Photoemission from Metallic Cesium Oxide Films

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Ultraviolet photoelectron spectra of Cs evaporated onto Ag and oxidized under ultrahigh-vacuum conditions have been measured. Time variation of the spectra indicates the formation of Cs suboxides (e.g., Cs_7O, $Cs_{11}O_3$). The high infrared photoelectric yield of Ag/O/Cs cathodes can be explained as due to the excitattion of surface plasmons in these compounds.

The infrared sensitivity of Ag/O/Cs photocathodes has been interpreted in terms of different mechanisms, such as defects in the lattice of Cs_2O formed during the production process of Ag/O/Cs cathodes,[1,2] as well as photoemission from silver.[3,4] All of these interpretations generally link the photoemission in the infrared region to the low work function of one of the cesium oxides.[5] Cathodes with an excess of cesium (compared to Cs_2O) show the highest infrared yield. Composition and thickness of the Ag/O/Cs layers as well as the electron emission process are still a matter of dispute. Bulk samples of metal-rich cesium oxides (suboxides, e.g., Cs_7O, $Cs_{11}O_3$) have recently been investigated by ultraviolet photoelectron spectroscopy (UPS).[6] It has been shown that the spectra reflect compositions and crystal structures of the bulk compounds.[6]

We report here UPS measurements of thin films of cesium deposited on a silver substrate and oxidized under ultrahigh-vacuum (UHV) conditions, simulating the active layers in Ag/O/Cs (S-1) photocathodes. The spectral response of films prepared in this way is similar to S-1 cathodes according to Heimann *et al.*[7] The UPS data of these films are almost identical to those of the bulk cesium suboxides.[6] A comparison with bulk data yields information about the composition of the films, the layer thickness, and the low-energy photoelectron emission process.

The measurements were performed at room temperature in a Leybold-Heraeus LHS 10 ESCA system equipped with a preparation chamber and a differentially pumped cold-cathode gas-discharge lamp using the He I resonance line ($h\nu = 21.2$ eV). The residual gas pressure in the analyzer chamber was 2×10^{-10} Torr. Evaporated silver served as a substrate and was etched by argon-ion bombardment. The photoelectron energy distribution curve of this sample is shown in Fig. 1(a). The energy scale is relative to the Fermi edge; the resolution is 0.1 eV. The photoelectron spectrum of Cs evaporated for 3 min at 390 K onto the Ag substrate at room temperature is shown in Fig. 1(b). Oxygen was leaked into the analyzer chamber (basic pressure $p = 2\times 10^{-10}$ Torr) at a partial pressure of 5×10^{-7} Torr for

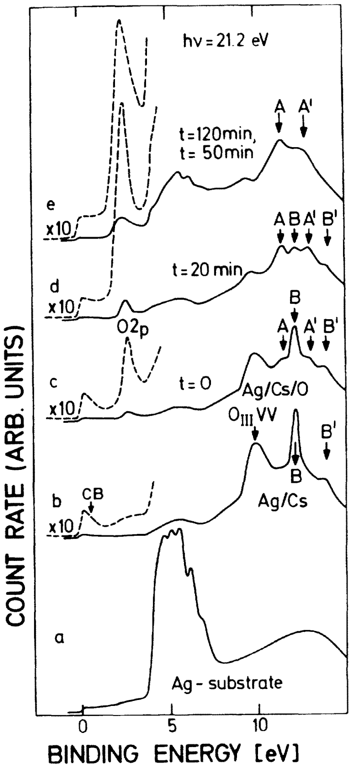

FIG. 1. Photoelectron energy distribution curves for silver, a cesium layer on silver, and reaction products with oxygen.

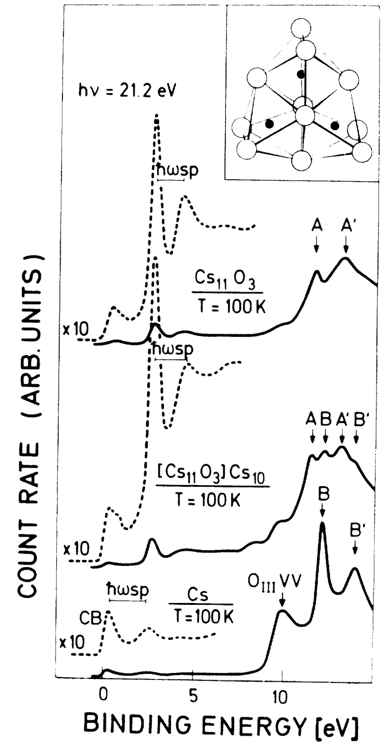

FIG. 2. Photoelectron spectra from Cs and the cesium suboxides Cs_7O and $Cs_{11}O_3$ (see also Ref. 11). The inset shows a $Cs_{11}O_3$ cluster.

20 sec, corresponding to an oxygen exposure of 10 L (1 L = 10^{-6} Torr sec). The spectrum recorded immediately after this procedure is given in Fig. 1(c). When the sample was left in the analyzer chamber ($p_{He} \approx 1\times 10^{-7}$ Torr during measurements; 99.999+% purity of He), the measured spectrum changed continuously and reached a final form after 50 min [Figs. 1(d), 1(e)].

Structure due to photoemission from the $4d$ bands of the Ag substrate[8,9] (in the energy range 4 to 7.5 eV) is observed in all of the spectra. This fact indicates a film thickness of less than 10 Å, as deduced from the short mean free path of electrons in Cs.[10] In the oxidized samples, photoemission from the $4d$ bands of the substrate increases with time, suggesting either a reduction of the layer thickness, island formation within the oxide layer, or both.

The spectrum 1(b), recorded from the evaporated Cs film, is equivalent to that of pure bulk[6] Cs in Fig. 2.[11] The structures of the two spectra show the filled conduction band (CB) of Cs followed by an energy loss ($\hbar\omega_{sp}$), an Auger transition (O_{III} VV) and the spin-orbit split $Cs\,5p$ levels (B, B'). The addition of oxygen leads to three new peaks (O $2p$, A, A'). These significant changes correspond definitely to cesium suboxide formation. Peaks A and A' strongly increase with time, accompanied by a decrease of the intensities of B and B'.

Cesium suboxides contain characteristic ion clusters of composition $Cs_{11}O_3$ shown in the inset of Fig. 2.[12] In the stoichiometric compound $Cs_{11}O_3$,[13] which is stable at room temperature, these clusters are close-packed.[14] The compound $Cs_7O \equiv [Cs_{11}O_3]Cs_{10}$ consists of $Cs_{11}O_3$ clusters intercalated with a stoichiometric amount of cesium.[15] If a melt of Cs_7O is kept in vacuum at room temperature, Cs evaporates, leading to crystallization of $Cs_{11}O_3$.[6] Cs_7O contains Cs atoms in two different bonding states.[12] Those in the clusters are partly ionic; the others are purely metallic. Consequently, two pairs of Cs $5p$ levels appear in the UPS spectra. Peaks A and A' in Fig. 2 correspond to the $5p$ levels of Cs incorporated in the $Cs_{11}O_3$ cluster, where B and B' refer to the intercalated cesium. In the spectrum of the compound $Cs_{11}O_3$, only the peaks A and A' are observed. The very sharp structure at 2.7 eV is due to photoemission from the nonbonding O $2p$ levels.[6] This characteristic peak was already observed by Gregory *et al.*[16] who interpreted it in terms of "oxygen atoms dissolved in the cesium metal" without considering the formation of metallic suboxides.

The appearance of the structures O $2p$, A and A' in Fig. 1(c) (Ag/Cs/O) indicates that the oxygen exposure is followed by the formation of some $Cs_{11}O_3$ clusters in the films. From the relative intensities of peaks A and B it can be concluded that Cs is still present in large excess to the clusters. The photoelectron spectrum taken after 20 min indicates a composition of the film which corresponds approximately to the stoichiometry of Cs_7O [Fig. 1(d)]. This change is due to the continuous loss of cesium. Further loss of Cs causes peaks B and B' to disappear. The remaining Cs $5p$ levels A and A' indicate that the film is composed mainly of $Cs_{11}O_3$ clusters. The filled conduction band (CB) as well as the very sharp O $2p$ peak, characteristic of all compounds containing the $Cs_{11}O_3$ clusters, definitely exclude the formation of (semiconducting) Cs_2O which shows only one broad valence band.[16,17] The observation of the characteristic O $2p$ peak in the photoelectron spectrum of an Ag-Cs_2O-Cs photocathode by Neil and Mee[18] is further evidence for suboxide formation in S-1 photocathodes.

All Cs suboxides are metallic. Plasma frequen-

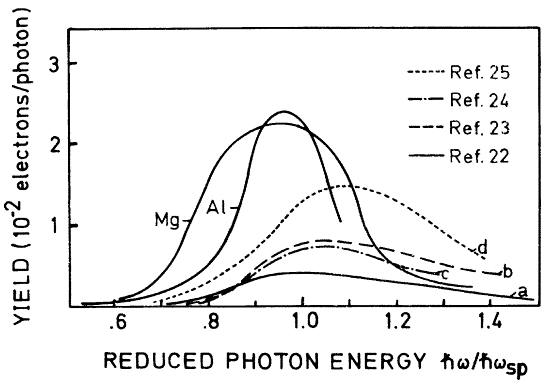

FIG. 3. Quantum yield of Mg and Al, normalized to their surface-plasmon energies, and comparison to the S-1 quantum yield, which is normalized to the surface-plasmon energy of $Cs_{11}O_3$ ($\hbar\omega_{sp}=1.55$ eV). The data were taken from Ref. 21 (Mg, Al) and Refs. 22–25 (S-1).

cies can easily be deduced from the energy-loss structures in the UPS spectra. With HeI radiation ($h\nu=21.2$ eV) as an excitation source, we observe surface-plasmon losses (see $\hbar\omega_{sp}$ in Fig. 2). With HeII radiation ($h\nu=40.8$ eV), both surface- and volume-plasmon energy losses could be separated. The decrease of the surface-plasmon energy of the Cs suboxides with respect to bulk Cs is caused by a lower electron concentration as discussed in detail in Ref. 6. The observed plasmon energies are 2.0, 1.75, and 1.55 eV for Cs, Cs_7O, and $Cs_{11}O_3$, respectively.

Surface-plasmon decay[19] has been used to explain photoemission from free-electron-like metals, e.g., Li and Na,[20] Mg, and Al, as well as from (Cs/O)-activated Ag.[21] If the photoelectric-yield curves[21] of Mg and Al are plotted versus excitation energy normalized to $\hbar\omega_{sp}$ (7.7 eV for Mg and 10.5 eV for Al), the yield maxima are found near unity in the reduced energy scale (Fig. 3). Similarly, the spectral responses of some commercial S-1 cathodes[22-25] are plotted (curves a–d in Fig. 3). The energy scale is reduced to the $\hbar\omega_{sp}$ of $Cs_{11}O_3$ (1.55 eV), since $Cs_{11}O_3$ clusters have here been proved to be the main constituent in the active layers of such cathodes. From the positions of the maxima in Fig. 3 we conclude that surface-plasmon-induced photoemission from metallic cesium-suboxide layers (especially $Cs_{11}O_3$) is the origin of the infrared sensitivity of S-1 photocathodes.

The present results are confined to Ag/Cs/O layers. Further investigations on all bulk cesium oxides and their chemical reaction with the substrate materials are necessary to understand the completely different UPS spectra of oxidized cesium layers on III-V (e.g., GaAs) substrates.[17,26]

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SPIN-FLIP RAMAN ECHO IN *n*-TYPE CdS. P. Hu, S. Geschwind, and T. M. Jedju [Phys. Rev. Lett. 37, 1357 (1976)].

The wavelength ω_L on Fig. 1(b) should read "$\omega_L \sim 4905.26$ Å." On page 1358, column 1, the seventeenth line from the bottom should read "...two longitudinal modes ω_L and ω_R, where $(\omega_L - \omega_R)/2\pi = 32$ GHz."

EXACT SOLUTION FOR THE INFLUENCE OF LASER TEMPORAL FLUCTUATIONS ON RESONANCE FLUORESCENCE. G. S. Agarwal [Phys. Rev. Lett. 37, 1383 (1976)].

In the process of printing Ref. 6 was changed. This reference should read as follows: J. H. Eberly, in Proceedings of the Symposium on Resonant Light Scattering, Massachusetts Institute of Technology, Cambridge, Massachusetts, April 1976 (to be published).