

art and Wooten⁶ and those of Pong.⁴ A possible reason for this disagreement has been given by Endriz¹⁷ 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.

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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 photoelectrons⁴ 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

those who may be anticipating either further experimental or theoretical work relating to the optical characteristics of the alkali metals.

The study which has been carried out was directed towards elucidation of the principal mechanisms of the effect of sulfur on photoemission from sodium.⁹ Such effects, which were referred to in the early literature as "sensitization" have, in general, received only slight attention in recent years.¹⁰⁻¹² Yet, it may very well be that a large portion of the available values of work functions and the results of photoemission studies include such effects. As an initial requirement for a study of photoelectric "sensitization" one must first produce clean, uncontaminated sodium surfaces. The sodium surfaces produced for this reason were found to exhibit a photoelectric work function of approximately 2.75 eV. Due to the highly reactive nature of the alkali metals, most studies of photoemission and the optical properties have been performed on films produced by vacuum evaporation. This procedure was also followed in this investigation, but the preparation of the films was carried out under more rigorous vacuum conditions than is usually considered necessary, which is an essential factor in obtaining the higher work-function sodium surfaces.

In order to maintain the requisite ultrahigh-vacuum conditions, the depositions were carried out using a two-chamber technique. The deposition sources were located in one ion-pumped chamber which was connected to another ion-pumped chamber by a straight-through valve. In the sample chamber the films were deposited onto the electrode of a quartz oscillator-microbalance crystal, which was at the temperature of liquid nitrogen. The two-chamber technique permitted pressures in the sample chamber during depositions to be maintained typically below 2.6×10^{-10} Torr as indicated by a nude Bayard-Alpert ionization gauge. Subsequent to the deposition, indicated pressures in the 10^{-11} Torr range were quickly attained.

Sodium for the deposition was procured in ampoules sealed under vacuum. Use of such ampoules as sources of highly reactive metals has become a quite-common experimental procedure. As has been reported by other investigators,^{13,14} a burst of gas was observed when the sodium ampoule was cracked in vacuum. For the investigation carried out, the ampoule itself was not used as an evaporation source, but the sodium was transferred under high vacuum into

another valved evaporation source. The sodium in this source was then outgassed until the base pressure of the evaporation-source chamber could be obtained with the sodium at about 220°C. The gas evolved was thought to be largely argon. The manufacturer of the ampoule indicated that the sodium had been processed under argon; and that after filling, the ampoule was then evacuated before sealing.

The curve shown in Fig. 1 for a sodium deposit of thickness 1207 Å is typical of the photoemissive yield obtained from uncontaminated sodium surfaces. This thickness represents a fresh deposition onto an already existing, much thicker, sodium film in order to obtain a fresh, uncontaminated sodium surface. The light inducing the photoemission was at near normal incidence ($\theta < 1\frac{1}{2}^\circ$) onto what appeared to be good mirror surfaces of sodium. As is shown in Fig. 1, the yield in the threshold region indicates a work function of approximately 2.75 eV, which is much higher than the usually reported value of approximately 2.25 eV. Typically, the work function for metals is obtained by fitting a Fowler¹⁵ curve to the photoemissive yield near the

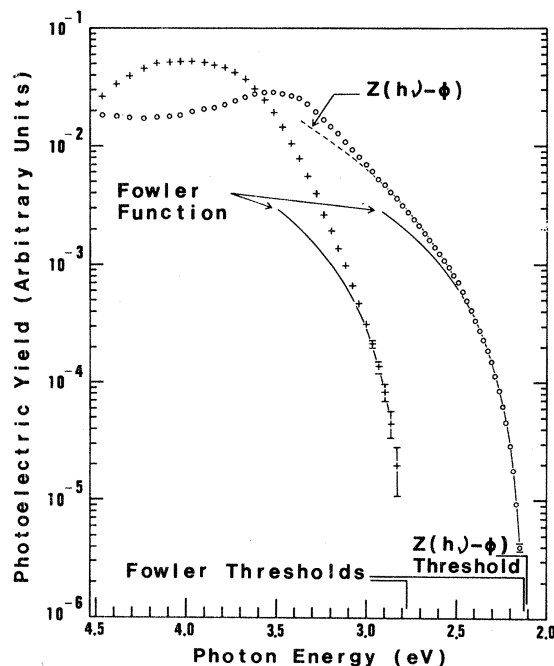


FIG. 1. The photoelectric yield per incident photon from an initial sodium deposition and from one of a subsequent sequence of sulfur depositions. The indicated uncertainty of the sulfur deposition represents the estimated accumulated microbalance-frequency-determination error limit. $Z(h\nu-\phi)$ is the ordinary Fowler function plus $0.01(h\nu-\phi)^3$. Crosses, 1207 Å initial sodium deposit; open circles, $(6.45 \pm 0.39) \times 10^{-8}$ g/cm².

threshold. This procedure was not completely suitable in this instance as the Fowler function did not provide a good fit to the emission obtained. As a consequence, the value adopted for the work function is somewhat arbitrary. The value found by using the Fowler curve (plotted in Fig. 1) and the adopted value agree within 0.05 eV.

Another feature which is quite prominent in the results obtained for clean sodium is the peak in the yield near 4.0 eV. The location of this peak is in accord with the energy at which the surface-plasmon oscillation is expected to occur for an uncontaminated surface, and is interpreted as being due to additional photoelectron excitation near this energy due to the surface plasmon. This is also essentially the experimental value of the surface-plasmon loss reported by Kunz¹⁶ in experimental studies of the characteristic energy losses of sodium.

The results which have been obtained by different investigators of the properties of the alkali metals in the optical region have been at least as noteworthy for their differences as for their agreements. Indication that the results reported here for clean sodium surfaces are not anomalous is shown in the behavior of the photoemissive yields (Figs. 1 and 2) for an uncontaminated sodium surface which has had small amounts of sulfur deposited onto its surface in a sequence of separate depositions. Measurements of the amount of sulfur deposited in each deposition were obtained from the frequency shift of the quartz oscillator microbalance used as a substrate for the depositions. As a result of the deposition of the sulfur, the threshold for emission was initially reduced and the location in the peak in the photoemissive-yield curve shifted to lower energies. Particular attention is called to the ability of extremely small amounts of sulfur deposited onto the surface to produce substantial alterations in the photoemission. Deposited amounts of sulfur of the order of a nominal "ideal"-monolayer coverage are sufficient to reduce the observed emission threshold by more than 0.5 eV, and amounts equivalent to several "ideal" monolayers are sufficient to produce a well-defined emission peak at the lowered energy.

The emission obtained for an amount of sulfur deposited on the surface sufficient to provide a threshold reduction to about 2.25 eV is quite similar to that reported by other investigators.^{17,18} In this case the emission is reasonably well fit

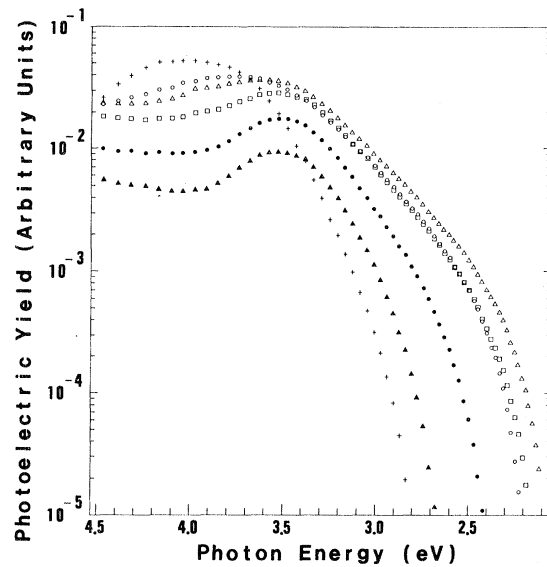


FIG. 2. The photoelectric yield per incident photon from an initial sodium deposition and from a subsequent sequence of sulfur depositions. The indicated uncertainties of the sulfur depositions represent the estimated accumulated microbalance-frequency-determination error limits. Crosses, 1207 Å initial sodium deposit; open circles, $(2.49 \pm 0.15) \times 10^{-8}$ g/cm²; open triangles, $(4.47 \pm 0.27) \times 10^{-8}$ g/cm²; open squares, $(6.45 \pm 0.39) \times 10^{-8}$ g/cm²; closed circles, $(8.52 \pm 0.50) \times 10^{-8}$ g/cm²; closed triangles, $(10.54 \pm 0.62) \times 10^{-8}$ g/cm².

by the Fowler theory for several decades near the threshold. A much improved fit can, however, be obtained by the addition of a small cubic term to the usual Fowler function. The threshold shift is interpretable in terms of the surface-potential contributions of the surface contaminant. More extensive data were obtained regarding the surface-potential contributions and are intended to be discussed in greater detail elsewhere.

The identification, made previously, of the origin of the emission peak with the surface plasmon is further indicated by the shift of its energy location as the amount of sulfur deposited on the surface was increased. A similar emission-peak shift was found to occur spontaneously on surfaces held for extended periods of time under somewhat poorer vacuum conditions.

Although this is the first observation of contaminate modification of the surface plasmon in an optical experiment, such modification has been observed in characteristic energy-loss experiments.^{19,20} An explanation of the modifications of the surface-plasmon frequency ω_{sp} observed in these characteristic energy-loss ex-

periments has been given in a classical model by Stern and Ferrell.^{21,22} In the case that the surface is bounded by a semi-infinite medium of dielectric constant ϵ , this treatment yields a particularly simple result for the surface-plasmon frequency: $\omega_{sp} = \omega_p / (1 + \epsilon)^{1/2}$. The shift in the emission peak found when adding sulfur to the surface is consistent with this prediction. Strict applicability of the classical approach to coverages on the order of several monolayers is, however, not to be expected.

The two aspects of the photoemission from sodium which have been dealt with here are relevant to results recently reported by others. The theoretical treatment of the work function of sodium was first rendered by Bardeen and yielded a value of 2.35 eV which was in good agreement with the then-known experimental values. Recently two separate calculations have been reported, yielding values of 2.75²³ and 2.95 eV.²⁴ These calculations were both rendered in a model which used the electron density as the basic variable, and with an approximate accounting being taken of the variation in the electron density at the surface. The experimental results reported here lend support to the interpretation that the more recent calculations do represent an improvement over the earlier theoretical treatment. One feature of the Smith calculation is that the difference in work function from that obtained by Bardeen was primarily due to a larger surface-potential contribution of as much as 0.74 eV. The work-function reduction observed with sulfur contamination is phenomenologically consistent with surface-potential contributions of this order of magnitude as work-function variations of the order of 0.6 eV were obtained as a result of surface contamination.

One significant factor suggested by the study reported here is that it is extremely likely that all previously reported experimental data regarding the photoemission of the alkali metals have been unsuspectedly influenced by surface contaminants. Such a case is not without precedent since recent investigators have found that the previously determined values for the work function of gold have been incorrect because of Hg contamination of the surfaces.^{25,26} Additional evidence for surface-contaminate effects have been reported for Al²⁷ and Be.²⁸

The surface-plasmon contribution as represented by the peak in the photoemissive yield has also been recently reported by other investi-

gators¹⁸ though the nature of its origin was not attributed to the surface plasmon. The interpretation rendered in that case was partially based on the use of optical-constant data obtained at a sodium-quartz interface. While the reported alterations of the optical constants of metals due to surface-plasmon absorption have been small,^{29,30} the demonstrated connection of the peak in emission with the surface plasmon and its sensitivity on boundary conditions suggests that the use of optical-constant data to explain features of the photoemissive yield will need to be restricted to optical-constant data measured on free surfaces.

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