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Optical Excitation of the Surface Photoelectric Effect of Metals Using Synchrotron Radiation

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By fully exploiting the properties of synchrotron radiation, a surface photoyield spectrum of a metal, namely aluminum, was obtained for the first time. This type of spectrum has been theoretically discussed since 1928. The extreme surface sensitivity, which is implicit in the transition matrix element for the surface photoexcitation process, was experimentally confirmed. The applied photoemission technique, therefore, provides one of the most powerful tools for the investigation of charge distribution and dielectric response at metal surfaces.

The surface photoelectric effect in metals has been one of the most long-standing problems in metal physics. Theoretical treatments of the effect began in the early days of quantum mechanics within the Sommerfeld model of a metal (see Fig. 1) and still continue (see, e.g., Refs 1, 6–13). Since the surface photoelectric effect is of fundamental importance for the understanding of the quantum mechanical perturbation applied by an electromagnetic field to electronic states in a one-dimensional potential box because of the existence of potential steps, numerous attempts have been made in the last forty years to detect the effect experimentally (see, e.g., Refs. 14 and 15). The first experimental evidence for the mere existence of the effect was photoyield data from Al obtained in 1971[16] which clearly showed contributions from the surface photoelectric effect excited by roughness-induced surface plasmons. Also, some evidence has been provided for the direct optical excitation of the effect.[17,18]

In this Letter we report the first experimentally obtained surface photoyield spectrum of a metal. A spectroscopic technique that fully exploits the properties of synchrotron radiation made it possible to separate unambiguously the photoyield caused by the surface photoelectric effect optically excited by p-polarized light from other contributions to the yield. The technique was applied to aluminum. Photoyield spectra were taken since it was shown by theory[11] that this type of photoemission spectra should most clearly exhibit features which are characteristic of the surface photoemission process in metals.

Figure 1(b) shows the geometry of the experiment. An aluminum surface, which is nature's best approximation to one side of a one-dimensional potential box, is rotated around two orthogonal axes with respect to a light beam with fixed orientation of the $\vec{E}$ vector. Rotation around the θ axis varies the angle of incidence of the light. Rotation by 90° around the φ axis changes the polarization from perpendicular to parallel to the plane of incidence and vice versa at arbitrary angles of incidence θ. The experiments were performed using monochromatized and highly

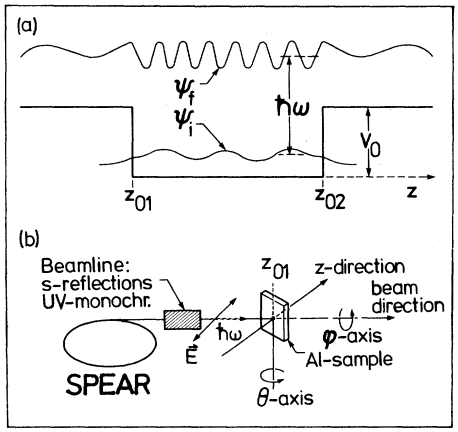

FIG. 1. (a) The symmetric, one-dimensional potential box established by a metal film gives a good intuitive understanding of the surface photoelectric effect (see Ref. 1). Within the Sommerfeld model of a metal (Ref. 2), this effect is the only possible photoexcitation process which conserves energy and momentum, with the surface acting as a momentum source [indirect processes (Refs. 3 and 4) or core excitations (Ref. 5) are not taken into consideration]. Because of the one dimensionality of the problem, only light with an $\vec{E}$ component in the z direction—p-polarized light—can couple to the surface photoelectric effect. For aluminum, $V_0 = 15.8$ eV. (b) Geometry of the experiment; the condition for incident p-polarized light. Rotation of the sample by 90° around the φ axis gives s polarization at arbitrary angles of incidence θ without altering any other parameters such as collector geometry.

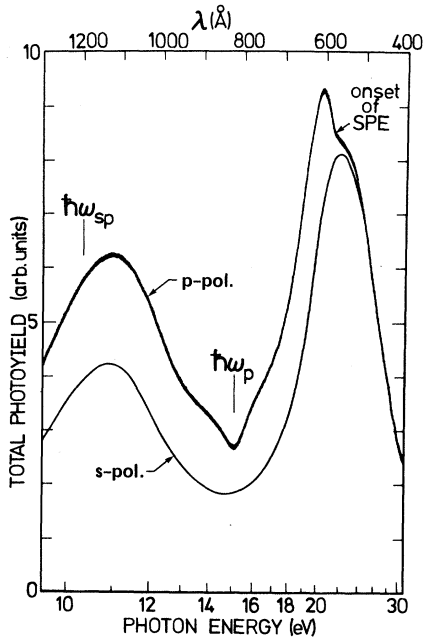

FIG. 2. The raw total photoyield spectra of Al for both s and p polarization of the incident light, angle of incidence $\theta = 45°$. The p curve is a facsimile of the x-y recorder trace. The photon flux decreases rapidly below 550 Å; the blaze wavelength of the osmium grating was 625 Å. The onset of surface photoemission is indicated.

polarized synchrotron radiation at the ultraviolet 8° beam line[19] of the Stanford Synchrotron Radiation Laboratory. The rotations described above were realized with use of a θ-φ manipulator.[20] The photoyield was directly determined by measuring the current into the sample and an electron collector was mounted at a fixed position relative to the sample. The sample was prepared by *in situ* evaporating an Al layer onto a smooth Al single crystal. Measurements were made at a pressure of 2×10^{-10} Torr.

Figure 2 shows the original photoyield spectra for s and p polarization at $\theta = 45°$. At photon energies above 24 eV the two spectra coincide within the statistical uncertainty which can be estimated from the spectrum taken at p polarization. The broad yield maximum around the surface plasma frequency of Al ($\hbar\omega_{sp} = 10.3$ eV) in both spectra is due to the decay of surface-roughness-induced surface plasmons, which form a highly effective mode for the excitation of the surface photoelectric effect.[9,16] In the energy range above this peak the most obvious difference in the spectral shape between p- and s-yield curves is a minimum in the p yield at 14.9 eV and a sharp maximum at 20.3 eV. These features can be clearly attributed to the optically excited surface photoelectric effect, as demonstrated in Fig. 3.

In Fig. 3 the total yield has been normalized to the photon flux of the monochromator which was estimated from an aged-Au-beam monitor and the yield has been decomposed into the contributions from volume excitations, from excitations caused by roughness-induced surface plasmons, and from the optically excited surface photoelectric effect. In the region between $\hbar\omega_p$ and 22 eV the volume yield curve for p-polarized light has been estimated by multiplying the s-yield curve by the volume absorption-ratio curve labeled "this experiment" in the upper part of Fig. 3. Some ratio values, which are indicated by dots on that curve, can be directly deduced from the experiment. The sharp minimum in the p-yield curve at $\hbar\omega_p$ is due to shielding of the z component of the electromagnetic field at the surface. Therefore only the volume photoeffect contributes to both p and s yields and the volume absorption ratio can be deduced. This can also be done in

the energy region above the onset of surface photoemission at 22 eV. Here the reflectivity for both s- and p-polarized light rapidly decreases to a few percent and the ratio values approach 1. Included is a theoretical ratio-value curve $(1-R_p)/(1-R_s)$ calculated using optical data for Al.[21] These values can only be obtained with perfectly smooth samples, 100% polarization, and a perfect geometry. The surface-roughness-induced yield below 15 eV photon energy should be the same for p- and s-polarization.[22]

The difference between the measured p-yield spectrum and the sum of the estimated contributions from volume photoemission and photoemission due to roughness-induced surface waves constitutes the photoyield spectrum of the optically excited surface photoelectric effect in Al (crosshatched area). It is given separately in the lower part of Fig. 3.

The correct transition matrix element[7] for the surface excitation process used in the included calculation[9] consists of two terms:

$$\langle M_f\rangle=\{[(e/mc)b_f]/2\pi|b_f|^2\}\int_{-\infty}^{+\infty}dz[A_z\partial\psi_i/\partial z+\tfrac{1}{2}\psi_i\partial A_z/\partial z](\psi_f{}^{+*}-\partial_f\psi_i{}^{-*}).$$

The first term in the matrix element reflects the decay of the Fermi sea's electronic wave functions at the surface because of the potential step. These changes extend over a distance of the order of the Thomas-Fermi screening length (~1 Å). The second term accounts for the contributions to the surface photocurrent which are caused by the variation of the electromagnetic field.[7] It occurs at the surface because of the variation of the dielectric response in the surface region. Another effect, which can give rise to a nonzero $\partial A_z/\partial z$ term—even in the region of bulklike dielectric response—is the optical exciation of volume-plasma oscillations at the surface.[23-25]

The observed sharp decrease of surface photoemission around 21 eV photon energy was predicted to occur[9,11] because $\vec{E}_z$ at the surface is much weaker in the refraction region —i.e., above $\hbar\omega=21$ eV for $\theta=45°$—than in the region of total external reflection below that energy. For energies between 16 and 20 eV the actually observed surface photoyield approaches the constant-field surface yield, while there are strong contributions at energies below $\hbar\omega_p$ which originate from the variation in the dielectric response at the surface (compare, e.g., Fig. 5 of the calculation of Endriz[9]).

At the limit of Landau damping (~18 eV) no increase in the surface photoyield is observed. It was predicted to occur[11] because of the decay of the optically excited volume plasma oscillations into single-particle excitations. Our result is consistent with the small effect which resonances of optically excited volume plasmons have on photoemission[26] and absorption[27] from thin metal layers on glass. These resonances as well as contributions from the decay of the so-called "optical plasmon" of frequency[28] ω_p are not to be expected in our experiment because of the nature of our sample.

At energies below 10 eV we can give only a rough estimate of the shape of the surface photoyield spectrum. Clearly, it does not show the theoretically predicted symmetric spectral shape with respect to $\hbar\omega_{sp}$. This reflects the sensitivity of the *ab initio* calculation[9] to the assumed surface potential at low photon energies. It em-

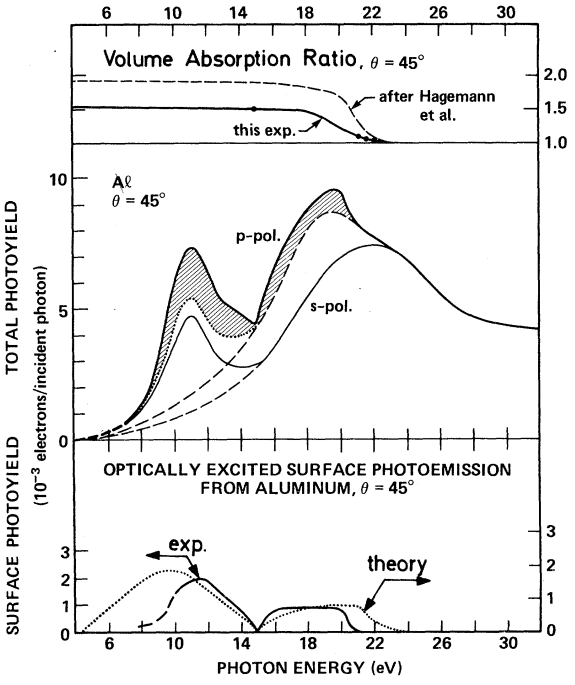

Fig. 3. Al photoyield spectra corrected for the photon flux. Below 7 eV the curves are extrapolated to zero yield at 4.2 eV. The crosshatched region under the p-yield curve represents the yield from the optically excited surface photoeffect. The surface photoyield spectrum is also shown separately and compared to theory (Ref. 9). Included is the ratio for volume excitations from s- and p-polarized light from this experiment and calculated (after Ref. 21).

phasizes the importance of the use of self-consistent wave functions in the surface region.[12]

The above observations experimentally confirm the extreme surface sensitivity, which is implicit in the transition matrix element of the surface photoemission process of metals. They seem to suggest that this surface photoemission technique provides one of the most powerful tools for the investigation of charge distribution and dielectric response at metal surfaces.

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