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Oxidation of Cs_2Te with superficial Te clusters studied by XPS

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The oxidation of alkali-metal (Cs, K) tellurides at room temperature and low oxygen pressure has been studied by X-ray photoelectron and Auger electron spectroscopies (XPS, XAES). The oxidation kinetics is faster than logarithmic and does not saturate for the exposures studied, while a migration of alkali ions to the surface is detected. These effects are strongly enhanced in a sample of overcaesiated telluride with elemental Te clusters on the surface. A strong gradient of the oxidation state (Te^{2-}, Te^0, Te^{4+}, Te^{6+}) is formed in a depth of the order of the XPS analysis depth. The oxygen concentration shows a similar gradient. Cs_2O_2 is formed too. The surface layer remains as Cs_2Te; the Te clusters also remain unreactive at the surface; they only transform into telluride when heavy oxidation of the Cs_2Te film is reached.

1. Introduction

Cesium telluride Cs_2Te is of significant technological interest as photocathode material in the near-UV range [1]; besides, the oxidation of metals and semiconductors promoted by alkali metals and oxides is also a field of recent interest [2–4].

In a previous work [5] we reported X-ray photoelectron and Auger electron spectroscopy (XPS and XAES) studies of the formation process of a Cs_2Te photocathode. Cs_2Te is an essentially ionic compound that is stable with a large excess of Cs in a near-surface region. From semimetallic Te with surface adsorbed Cs (no telluride bonds) to Cs_2Te, the Cs–Te relative chemical shift increases by 1.7 eV while the Te Auger parameter decreases by 3.1 eV. The Cs excess cannot be compensated by Te evaporation on the photocathode; very stable small clusters of elemental Te seem to be formed instead. In this work [5], a quantitative XPS method, taking into account spectra taken at 0° and 30° emission angle, allowed us to determine the Te clusters coverage to be 0.4 ML. These Te clusters allowed further caesiation of the photocathode without reacting with the Cs vapor. They were characterized by their Cs–Te relative chemical shift and Auger parameter.

In this work we present XPS/XAES studies of the reaction of the $Te^0/Cs_{2.6}Te$ surface with oxygen at low pressures and room temperature. It has been found that Te^{2-} is easily oxidized to Te^{6+} in contrast with the no oxidation of pure semimetallic Te.

2. Experimental

The XPS spectrometer was a commercial ESCA LH 10 (Leybold Hereaus) with non-monochromatic Mg Kα source [5]. Spectra taken by tilting the sample allow one to detect atomic concentration gradients near the surface. In these conditions, the escape depth of photoelectrons decreases with the emission angle.

Saturated cesium telluride with composition $Cs_{2.6}Te$ was prepared by reaction of a thin Te film with Cs vapor [5]. After the formation of the cesium telluride with Cs excess, Te was evaporated again onto the surface with an equivalent coverage of ~ 0.4 monolayers (ML) forming clusters of elemental Te [5]. A potassium telluride was also formed; however, Cs contamination from the walls of the preparation chamber was detected mainly at the surface, giving a composition: $K_{1.6}Cs_{0.6}Te$.

Oxidation of the tellurides was performed at room temperature in the preparation chamber by means of a leak valve using high purity oxygen. The oxygen pressure was 5×10^{8} Torr for exposures lower than 300 L. For larger exposures up to 10^{4} L, the oxygen pressure was varied between 1×10^{-7} and 5×10^{-6} Torr. After each oxidation, the samples were transferred to the analysis chamber in order to perform XPS and XAES measurements.

In order to compare the oxidation kinetics, an evaporated Te semimetal thin film was exposed to oxygen at room temperature up to 1000 L ($P_{O_2} = 5 \times 10^{-6}$ Torr). The same experiment was repeated at 200 °C. In both cases, no oxide formation was detected.

3. Results and discussion

Fig. 1 shows experimental spectra of the Te 3d and O 1s core levels corresponding to the $Cs_{2.6}Te$ sample, covered with Te clusters with an equivalent coverage of 0.4 ML, after an exposure to oxygen of 350 L. These spectra have been taken at 0 ° (a), 30 ° (b) and 40 ° (c) emission angle. Te 3d spectrum (a), at normal emission shows one $3d_{5/2}$ peak at $E_B = 572.51$ eV corresponding to Cs_2Te (Te^{2-}), with a shoulder, corresponding to a peak at $E_B = 674.09$ eV, due to Te clusters (Te^0) [5]. Apart from these two peaks, a larger one appears at $E_B = 577.20$ eV, assigned to TeO_3 (Te^{6+}), in good agreement with reported values [6]. With respect to the O 1s core level, the spectrum shows a peak centered at 531.65 eV with a weak asymmetry at lower binding energies. In comparing these spectra with those obtained at 30 ° and 40 ° emission angles (b, c), it can be seen that the peaks corresponding to TeO_3 and O decrease strongly. These results indicate that TeO_3 has grown in the bulk and is not present in a near-surface region of the order of the XPS analysis depth.

In order to obtain more precise information, lineshape and quantitative analysis were performed following a method described elsewhere

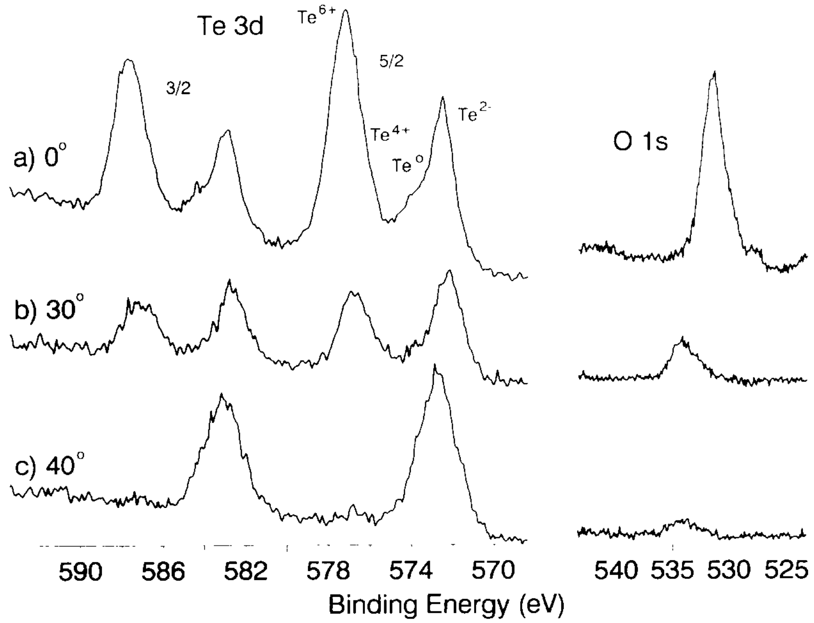

Fig. 1. Experimental XPS Te 3d and O 1s core level spectra of a $Cs_{2.6}Te$ sample with Te^0 clusters at the surface after exposure to 350 L O_2, taken at different emission angles: (a) 0 °, (b) 30 ° and (c) 40 °. Mg Kα satellites have been substracted. Energies are referred to the Fermi level.

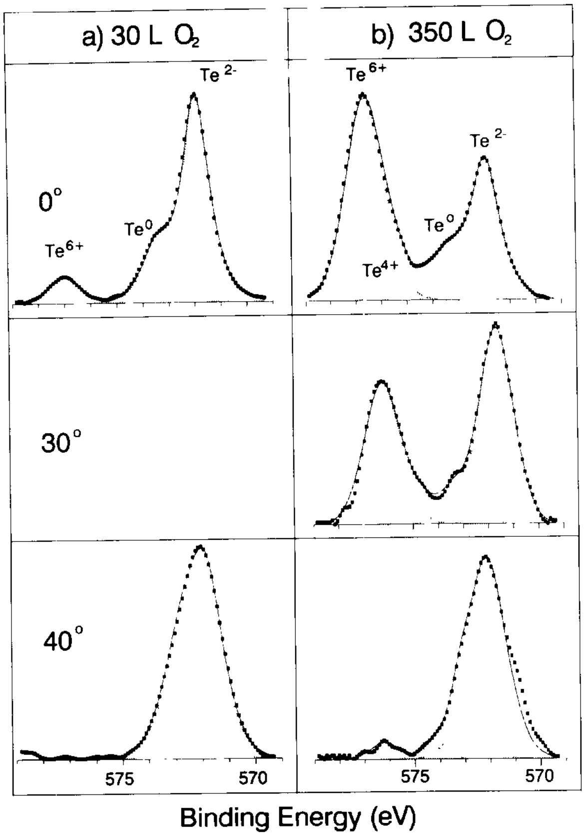

Fig. 2. Fitting of the XPS Te $3d_{5/2}$ core level spectra corresponding to the $Te^0/Cs_{2.6}Te$ sample of fig. 1, for 30 and 350 L O_2 exposures, by Te^{2-}, Te^0, Te^{4+} and Te^{6+} components. Energies are referred to the Fermi level.

[7]. In fig. 2 we present the fittings obtained for Te $3d_{5/2}$ peaks of the sample with oxygen exposures of 30 L (a) and 350 L (b), this latter corresponding to the sample in fig. 1. In fig. 2a, at 0 ° C, three lineshapes have been used to fit the spectrum. These peaks correspond to the species Te^{6+}, Te^0 and Te^{2-} at the binding energies mentioned above. In the spectrum at 40 °, the Te^{6+} peak disappears, while both Te^0 and Te^{2-} peaks remain, but the former has increased with respect to the latter. That means that TeO_3 molecules are deeper than those of Cs_2Te, the Te clusters remaining on the surface. In fitting spectra of the sample with 350 L oxygen exposure, a new peak was needed as can be seen in fig. 2b. This has been determined to corresponding to TeO_2 (Te^{4+} species), in good agreement with published values [6].

From XPS quantitative analysis, the sample corresponding to 30 L, fig. 2a, has been approximately fitted with 0.4 ML of Te^0 at the surface, followed by a 25 Å thick layer containing mainly Cs_2Te and Cs_2O_2. The composition of the bulk of this sample have been fitted as a mixture of TeO_3, Cs_2O_2 and a small amount of Cs_2Te. The sample corresponding to 350 L, fig. 2b, is approximately explained by 0.1 ML of Te^0 in a 3 Å thick layer of Cs_2Te followed in depth by a 10 Å thick layer of Cs_2O_2 and TeO_2. The bulk corresponds to a mixture of TeO_3 and Cs_2O_2.

It is interesting to point out that not only the oxidation of Te atoms occurs in the bulk region, but also the Te atoms change strongly their chemical environment from Te^{2-} to Te^{6+}. At this point we have to note that the exposures to oxygen at room temperature and even at 200 ° C, did not produce any oxidation of a Te semimetal thin film. Obviously Cs atoms have played an important role promoting the oxidation of Te atoms.

The XPS Cs 3d peak and the Cs MNN Auger structure of the sample with 350 L oxygen exposure show single lineshapes very similar to those in CsI, giving an Auger parameter for Cs in this sample $\alpha(\mathrm{Cs}) = 1294.06$ eV. This value is between those for Cs_2Te (1295.07 eV [5]) and for Cs_2O_2 (1293.36 eV [8]), suggesting the presence of only one Cs–Te–O phase. However, it is well known that Cs photoemission peaks do not show important chemical shifts in a given sample [8]. In the sample analyzed, according to the results above, at least two different phases containing Cs are present: Cs_2Te and either Cs_2O_2 or Cs_2TeO_4. However, the binding energy of the Te^{6+} 3d peak agrees much better with the first supposition, compared with $E_B = 576.8$ eV reported for Na_2TeO_4 [9].

Cs_2O_2 (chemical species O_2^{2-}) has been assigned as the cesium oxide formed. This assignment is based not only on the quantitative results, but also on the value of the binding energy of the O 1s core level [8,10]. In fig. 1a, it can be observed that the O 1s peak is asymmetric at lower binding energies. This peak can be decomposed in two lineshapes centered at 531.65 and 530.00 eV, respectively. The former can be attributed to oxygen in TeO_3 [6], and the latter to oxygen in cesium peroxide Cs_2O_2 [8,10].

The Te MNN Auger structure, for the mentioned sample, shows a very complex lineshape, as can be expected from the complex lineshape of Te 3d XPS peak. After an approximate fitting with two single structure spectra, we obtained the Auger parameters: $\alpha(Te) = 1061.7$ eV for Cs_2Te, and $\alpha(Te) = 1061.0$ eV for TeO_3. These values, even with some error in their measurement, agree with the value obtained for Cs_2Te [5] and with the fact that tellurium oxide should have a lower Auger parameter than cesium telluride. This is based in the larger polarizability for Cs^+ and Te^{2-} than for O^{2-} and Te^{6+}.

A similar analysis was performed for the sample of potassium telluride, free of Te clusters, whose average composition resulted to be $K_{1.6}Cs_{0.6}Te$, because of Cs contamination. This contamination is mainly at the near surface region, as can be deduced from the average composition in spectra taken at 35° emission angle: $K_{1.5}Cs_{0.7}Te$.

Fig. 3 shows the Te 3d spectra from this sample at different oxygen exposures and taken at 0° and 35° emission angle. In this case, an oxide peak also appears whose intensity increases with oxygen exposure. The binding energy is $E_B = 577.63$ eV, thus it seems to correspond to Te^{6+}. The main difference with the sample of Cs_2Te with Te clusters is that, in this case, the peak does not decrease when tilted the sample. Instead, the relative intensity of this peak in the spectrum for 10^4 L oxygen exposure and at 35° emission angle, increases by 70%. Thus, this indicates that TeO_3 is formed mainly at the surface, just the opposite of what occurred in the first sample analyzed. In that case, the Te clusters seemed to play an important role in the kinetics of such an oxidation. Besides, no formation of TeO_2 seems to be produced, as can be inferred from the valley between Te^{2-} and Te^{6+} peaks.

In fig. 4, the average concentrations obtained from XPS intensities have been represented versus the oxygen exposure, where the first three points correspond to the initial sample with no oxygen exposure. In this figure it can be observed that, in the early stages of oxidation, both alkali metals, Cs and K, slightly increase their relative con-

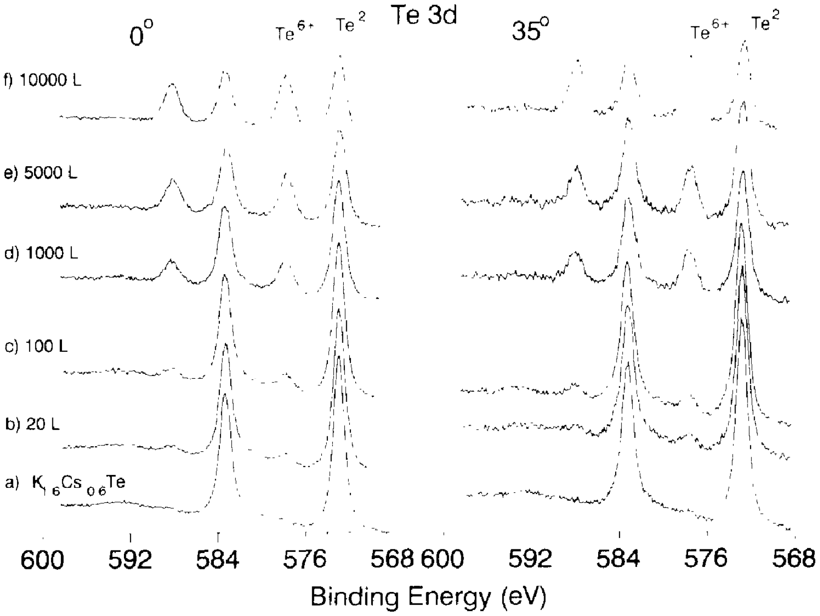

Fig. 3. Experimental XPS Te 3d core level spectra of a $K_{1.6}Cs_{0.6}Te$ sample at different O_2 exposures and taken at 0° and 35° emission angle. Mg Kα satellites have been subtracted. Energies are referred to the Fermi level.

centrations, but, while K concentration continues increasing with oxygen exposure, Cs concentration drops for exposures larger than 100 L. This seems to indicate a migration of K atoms to the surface larger than that of Cs. It should be pointed out that the oxidation processes at a rate faster than logarithmic and does not seem to reach a saturation region. This behaviour has also been observed in the oxidation of a bialkali antimonide photocathode Cs_2KSb [8].

The Te MNN Auger structure, for the sample with largest TeO_3 content, presents a well defined double lineshape, where subtractions can be done easily. From this spectrum the Auger parameter has been determined more accurately than before, giving for TeO_3 the value $\alpha(Te^{6+}) = 1061.51$ eV. For the alkali telluride we obtain a value for $\alpha(Te^{2+}) = 1061.84$ eV, the same value as for $Cs_{2.6}Te$.

4. Conclusions

The results for the cesium telluride with surface Te^0 clusters show that for low oxygen exposures (10 L range) oxygen is chemisorbed and diffuses into the bulk, oxidizing Cs and Te atoms, but Te^0 clusters remain unreactive at the surface. It should be recalled that Te^0 clusters were unreactive on overceasiated Cs_2Te. On further oxygen exposures (10^2 L range), the bulk becomes completely oxidized in the form of TeO_3 and Cs_2O_2 while TeO_2 and Cs_2O_2 are formed in a near-surface region. However, the surface layer is still formed by Cs_2Te and Te^0. The Te^0 clusters might have reacted with Cs since their equivalent coverage has decreased to 0.1 ML. An oxidation-state gradient is formed in a depth of approximately 70 Å and is clearly shown by XPS analysis at different photoelectron emission angles, both by the gradient of oxygen concentration and the ordering of the tellurium species Te^{2-}, Te^0, Te^{4+} and Te^{6+} for increasing depth. This seems to reflect the existence of a strong electric field between the Te^{2-} at the surface and the Te^{6+} in the bulk, and consequently the Cabrera–Mott mechanism for oxidation at low temperatures could be invoked [11,12], since the Te electron affinity is larger than that of oxygen. However, the chemical driving force for that gradient is probably of a different nature since it is clearly related to the presence of the Te^0 clusters at the surface, that favors in some way the Te^{2-} species against O^{2-}.

The oxidation kinetics as measured by the XPS

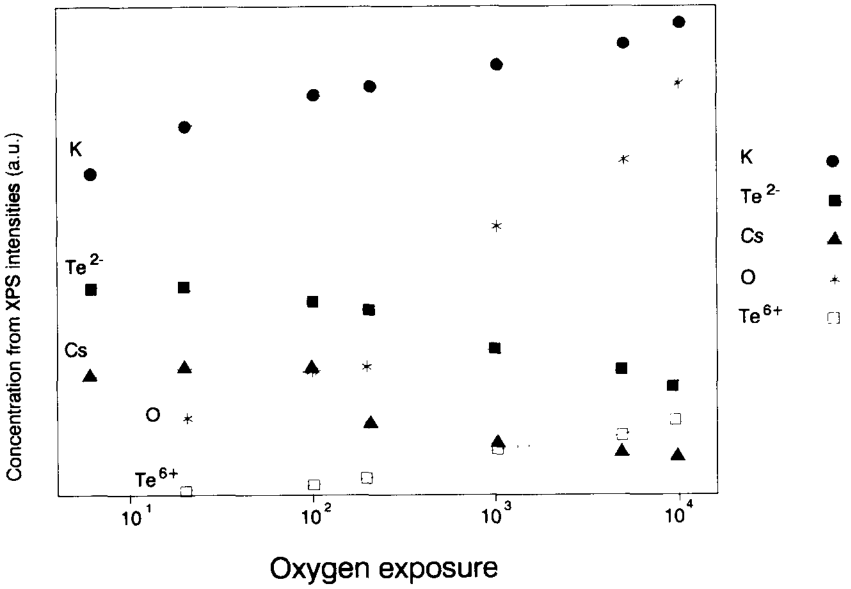

Fig. 4. Concentration from XPS intensities versus oxygen exposures, corresponding to the sample of fig. 3.

intensity of Te^{6+} 3d is many orders of magnitude faster for the alkali metal tellurides than for the pure semimetallic Te. It is also faster for $Cs_{2.6}Te$ with Te^0 clusters at the surface than for $K_{1.6}Cs_{0.6}Te$. This is probably due to the Te^0 clusters that in some way produce an strong chemical gradient for oxygen ions to diffuse into the bulk, allowing the Cs_2Te surface to remain very reactive for oxygen chemisorption.

Acknowledgements

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