INTERACTION OF CESIUM AND OXYGEN ON W(110) [†] II. Codeposition: cesium oxide formation

C.A. PAPAGEORGOPOULOS * and J.-L. DESPLAT **

Stanford/NASA Ames Joint Institute for Surface and Microstructural Research, NASA-Ames, Moffett Field, California 94035, USA

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The codeposition of cesium and oxygen on W(110) has been studied by work function measurements, Auger electron and energy loss spectroscopies and thermal desorption. Thick layers of cesium oxide are grown on the substrate and their properties depend on which of the two constituents is in excess in the incident fluxes. With an excess of cesium, work functions between 0.9 and 1 eV are obtained for thicknesses around 30 Å, and the main cesiated desorption product is Cs_2O which has a desorption energy of 1.2 eV. We propose that Cs_2O is grown on the surface and that it does not include a large amount of Cs doping. With an excess of oxygen, it is suggested that part of it is imbedded in the Cs_2O matrix. A reaction with the substrate occurs below 900 K, leading to the formation of a ternary compound, possibly a cesium tungsten bronze.

1. Introduction

In a previous publication [1], we have shown that work functions around 1 eV could be obtained by adsorbing Cs on a particular oxygen structure formed on W(110). This "2D-oxide" structure is stable up to 1250 K: in a thermionic converter, such a surface could be used as a collector (maximum temperature ~ 800 K) without a permanent oxygen supply.

On the other hand, earlier studies have shown that cesium oxide layers on semiconductors can lead to work functions as low as 0.8 eV [2]. Work functions below 1 eV have been measured, by thermionic emission, on W(100) with steady cesium and oxygen fluxes [3], but these experiments lacked the informations provided by complementary analytical techniques and the nature of the emitting surface was not established. The purpose of the present work is to study the compounds formed during cesium and oxygen codeposition and to determine their thermal stability.

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^{*} Permanent address: Department of Physics, University of Ioannina, Ioannina, Greece.

^{**} Rasor Associates, Inc., 253 Humboldt Court, Sunnyvale, California 94086, USA.

2. Experimental

The experimental setup has been described in a preceding publication [1]. The technique used in this work is to expose the W(110) sample to steady cesium and oxygen fluxes for a given amount of time, and then to study the characteristics of the resulting surface. The opening and closing of the oxygen leak valve are fast enough not to introduce significant transients, as seen on the residual gas analyzer (the Bayart-Alpert gauge reading usually exhibits a tail at the closing).

The substrate used in this work is the same W(110) sample used previously. Its particular orientation is not important here, and it acts merely as a support on which thick layers are formed by codeposition, as will be seen later.

2.1. Escape depths in cesium and cesium-oxygen layers

To determine thicknesses we used the peak-to-peak heights in the derivative mode of the W Auger signals appearing at ~170 eV and ~1730 eV. The only unknown quantities are the inelastic mean free paths (imfp) λ at those energies in the material grown on top of the substrate. It is fairly easy to determine the ratio $\lambda(1730 \text{ eV})/\lambda(170 \text{ eV})$: in a succession of experiments we found that this ratio is the same (3.1 ± 0.1) for pure Cs layers and for the thick layers formed by codeposition of Cs and oxygen. Unfortunately no data exist for $\lambda(170 \text{ eV})$ in Cs, although a lower limit is given by Thomas and Haas [4]. They clearly indicate that a 6.7 Å Cs layer attenuates the W-170 eV, measured in the derivative mode with a CMA, by only 46%. This attenuation is far too small to correspond to an imfp of 6.7 Å, inaccurately reported [5] as "measured" by Thomas and Haas.

Our measurements show that at completion of the first Cs layer on W(110), W-170 is attenuated by 38%. Fedorus and Naumovets [6] determined that the closest approach between Cs atoms, at saturation of the hexagonal closed packed structure of Cs on W(110), is 4.7 Å. This gives an estimate of the effective diameter of a Cs atom in the first layer. If we assume that the Cs layer has a thickness equal to that diameter, applying Seah's formulation for a CMA [7] gives $\lambda(170 \text{ eV}) \sim 13$ Å, which lies above the cloud of experimental values in other materials. On the other hand, if we introduce an effective thickness d_{eff} such that the atomic volume density of the HCP array of hard Cs spheres (radius R) is equalled to that of a uniform slab, then $d_{eff} = R 2\pi/3\sqrt{3}$, which brings $\lambda(170 \text{ eV}) \sim 8$ Å. In view of the approximations involved in these two different approaches, we chose a mean term, i.e.

 $\lambda(170 \text{ eV}) \sim 10 \text{ Å}$ and $\lambda(1730 \text{ eV}) \sim 30 \text{ Å}$.

2.2. Estimation of the quadrupole mass spectrometer mass discrimination

In order to compare quantitatively desorption spectra of different species, one has to evaluate the sensitivity of the mass spectrometer as a function of the mass number m/e. This sensitivity can be expressed as [8]

 $S = \sigma \tau G$,

where σ is the ionization cross section of the species to be detected, τ is the transmission efficiency and G is the secondary electron coefficient of the first dynode of the electron multiplier. Each of these factors depends on the species and its related ions.

In the present study, we want to determine the sensitivity for Cs_2O -282 compared to Cs-133. (As will be seen later, Cs and Cs₂O are the main cesiated desorption products.)

The ionization cross-section ratio $\sigma(282)/\sigma(133)$ is estimated to be 1.9 from the linear plot of Flaim and Ownby [9]. The product τG is then determined for our quadrupole according to the following procedure. A vapor, perfluorotributylamine $C_{12}F_{27}N$, is leaked into the system and peak areas of fragmentation products at m/e = 281 and 131 are compared to a standard spectrum of the same substance [10]. The standard spectrum was obtained at the same ionization energy in a magnetic deflection mass spectrometer where the magnetic field is scanned (this technique introduces little or no mass discrimination in the ion transmission [11], and the ion current is received on a collector).

Assuming that τG depends primarily on m/e and not on the chemical nature of the ion, the ratio $\tau G(133)/\tau G(282)$ is about 18 and the final sensitivity ratio S(282)/S(133) is close to 0.1.

3. Results

3.1. Work function measurements

Work function plots versus exposure time to both cesium and oxygen sources are shown in fig. 1. They were obtained for one cesium flux μ_{Cs} and 3 different oxygen pressure P_{O_2} , with the sample at room temperature. During these experiments the sample was facing the cesium Knudsen cell, and no attempt was made to estimate the oxygen pressure in the immediate vicinity of the sample. The reported P_{O_2} are the uncorrected BA gauge readings.

The evolution of the work function with the coexposure changes widely when P_{O_2} is varied: at 5×10^{-8} Torr a nearly constant value close to 2 eV is reached, while at pressures 3 and 10 times smaller, flat minima smaller than or close to 1 eV are obtained. It is not possible to find a time conversion factor (according to the various P_{O_2}) which would reconcile the data. Therefore it appears that for a given μ_{Cs} the properties of the surface depend upon the oxygen pressure used. With the previously mentioned uncertainty about the real value of P_{O_2} , the atomic oxygen flux at room temperature incident onto the sample is

 $\mu_0 = 7.2 \times 10^{20} P_{O_2}(\text{Torr})$ in atoms cm⁻² s⁻¹.



Fig. 1. Evolution of the work function during simultaneous exposure to cesium and oxygen fluxes. The cesium flux was kept constant and the oxygen pressure was varied as indicated. The effect of additional Cs exposure on the work function is also shown after codeposition at the highest oxygen pressure.

Then the ratio $\mu_{\rm Cs}/\mu_0$ of atomic fluxes varies from 5 to 0.5 for the highest $P_{\rm O_2}$ used: we will call this last case oxygen-rich as opposed to cesium-rich for the two other oxygen pressures.

In the oxygen-rich case, when a 2 eV work function is reached (point A on curve 3 of fig. 1), an additional exposure to cesium alone lowers the work function below 1 eV (point B): this will be discussed later after acquiring complementary informations from AES and TDS.

3.2. Auger electron spectroscopy and energy loss spectroscopy

3.2.1. Auger signal amplitudes

W-1730, O-510 and Cs-560 Auger signals are plotted against exposure in figs. 2a



Fig. 2. Variation of W, O and Cs Auger signals with exposure to cesium and oxygen: (a) same conditions as for the work function plot 2 in fig. 1; (b) same conditions as for plot 3 in fig. 1.

and 2b for $P_{O_2} = 1.5$ and 5×10^{-8} Torr respectively. As the substrate signal decreases steadily with the coexposure, it can be concluded that a thick compound is grown on the substrate, which involves only cesium and oxygen. In the oxygenrich situation (fig. 2b), exposure of the thick layer (~64 Å) formed after 10 min of codeposition to additional Cs alone does not substantially affect the oxygen and cesium Auger signals, while the work function drops below 1 eV (curve 3 of fig. 1): the dramatic change in the electronic structure is not reflected in a substantial change in the chemical composition as detected within the escape depth around 500 eV.

3.2.2. Oxygen Auger peak shape

During the growth of the cesium-oxygen compound, the oxygen KLL Auger spectrum undergoes a profound change in shape as shown in the derivative mode in fig. 3a, the main oxygen peak being also shifted upward by 3.2 eV when compared to oxygen chemisorbed on W(110).

3.2.3. Electron energy loss spectra

Corresponding energy loss spectra are shown in fig. 3b. Although a full interpretation of loss spectra is quite beyond the scope of this paper as it requires the knowledge of the loss function, a comparison of some losses with reported electronic binding energies (referred to the Fermi level) suggests that these losses correspond to electronic transitions between core levels and the Fermi level. Losses between 10 and 15 eV have been associated with Cs 5p levels, and the loss near 26



Fig. 3. Evolution of (a) the oxygen KLL Auger spectrum, and (b) the energy loss spectrum with exposure to cesium and oxygen. Experimental conditions as indicated.

eV to Cs 5s levels [12]. The growth of the thick cesium—oxygen compound introduces two prominent losses at 4.8 and 7.8 eV which cannot be matched with Cs core levels: we propose to associate them with O 2p levels and/or interband transitions in the Cs—O compound. As will be seen later, loss spectra can be used qualitatively as fingerprints of chemical compounds.

Comparing the work function curve 2 of fig. 1, with the oxygen KLL peak shapes and loss spectra (all obtained under the same conditions) it is interesting to note that the changes occurring in figs. 3a and 3b are all completed when the work function reaches its very flat minimum around 0.9 eV for an estimated thickness of 18 Å. Beyond, very little change takes place, although the thickness is increasing.

If the Cs–O compound is grown under oxygen-rich conditions, the evolution of the oxygen KLL spectrum is not fully achieved. The small peak at \sim 508 eV is not present and the ultimate shape is that of an intermediate stage such as the one obtained after 4 min of codeposition under cesium-rich conditions (fig. 3a). The energy loss spectrum exhibits losses at 4.1 and 8.1 eV. Addition of extra cesium brings back the oxygen peak shape and losses obtained under cesium-rich conditions.

3.3. Thermal desorption spectroscopy

The significant cesiated desorption products are Cs and Cs₂O, (up to m/e = 500, limit of our mass spectrometer), even when the Cs–O compound is grown under oxygen-rich conditions. Very small amounts of Cs₂ and CsO are observed, likely to be fragmentation products from Cs₂O. No suboxide Cs₃O is detected in the cesium-rich case. In the oxygen-rich case, reducing the electron energy in the ionizer from 75 to 15 eV, which reduces the fragmentation probability and makes the parent molecule more readily observable, failed to reveal any superoxide CsO₂ or peroxide Cs₂O₂.

3.3.1. Cesium-rich case

Figs. 4a and 4b show flash desorption spectra for Cs and Cs₂O respectively after a codeposition under cesium-rich conditions (the corresponding work function plot versus exposure is curve 2 of fig. 1). The two sets of desorption spectra were recorded using the same electrometer sensitivity, and no correction was applied to the vertical scale on fig. 4b.

After 3 min of codeposition (estimated thickness 12 Å), the Cs desorption spectrum is dominated by a large low temperature peak (desorption energy 0.91 eV) already seen in Cs desorption from oxygenated W(110) [1] and no Cs₂O is yet desorbed.

After higher exposures this low temperature peak is replaced by a peak near 700 K and Cs_2O desorption occurs at the same temperature. As an atomic oxygen desorption peak is also observed at that temperature, it seems likely that at least part of the Cs signal observed at ~700 K comes from fragmentation of Cs₂O in the



ionizer of the mass spectrometer. It is not possible to estimate the magnitude of this effect however, as the corresponding cross section is not known.

A second Cs desorption peak is observed at ~1060 K. In a previous publication [1], a similar peak was reported at the same temperature, associated with the decomposition of a Cs-O-W compound formed by cesiation of thick tungsten oxide layers, which we tentatively described as a bronze $Cs_{0.3}WO_3$. A comparison of energy loss spectra from this "bronze" and from the surface obtained after annealing at 900 K a cesium oxide layer deposited on W(110) shows that they are nearly identical (fig. 5). This provides a strong evidence that, during the flashing, part of the cesium oxide is not desorbed and reacts with the substrate below 900 K to form a ternary compound.

The ascending edge of the Cs₂O desorption peak does not depend on the amount of material, and can be fitted reasonably well with a simple exponential law, indicating a zero-order desorption process. The corresponding desorption/sublimation energy is 1.2 ± 0.1 eV.

Using the mass spectrometer sensitivity ratio determined earlier, the amount of



Fig. 5. Comparison of energy loss spectra obtained after cesiation of a thick (~600 Å) layer of WO_2 , and after annealing at 900 K a ~60 Å Cs_2O layer on W(110).



Fig. 6. Comparison of the amount of cesium desorbed as Cs and as Cs_2O after a codeposition under the indicated conditions.



Fig. 7. Effect of an additional Cs exposure on (a) the Cs desorption spectrum and (b) the Cs_2O desorption spectrum following a codeposition under oxygen-rich conditions. Points A and B are identified on curve 3 of fig. 1.

Cs desorbed as Cs_2O is 2 × 10 times the integrated area of Cs_2O desorption spectra. As it appears in fig. 6, much more Cs is desorbed as Cs_2O than as atomic Cs, for initial doses which give work functions below 1 eV. In fact as part of the Cs spectrum is artificially produced by fragmentation of Cs_2O , the real ratio of the amount of Cs desorbed as Cs_2O to the amount of desorbed atomic Cs is certainly larger than the experimental one which is 4 as deducted from fig. 6. We realize that the conclusion that Cs_2O is the main desorption product in this case is based on the sensitivity determination explained in section 2.2. In order to reverse this conclusion, we would have to admit a systematic error by a factor larger than 4, which seems unlikely.

3.3.2. Oxygen-rich case and the effect of additional Cs

When a Cs–O compound is grown on the substrate under oxygen-rich conditions (point A of curve 3 in fig. 1, work fuction ~2 eV), the desorption spectrum of atomic Cs (fig. 7a) is very different from a cesium-rich one, with the prominent peak being now around 1060 K. Additional cesiation bringing down the work function to ~0.9 eV (point B in fig. 1) induces a dramatic change in the Cs desorption spectrum related to a very large increase in the amount of Cs₂O desorbed (fig. 7b). After the additional cesiation, the Cs desorption spectrum is similar to spectra obtained under cesium-rich conditions.

4. Discussion

From the results of work function measurements and thermal desorption spectroscopy, it appears that the chemical nature of the Cs–O compound grown on the substrate depends on which of the two fluxes is predominant. Little difference is detected by AES in the respective amplitudes of O and Cs signals from layers grown under cesium or oxygen-rich conditions, although the substantial difference in the O peak shape in the derivative mode between the two cases probably makes the use of the peak to peak height unreliable as a measure of the O concentration. The use of thermal desorption can also be questioned whether it can reflect the chemical composition prior to the desorption itself.

4.1. Formation of Cs₂O in the Cs-rich case

It is very tempting to associate the very low work functions and the appearance of Cs_2O as the main cesiated desorption product, in the Cs-rich case, but the possibility that Cs_2O is formed during the heating has to be examined.

The formation of Cs_2O from its constituents in the gas phase is an exothermic reaction (76 kcal mole⁻¹) and should not therefore require any heating. Oxidation of bulk Cs occurs readily below 140 K [13], where the rate limiting process seems to be the diffusion of O in the bulk to form one or several oxides. In our experi-

ment, the two constituents are supplied at the surface of the layer already grown, where the reaction can take place without involving any diffusion, and therefore any activation energy.

The work functions obtained at room temperature under Cs-rich conditions (~0.9 eV) also favor the assumption that Cs₂O already exists at that temperature, possibly with some extra Cs acting as a dopant. Work functions as low as 1.05 eV on Ni have been masured after decomposition of Cs₂CO₃ mainly into Cs₂O, according to Briere and Sommer [14]. Suboxides such as Cs₇O and Cs₁₁O₃ are reported to have work functions of 1.75 and 1.35 eV respectively (from Simon and Ebbinghaus, cited in ref. [15]), so to bring the work function further down, one would have to consider oxides with a higher oxygen content. But there are no work function data available and it is unfortunate that the stoichiometry of the oxide, formed during oxidation of bulk cesium, which had a work function around 0.7 eV, could not be determined in the experiments performed by Gregory et al. [13]. As assumed in ref. [15], it is very tempting to associate the cusp at 0.7 eV in their work function versus oxygen exposure plot with the completion of the Cs₂O stage thoughout the sample.

The extreme sensitivity of the low work function to a small exposure to additional oxygen stronly suggests that the amount of extra Cs embedded in the Cs–O compound grown under Cs-rich conditions, and responsible for the low work function, is quite small. If a large amount had been present, we would have expected the additional oxygen to diffuse in the layer and react with Cs as in ref. [13], leaving the work function unchanged or decreasing it. The cesium desorbed before the onset of the Cs₂O desorption at 550 K (see figs. 4a,b) could correspond to this extra Cs; its amount does not change as the thickness of the Cs–O layer increases.

In the case where the layer is grown under Cs-rich conditions, we then tentatively conclude that a cesium oxide having a stoichiometry close to the monoxide Cs_2O is formed.

4.2. Oxygen-rich case and the effect of additional cesium

When the Cs–O compound is grown under oxygen-rich conditions, we still observe Cs₂O in the desorption products, but no Cs₂O₂ or CsO₂ are detected at levels 10^3 times smaller than the Cs₂O peak. Comparing the amount of Cs and Cs₂O desorbed for a given exposure (10 min) for two oxygen pressures (1.5 and 5×10^{-8} Torr), although the amount of desorbed Cs is 2.5 larger for the higher oxygen pressure, the amount of desorbed Cs₂O is virtually the same. The amount of combined Cs being larger (and the layer thicker), the absence of oxygen rich oxides in the desorption products seems puzzling. CsO₂ by heating is transformed into Cs₂O₂ [17] which should then be observed. Based on the fact that most of the Cs in the oxygen-rich case, is desorbed at 1060 K (see fig. 7a), we suggest that Cs₂O₂ eventually formed in this case reacts with the tungsten substrate during the flashing, forms a bronze which subsequently is decomposed.

When additional Cs is added to the oxygen rich oxide all the properties revert to those obtained in the cesium rich case (which we associate with Cs₂O). We can rule out a pure surface effect, like adsorption of an extra Cs layer, as a possible mechanism, because of the large increase in desorbed Cs₂O which involves the equivalent of several tens of Cs layers. It appears therefore that the added Cs is included in the thick layer previously grown and that it reacted with oxygen to form Cs₂O. No reaction of this kind is reported in the rather sketchy literature dealing with the chemical properties of the different cesium oxides.

5. Conclusions

Cesium oxide layers were grown by exposing a W(110) substrate to cesium and oxygen fluxes at the same time, in order to study the possibility of reaching very low work functions in thermionic converters.

When the ratio of the incident cesium flux over the incident atomic oxygen flux is larger than 2, the composition of the grown oxide does not appear to lie very far from the ideal monoxide Cs_2O . Work functions between 0.9 and 1 eV can be obtained for thicknesses around 30 Å. Desorption of Cs_2O begins to be significant above 550 K and its desorption energy is 1.2 ± 0.1 eV.

When there is an excess of oxygen in the incident fluxes, the oxide is richer in oxygen than Cs_2O and the work function is much higher. The extra oxygen can eventually react with additional cesium, bringing back very low work functions. No evidence of the existence of the peroxide Cs_2O_2 has been found, although it is suggested that this is due to a reaction near 900 K with the W substrate to form a ternary compound, such as a bronze.

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