Experimental Evidence for the Surface Photoelectric Effect in Aluminum

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Experimental evidence is presented for the existence of both the volume and surface photoelectric effects in aluminum. Good agreement is obtained between the observed strengths of the surface effect and the predictions of the Mitchell-Makinson theories when the photoemission due to surface plasmon decay is divided into surface and volume photoeffect components.

The controversy over the applicability of volume versus surface theories of photoemission from nearly free-electron metals dates back nearly 40 years and, yet, it has not been resolved. In this Letter we report what we believe to be the best experimental evidence to date for the surface effect. We give a measure of the relative strength of surface and volume photoeffects in aluminum for specific modes of excitation and show that the Mitchell-Makinson surface-effect theory[1] is in reasonably accurate agreement with our results. This paper applies to Al in particular and the nearly free-electron metals in general. Great care should be taken in extrapolating it to other solids.

The surface-effect theories of the 1930's[1] and associated experiments[2] on the alkali metals have given way to volume-effect theories[3,4] and volume-effect interpretations of more recent experiments on the alkalis.[5] Unfortunately, order-of-magnitude differences exist between the results of these experiments. Additional uncertainty has been introduced by a recent interpretation of the volume-effect data[5] in terms of a strong surface effect.[6] The unsettled nature of this controversy takes on additional importance with the recent theoretical interest in photoemission from nearly free-electron metals.[7]

In principle it should be possible to experimentally resolve the surface and volume photoeffects by recognizing that the surface effect can only be excited by oblique incidence p-polarized light when the surface is sufficiently smooth.[1] The reality that experiments to date have not resolved this question may be due to the extreme reactivity of the alkali metals,[8] and to the lack of recognition of the importance of surface[9] and volume[10] plasmon effects. In the present work, great care was taken to protect against contamination of the Al samples, with measurements made at pressures below 10^{-10} Torr. The effects due to optical excitation of surface plasmons (surface waves) were systematically studied by utilizing the surface-wave excitation theories of Ritchie[11] and his co-workers and by recognizing that such surface waves are analytically identical to p-polarized light waves at complex angles of incidence.[12] These surface waves thus provide the field configuration and mechanism necessary for surface-effect excitation. The photoyield from these waves should in principle include both a surface and volume effect component.

Surface waves were excited with normal incidence light upon relatively smooth and roughened surfaces of Al. By measuring reflectance and photoyield from the rougher surfaces upon which surface-wave excitation was strong, the photoyield per decaying surface wave could be determined; and by measuring reflectance and photoyield from smoother surfaces, the Al, ideally smooth-surface (volume-effect) photoyield per absorbed photon could be estimated.

Theoretical[11] and experimental[13-15] details of roughness aided excitation and photoemissive decay of surface oscillations are available elsewhere. It is sufficient for the present discussion to state that such oscillations exist and may be excited via surface roughness[11] coupling at any energy below $\hbar\omega_p/\sqrt{2}$ for nearly free-electron metals (10.55 eV for Al).[16] The fields of these surface waves are very similar to grazing-incidence optical excitations at low-k, low surface-oscillation energies, but become very concentrated near the surface for high-k energies near $\hbar\omega_p/\sqrt{2}$. It is in this high-energy range that the surface photoeffect can become particularly strong.

An example of one of several films used to ex-

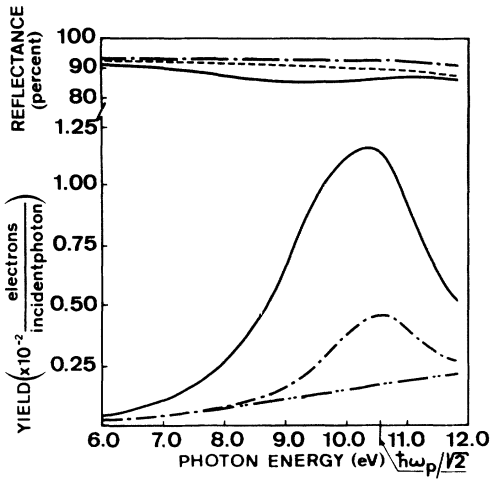

FIG. 1. Reflectance and photoyield measurements on Al. Solid curves, measurements taken on one of the slightly roughened films with coupling to surface waves appreciable; dot-dashed lines, reflectance and photoyield measurements on the smoothest Al films that we made. The dashed line is the scattered-light–induced reflectance drop in the rougher film (Ref. 17). The double-dot–dashed curve is our estimate of the ideally smooth-surface photoyield, i.e., no surface-wave contribution.

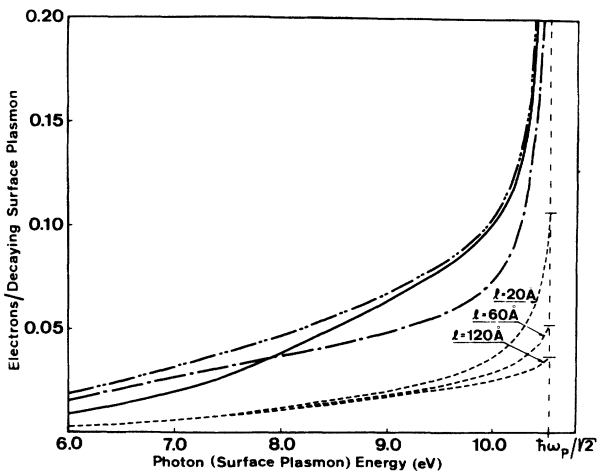

FIG. 2. Experimentally determined and calculated electrons per decaying surface plasmon (surface wave) in Al. Solid curve, experiment; dashed curve, surface-wave decay in the volume photoeffect theory; dot-dashed curve, surface-wave decay in the surface theory; double-dot–dashed curve, the sum of the volume and surface theories.

perimentally determine the photoyield per excited (decaying) surface wave in Al is shown in Fig. 1. The deviation in reflectance from smooth-surface values may be corrected for scattered light[15,17] (shown as a dashed line), and used to estimate the number of surface waves excited, while the deviation in photoyield from smooth-surface values may be used to directly determine the yield per excited (decaying) surface wave. At high surface-wave energies (>10 eV), where the density of surface-wave states is great,[16] lifetime broadening prevents direct determination of photoyield per surface wave, and only the mean photoyield of surface waves within a surface-wave linewidth may be directly determined (exceeding 0.2 electrons per surface wave in several films). We have, however, assumed physically reasonable roughness spectra for our films studied[15] which allowed estimation of the photoyield per decaying surface wave to even the highest frequencies. This result, which represents an average over all films studied, is plotted versus surface-wave energy in Fig. 2.[18] The estimated accuracy is ±20%.

The experimental smooth-surface Al reflectance and photoyield shown in Fig. 1 were obtained from two different but very smooth Al films. The reflectance data show no coupling to surface waves and agree well with previous Al reflectance data,[19] while the photoyield shows appreciable residual coupling to surface waves necessitating an estimation of the ideally smooth-surface (volume-effect) photoyield as indicated in Fig. 1.[15]

Theoretical calculations of the photoyield per decaying surface oscillation have been carried out in both the volume and surface photoelectric theories. One may reasonably assume that the polycrystalline form of our films, possible elastic scattering processes, and the more complicated band structure of Al all combine to make the volume-theory directionality effects described by Mahan for the alkalis[7] of lesser importance in Al. If we thus assume isotropic photoexcitation, the commonly accepted volume photoeffect theories[4] can be used to calculate photoyield per decaying surface oscillation in the volume theory.[14] The photoyield in this theory is given by the ideally smooth-surface yield per absorbed photon modified by an enhancement factor depending on the easily determined surface-wave–field penetration depth and the electron escape depth l. Values available for l range from 70 Å calculated by Wooten[20] from our ideally smooth Al photoyield (Fig. 1) for electrons 10 eV above the Fermi level (E_F) to 50 Å measured by Kanter[21] for energies 5 eV above E_F.

The results of calculations for volume-photoeffect surface-oscillation decay are shown for

several values of l in Fig. 2. It is quite clear from these curves that neither the value $l = 70$ Å determined from our experimental data nor the value $l = 50$ Å determined by Kanter gives at all good agreement with experiment. Photoyields of over 0.2 electrons per excited plasmon have been observed on several of our films near the high-k surface plasma frequency. It is peculiar to the volume-effect decay theory that once the high-k plasmon field depth becomes less than l, enhancement saturates to a finite value (shown as horizontal bars in the calculations of Fig. 2), and none of these values even approaches 0.2 electrons per plasmon. Failure of the volume-effect theory at lower surface-oscillation energies is even more acute since there is no possibility for the descrepancy to be explained in terms of electron-escape-depth effects. It is extremely doubtful that these disagreements between theory and experiment can be due to theoretical uncertainties in this volume theory.

Photoyield in the surface-effect theory was calculated from the model of Mitchel.[1] Surface-wave excitation fields were obtained from the theory of Crowell and Ritchie,[11,15,22] and their magnitudes specified by making the reasonable assumption[23] that volume electronic excitation dominates the surface-oscillation decay mechanism. The corrections to the Mitchell theory first suggested by Makinson[1] were included, an image-charge potential was assumed, and a modification of Makinson's treatment of the fields at the surface was used which we believe represents a definite improvement.[24] This model is believed to be as accurate as any used to date for surface-photoeffect calculations. The result of this calculation is shown in Fig. 2. It should be emphasized that the model used has no adjustable parameters, but surface-field configurations and the surface potential were intentionally varied[25] in order to check the reliability of our result. Resultant variations in calculated yield were found to be less than ±20%.

It has recently been noted[7] that when both the surface and volume photoeffects are appreciable, they may coherently interfere at specific emission energies and angles; but since the present photoyield is taken over all emission angles and energies, we have chosen to combine these two effects by simply adding them as indicated in Fig. 2. The exceptional agreement between this theoretical curve and experiment at high energies must be considered somewhat fortuitous. The discrepancy occurring at lower energies is

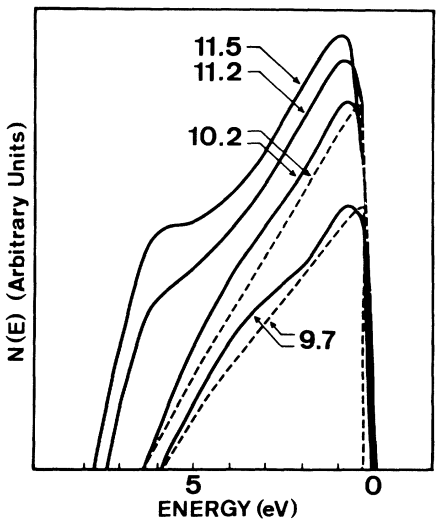

FIG. 3. Electron distribution curves for excitation energies just above and just below the Al surface plasma frequency (10.55 eV). Dashed curves are theoretical EDC's calculated in the surface photoeffect theory (Refs. 1, 11). EDC's were plotted for comparison of shapes and are *not* normalized to photoyield.

believed to be associated with a possible breakdown of our volume-effect decay-mechanism assumption[23] at these energies. Despite this shortcoming, the curves of Fig. 2 clearly indicate the inability of the conventional volume-effect theory to adequately explain surface-wave decay, while presenting very strong evidence for the need to invoke the surface photoeffect. The calculations represent the first quantitative agreement obtained between experiment and the Mitchell-Makinson surface-effect theory.

The tendency in the past to invoke either a pure surface or a pure volume interpretation for nearly free-electron metals makes it important that we emphasize the evidence for both of these effects in the present result. The combined surface-volume nature of the photoemission is further illustrated by Fig. 3 which shows measured and calculated energy distribution curves (EDC's) from one of our smoother surfaces. At energies below or equal to $\hbar\omega_p/\sqrt{2}$ (10.55 eV), the surface effect should dominate. Here we find good agreement with shapes predicted in the surface effect theory.[1,11,15,22] Smith and Koyama[26] obtain similar agreement with a volume theory. For $\hbar\omega > 10.55$ eV, the surface effect should diminish and the volume effect become dominant. The low-energy shoulder which appears for 11.2 and 11.5 eV is characteristic of scattered electrons, and these would be expected in a volume-effect ex-

citation.[27]

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[8]R. J. Whitefield and J. J. Brady, Phys. Rev. Lett. 26, 380 (1971).

[9]It is doubtful that previous alkali films studied were smooth enough to avoid the type of surface plasmon yield effect discussed in this Letter.

[10]In thin-film studies, the large optical penetration depths near the plasma frequency can give rise to the excitation of "radiative" surface oscillations.

[11]J. Crowell and R. H. Ritchie, J. Opt. Soc. Amer. 60, 794 (1970); J. M. Elson and R. H. Ritchie, Phys. Lett. 33A, 255 (1970).

[12]The most general classical expressions for reflection-refraction of p-polarized light at an arbitrary vacuum-complex dielectric interface, e.g., T. S. Moss, *Optical Properties of Semiconductors* (Academic, London, 1959), yield a complex angle of light incidence such that the incident and refracted waves decay away from the surface, while the reflected wave is zero. The criterion on the complex angle to yield these surface waves at a given frequency corresponds to the surface-plasmon dispersion relation.

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[15]J. Endriz and W. E. Spicer, "Study of Aluminum Films I. Optical Studies of Reflectance Drops and Surface Oscillations on Controlled Roughness Films" (to be published), and "Study of Aluminum Films II. Photoemission Studies of Surface Plasmon Oscillations on controlled Roughness Films" (to be published). The experimental data of this Letter are taken from the more extensive results of these references.

[16]ω_p is the volume plasma frequency.

[17]J. M. Elson and R. H. Ritchie, "Photon Interactions at a Rough Metal Surface" (to be published).

[18]The solid curve in Fig. 2 was calculated directly from the experimental "fitted" curve of Fig. 13, "Study of Aluminum, II," Ref. 15.

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[20]F. Wooten, private communication.

[21]H. Kanter, Phys. Rev. B 1, 522 (1970).

[22]The Crowell and Ritchie formalism (Ref. 11) gives the detailed surface-polarization charge-density decay coefficient $\Gamma \simeq 1$ Å^{-1} in terms of the Fermi velocity. It is thus superior to the less-sophisticated derivation of the surface-wave field of Ref. 12.

[23]This is analogous to the assumption made throughout the literature that volume-effect energy absorption dominates surface-effect absorption in an optical excitation.

[24]The exponentially decaying surface-polarizarion–charge fields of Refs. 11 and 23, derived assuming a step-charge discontinuity at the surface, were convolved with the calculated charge variation associated with an image-charge potential. This treatment includes effects of finite electron Fermi velocity as well as charge-density variation effects of Makinson (Ref. 1), but it avoids field singularities of Makinson's treatment.

[25]The surface-polarization charge thickness was assumed 50% larger and 50% smaller than the value derived in Ref. 11, and a separate calculation was carried out assuming a step rather than an image potential.

[26]R. Y. Koyama and N. V. Smith, Phys. Rev. B 2, 3049 (1970).

[27]Comparable observations have been noted just above $\hbar\omega_p/\sqrt{2}$ in magnesium by T. F. Gesell and E. T. Arakawa, private communication.