest.[1-3] In the case of the optical constants this interest has been occasioned by a persisting lack of agreement between theoretical computations and the experimental results for the optical conductivities. Recently experimental and theoretical attention has also been directed towards photoemission from the alkali metals. Some characteristics of the reported experimental photoemissive energy distributions have been interpreted variously in terms of surface-plasmon excitation of photoelectrons[4] and in terms of surface plasmarons,[5] and have been related tentatively to models of the excitation of the photoelectrons. The most recent theoretical computations of the work function to be expected for sodium have resulted in values much higher than the results usually obtained experimentally.[6,7] The results of these presumably improved computations are in poorer agreement with the reported experimental values of the work function for sodium than was the earlier computation by Bardeen.[8] As a consequence of the foregoing, the experimental results which are reported here are thought to have immediate relevance for