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Photoemission from Ag-O-Cs

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X-ray photoelectron spectra of Ag, O, and Cs and quantum yield distributions from surfaces prepared by evaporating Cs onto Ag oxidized in ultrahigh vacuum have been measured. The structure of this surface determined from these measurements consists of silver particles dispersed in a matrix of Cs_2O with a layer of $Cs_{11}O_3$ on top. The threshold at 1.2 μm is due to a lowering of the surface barrier by the $Cs_{11}O_3$ and the yield in the visible and near infrared is explained as due to the excitation of Mie or optical resonance absorption in the silver particles.

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The Ag-O-Cs or *S*-1 photocathode is unique among photoemissive materials with useful sensitivity to visible light. It was the first, and for many years the only, cathode available for practical applications.[1] Because of its useful response in the visible and near-infrared region of the spectrum, it continues to find widespread use in many photoelectronic applications. In spite of this no explanation of the observed quantum yield in this spectral region has been previously

given that is consistent with the experimental results on this surface, since it was discovered fifty years ago. Only recently has the chemical composition been established in detail.[2]

In particular no model of this surface that has previously been proposed[3-6] can explain the long wavelength threshold at 1.2 μm nor the high yield in the visible and near infrared. Earlier treatments by Eckart,[3] Davey,[4] and Parker[5] that consider the S-1 as being a homogeneous cesium monoxide (Cs_2O) semiconductor containing silver as an impurity, fail to recognize, as pointed out by Sommer,[7] that the concentration of silver in such cathodes is so great that the representation of silver by a single narrow donor level is unrealistic. A more recent study by Ebbinghaus *et al.*[6] attributes the yield in the visible and near infrared to the excitation of surface plasmons in $Cs_{11}O_3$ and definitely excludes the formation of Cs_2O.

The generally accepted structure of the S-1, obtained from many studies over the years and before this work was undertaken, consisted of silver particles up to about 200 Å in linear dimensions approximately spherical in shape, and distributed throughout a matrix 200–400 Å thick with a stoichiometry determined to be close to Cs_2O.[7] This picture, however, does not provide an explanation for the 1.2 μm threshold, and only a highly speculative explanation for the yield between 4000 and 9000 Å has been provided.

The purpose of this Letter is to report on x-ray photoelectron spectroscopy and quantum yield measurements that give a modified structure for this surface, a structure that successfully explains the quantum yield in the visible and near infrared and the threshold at 1.2 μm. The structure consists of Ag particles dispersed in a Cs_2O matrix with a $Cs_{11}O_3$ overlayer. The experiments leading to this structure and the interpretation of the quantum yield based on this new composite surface will now be given.

The quantum yield versus wavelength for a typical Ag-O-Cs or S-1 photocathode is shown in Fig. 1. The peak position of the maximum yield in the visible λ_R, has been found to vary by a substantial amount. It has definitely been established that the long wavelength response of Ag-O-Cs must be associated with the Ag because at wavelengths above 4000 Å, the Cs-O matrix shows neither light absorption nor photoemission.[7] Asao[8] in his studies on this surface found this peak to be at 6500 Å. We have found this peak to vary from about 6000 to 8000 Å depending upon the

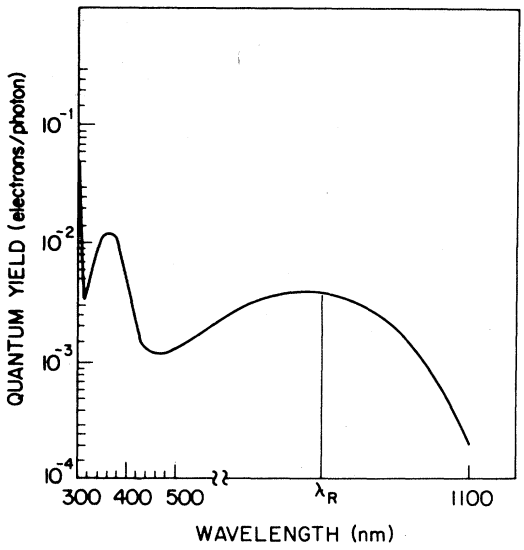

FIG. 1. Quantum yield of S-1 photocathode.

method of preparing the initial silver film.[2] A proper explanation of the observed quantum yield must contend with this variation of λ_R and the fact, known for many years,[7] that if silver is replaced by another metal in this surface photoemission in the region of interest is considerably reduced over that for silver, or is nonexistent. The plasmon model of Ebbinghaus *et al.*[6] cannot consider the variability of λ_R as $Cs_{11}O_3$ has a single plasmon at 1.55 eV.

The surfaces were prepared and examined in ultrahigh vacuum (10^{-7} Pa) in a system previously described.[9] The preparation procedure may also be found in the literature.[7] The spectral response shown in Fig. 1 is taken from a surface prepared in our system, though the position of λ_R varied from about 6000 to 8000 Å. The quantum yield from 4000 Å to shorter wavelengths has been definitely attributed to interband transitions in the Cs-O matrix.[7]

In Fig. 2 we show (a) the quantum yield in an incomplete and completely processed S-1 photocathode and (b) the respective x-ray photoemission O 1s core-level spectra. What is obvious here is that there exist two types of oxygen in both the incomplete and completely processed surface. The peak at 527.5 eV is due to oxygen in Cs_2O and the one at 531.5 eV we attribute to oxygen in $Cs_{11}O_3$. The experiments from which we obtained these assignments have been described in previous works,[2] though we briefly give the results here. The Cs_2O was produced in a separate experiment by the complete reduction

of Ag_2O (produced by a glow discharge of Ag in oxygen) by cesium through the reaction $Ag_2O + 2Cs \rightarrow 2Ag + Cs_2O$. In this experiment we observed only one Ag peak in all core-level spectra located at the values for metallic Ag. We observed one O 1*s* peak at 527.5 eV. The measured Cs/O ratio was very close to 2:1.[10] The position of the Cs 3*d* peak is also in reasonably good agreement with the work of Ebbinghaus and Simon[11] (725.5 eV, Ref. 11; 725.3 eV Ref. 2) who also measured the core-level spectra of Cs_2O. The O 1*s* peak at 531.5 eV was assigned to oxygen in $Cs_{11}O_3$ on the basis of work by Ebbinghaus and Simon[11] who studied the properties of $Cs_{11}O_3$ in great detail. They give a value of 531 ± 1 eV for this peak and noted a broad asymmetric peak for the Cs 3*d* core-level spectra for all suboxides of cesium, whereas Cs_2O and the cesium peroxides have sharp symmetric Cs 3*d* core-level spectra. We have observed the same behavior.

In the present experiments we varied the angle of observation of the photoemitted electrons and, from a measurement of the areas and the published data for photoionization cross sections,[10] established that the $Cs_{11}O_3$ exists as an overlayer on Cs_2O. In another series of experiments on the oxidation of cesium in ultrahigh vacuum[12] on various substrates we found the same general behavior, i.e., $Cs_{11}O_3$ is produced along with Cs_2O as an overlayer on Cs_2O. These experiments further indicate that after a "certain" thickness of $Cs_{11}O_3$ is grown cesium peroxides begin to form upon further oxidation. This is noted as a shift of the O 1*s* peak at 531.5 to 530 eV and a gradual attenuation of the Cs_2O O 1*s* peak at 527.5 eV[2]. This layer of $Cs_{11}O_3$ appears to form over a narrow range of oxygen exposures[2] and from varying the angle of observation of the photoemitted electrons we estimated this layer to be 10–20 Å over a Cs_2O layer >40 Å thick. This provides an explanation for why Ebbinghaus *et al.*[6] in their ultraviolet photoelectron spectroscopy work on oxidized cesium only detected $Cs_{11}O_3$. The He I resonance line at 21.2 eV would only sample electrons from a depth of a few angstroms.

A band diagram for the model of the *S*-1 consisting of silver particles in a matrix of Cs_2O, the so called Sommer-Borzyak model, is shown in Fig. 3. The data for Cs_2O are taken from the work of Borzyak, Bibik, and Kramerenko[13] but has been substantiated by more recent studies.[14] This model successfully explains the photoemission in the blue (interband transitions in Cs_2O), but completely fails to account for the long wavelength threshold of ~ 1.2 μm and why the silver particles have a quantum yield in the visible of ~ 10^{-3} electrons/photon when a continuous solid silver film has a value of only ~ 10^{-5} electrons/photon, i.e., two orders of magnitude smaller

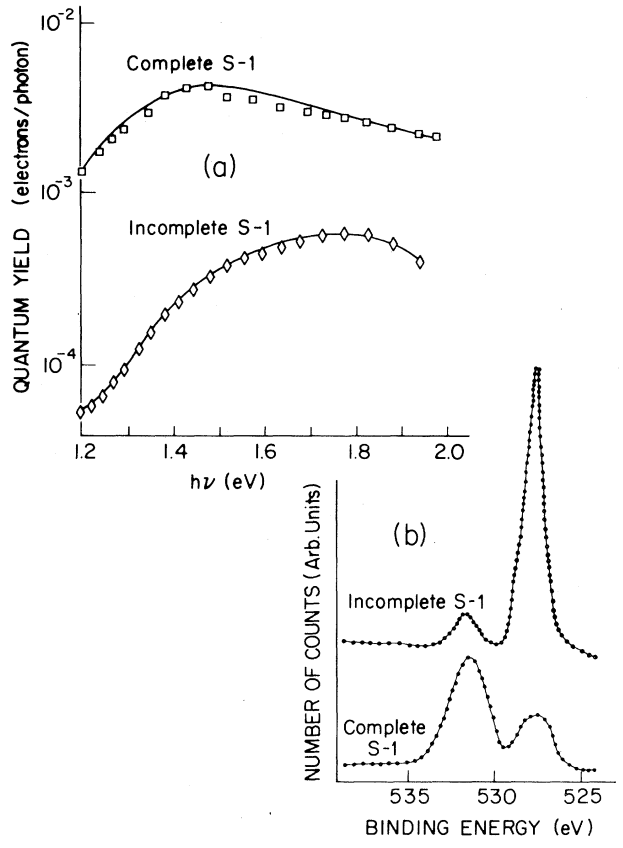

FIG. 2. (a) Quantum yield of an incomplete and complete *S*-1 photocathode. (b) O 1*s* core-level spectra for an incomplete and complete *S*-1 photocathode.

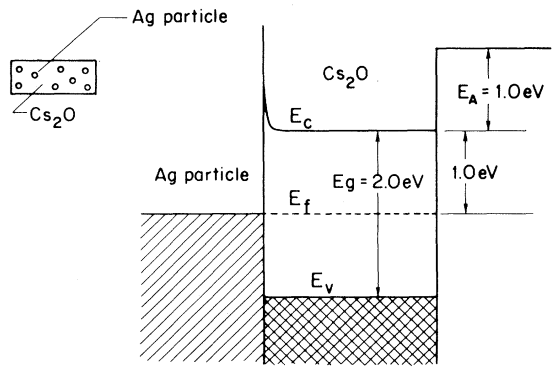

FIG. 3. Sommer-Borzyak model of *S*-1 photocathode.

in the same spectral range. We can account for the threshold if we consider that the $Cs_{11}O_3$ surface with a work function of only 1.35 eV (Ref. 15) can lower the electron affinity to negative values. This would provide of threshold of 1 eV or 1.25 μm, the observed value. The considerations of the $Cs_{11}O_3$ surface layer are completely consistent with the observations of Uebbing and James[14] who observed a continuous decrease in the work function of Cs_2O layers with increasing layer thickness, to the low value of 0.6 eV. They also support the studies on oxidized cesium films made by Gregory *et al.*[16] who noted a sharp minimum in the work function of 0.7 eV within a narrow range of oxygen exposures. This present work suggests that a thin layer of $Cs_{11}O_3$ was formed over the Cs_2O in these two cases resulting in a lower work function.

The enhanced yield of the silver particles is another matter. Just recently Schmidt-Ott and coworkers[17] observed an enhancement of the photoelectric yield if ultrafine silver particles with radii ≤ 50 Å are used as photoemitters. The system obeyed the Fowler-Nordheim law $Y = C(h\nu - \varphi)^2$ for $(h\nu - \varphi) \leq 1.5$ eV. They noted that the yield for particles 20 Å in diameter was a factor of 110 over that for a macroscopic, smooth surface of silver. φ changes by a very small amount so it does not enter into the description of the phenomena. Resonance absorption of radiation by small metal particles suspended in a dielectric has been known for many years and was obtained from a theory developed by Maxwell-Garnet[18] for small metal particles dispersed in a dielectric or, in the limit of small isolated spheres, from Mie scattering theory.[19] Provided the small metal particles and their separations are much smaller than the wavelength of the incident light, this resonance or Mie absorption corresponds to the collective absorption of the metal particles much like plasma resonance. The resonance wavelength λ_R is strongly dependent on the density of the metal clusters, the ambient dielectric constant, and the presence of nearby interband transitions as indicated by the following equation given by Moskovits[20]

$$\lambda_R = \lambda_p \left[1 + \epsilon_b + \left(\frac{2+q}{1-q} \right) \epsilon_0 \right]^{1/2} . \quad (1)$$

In Eq. (1) λ_p is the plasma wavelength for the metal, ϵ_b the interband contribution to the complex dielectric constant of the metal, and q is the volume fraction of the metal within a dielectric of dielectric constant ϵ_0. Though this simple expression does not give the details of the variation of λ_R with the particle size specifically (this is somehow related to q) it suffices for our interpretation of the photoyield of S-1 surfaces in the visible and near infrared. The model for which this expression was derived, i.e., small particles with linear dimensions $\ll\lambda$, the incident wavelength, suspended in a dielectric, is a good approximation to the structure of S-1 photocathodes. For silver, ϵ_b is approximately a constant in the visible region of the spectrum equal to 4 and λ_p is 1360 Å. If one assumes a value of $\epsilon_0 = 3$ for Cs_2O and 0.75 for q, λ_R is 8000 Å. For small values of q, λ_R occurs at shorter wavelengths and for large values, λ_R is in the red. Thus λ_R is a function of the specifics of the particle size distribution and their volume content in the dielectric. These numbers are presented to show that reasonable values for the parameters involved in the determination of λ_R give the experimentally observed λ_R.

In the work of Schmidt-Ott, Schurtenberger, and Siegman,[17] the yield was a factor of 25 larger for 30 Å diameter silver particles and 110 larger for 20 Å particles, both relative to a macroscopic silver surface, indicating a significant particle size effect. Asao's[8] data for the S-1 shows a photoyield peak at $\simeq 6500$ Å. The silver films from which he made his cathodes show a broad absorption maximum at $\simeq 6000$ Å as a result of the specific silver particle size distribution and the fact that the dielectric was vacuum.

The reason that silver works better than any other metal is a reflection of the fact that it forms small spherical agglomerates in thin films and the optical constants of silver as a function of wavelength (ϵ_b is large due to d-s transitions) place λ_R in the visible to near infrared. Other materials such as Cu with $\epsilon_b = 10.9$ and Au with $\epsilon_b = 8.2$ should absorb better in the infrared if a matrix could be found with a relatively small band gap where the Fermi level of the metal and matrix would be < 1.0 eV from the conduction-band minimum of the matrix.

In conclusion we have presented a theory of the yield of the S-1 photocathode which for the first time is consistent with the observed experimental data. The structure of this surface consists of silver particles distributed throughout a matrix of Cs_2O with a thin layer of $Cs_{11}O_3$ on its surface. The $Cs_{11}O_3$ lowers the electron affinity at the surface so that the S-1 is a negative electron affinity surface. This accounts for the threshold of $\simeq 1.2$ μm. The peak in the yield in the visible

and near infrared is due to resonance absorption in the silver particles. A solid continuous specular film of silver reflects most of the light incident on it in the visible and hence has a low quantum yield. Another factor is that most of the silver particles are smaller than the electron scattering length and hence the escape probability of photoelectrons from small particles is higher than from a semi-infinite solid. The resonance absorption, however, appears to be the dominant enhancement mechanism.[17]

Discussions with Dr. A. H. Sommer on the S-1 photocathode have been extremely valuable.

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Proximity-Effect Tunneling in Pd-Pb Sandwiches

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Tunneling characteristics of junctions of the form AlO_x-Pd-Pb are reported. From the thickness dependences of T_c and the induced gaps we find that the total BCS interaction (NV) in Pd is 0 ± 0.05. We find a Fermi velocity of $\sim 0.2 \times 10^8$ cm/sec indicating that the narrow d-band electrons dominate our measurements. Pd phonon structure is not resolved, setting an upper limit of $\lambda \lesssim 0.2$ for the effective electron-phonon interaction. These results indicate that paramagnon effects are substantially less important for superconductivity than was previously envisioned.

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Palladium is a nearly ferromagnetic metal with a strongly exchange-enhanced susceptibility.[1] This has led several authors to suggest that long-lived spin fluctuations (paramagnons) play a fundamental role in preventing Pd from becoming superconducting.[2] Recently interest has grown in related T_c reductions in Nb and V,[3,4] in the possibility of superconductivity in Pd-Ag alloys,[5] and in the possibility of triplet superconductivity in exchange-enhanced metals.[6]

In this Letter we report on a series of proximity-effect studies aimed at evaluating the total effective electron-electron interaction and its electron-phonon component (λ) in pure Pd. Previous studies of induced superconductivity in noble metals have measured NV[7,8] (the BCS coupling parameter, i.e., the density of states at the Fermi energy times the effective electron-electron interaction) from the pair amplitude and energy gap as a function of normal and superconducting met-