Spectroscopic investigation of *in situ* prepared multialkali-based photocathodes

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Abstract

Alkali-based electron sources are characterised by high quantum efficiency and low work function, therefore they are the best candidate to met the specification of laser-driven RF gun. Preparation technology of such a photoemitters is in rapid progress, and the development of multialkali materials represent a promising step.

We used Auger Electron Spectroscopy (AES) to investigate in situ grown multialkali photoemitters. Thin films (tens of nanometers scale) of Sb, K and Cs were sequentially deposited on different substrates (Mo and stainless steel AISI 304). The procedure has been separately proved to result in an high efficiency photoemitter. At each preparation stage and in the final configuration the film was monitored as far as the interfacial intermixing (also with respect to the substrate), the chemical bonding and the presence of contaminants are concerned. In particular, AES was used in conjunction with sputter erosion to obtain the in-depth profile of the film. Emphasis was also on the characterisation of the outermost layers, which is known to mainly determine the photoemissive behaviour of the material.

INTRODUCTION

Multialkali photoemissive materials has been widely used in photomultiplier devices technology. Several interesting studies on this topic are available in literature [1,2]. The interest in these materials has been recently renewed for the applications that photocathodes can have in high quality electron sources for particle accelerators [3,4,5]. However, the development of photocathodes is still more or less empirical. The growth is usually monitored only by measuring the photosensitivity at various stages of the growth. This does not give much information about the various processes that occur during the deposition of the photocathode. An understanding of these processes may be very useful for improving the reproducibility of the growth and the photosensitivity of the photocathodes.

For a relevant analysis, the study of alkali antimonide compounds needs measurements combining both the physics of thin layers under Ultra High Vacuum (UHV) conditions and the chemistry of these materials. The presence of contaminants on the substrate and/or in the photoemissive material require a chemical-sensitive analytical technique, and the nanometric scale of these photoemissive devices demand a high surface sensitivity. AES and X-ray Photoelectron Spectroscopy (XPS) [6] are well established analytical tools, which fulfils the above requirements [7,8].

The study of multialkali photocathodes applied to RF electron guns require an expertise that extend over a wide field of interest. This work is the result of a collaboration which involves three research centres (S.E.S.A.MO, TASC and LASA) with specific competences.

The effect of different substrates and cleaning procedures on the growth of K_2CsSb photocathodes has been investigated, and particular attention has been dedicated to illustrate how such complex situation can be studied by Auger electron spectroscopy in conjunction with photoemissivity measurements.

EXPERIMENTAL

A UHV system has been purposely designed for the growth of multi-alkali photocathodes. The alkali metals were evaporated from Ni-Cr dispensers (SAES Getters) filled of Me_2-CrO_4 (Me = K,Cs) and 84% Zr - 16% Al (ST 101) non-evaporable getter powders. Similar dispensers filled with 99.5 % purity antimony powder was used as Sb source. The evaporation rate and the thickness of the deposited film has been monitored by means of a quartz microbalance.

The photocurrent was excited through a 0.95 mW He-Ne laser (λ=543.5 nm, $h\nu$=2.28 eV) and collected by a ring-shaped anode placed in close proximity to the photocathode. The anode has been polarised to +50 V with respect to ground to avoid space-charge effects on the photocurrent.

The substrates was made of stainless steel AISI 304 or 99 % Mo, optically polished by 0.25 μm diamond powder and successively cleaned in high purity trichloroethylene (C_2HCl_3), acetone ($CH_3CO.CH_3$) and ethanol (C_2H_5OH).

The substrates have been introduced in the growth chamber (base pressure < $7 \cdot 10^{-11}$ mbar) through an air-lock device, and successively heated to 723±1 K for 30 minutes by electron bombardment. During growth the substrate temperature was held to 393±1 K, and the pressure raises $3 \cdot 10^{-10}$ mbar.

We deposited 5.0±0.1 nm of Sb and successively 3.0±0.1 nm of K at a growth rate of about $1 \cdot 10^{-2}$ nm/s.

While monitoring the photocurrent, Cs was deposited at the aforementioned rate until a maximum of the photocurrent was reached. The substrate was then cooled at a rate of about 0.1 °C/s and the Cs source was not turned off until the substrate temperature was lower than 363 K. From the microbalance reading we can estimate that about 50 nm of Cs were deposited during this phase. The quantum efficiency of the photocathodes after Cs deposition was typically 1-5 %.

The same substrate has been utilised several times by heating the photocathode at 723±1 K for 30 minutes (in the
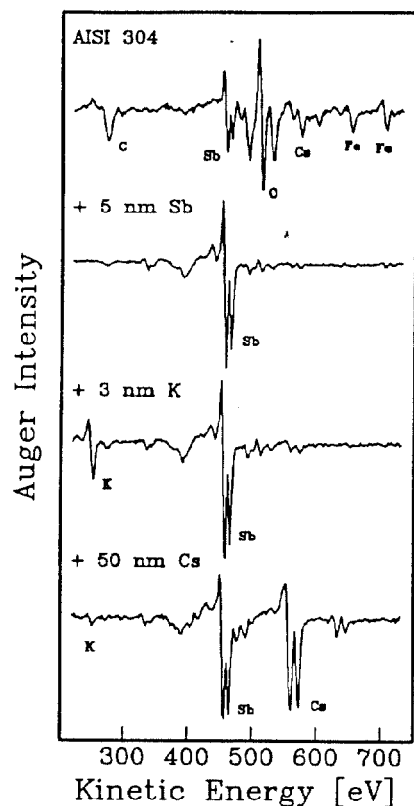
Fig. 1: Auger spectra taken before each deposition step on a regenerated substrate. The main contaminants are C and O. Traces of Sb and Cs from the previous depositions are still detectable even after 30 min heating at 723 K.

followings we refer to this procedure as the "regeneration of the substrate").

Further details about the growth procedure and the UHV system are given elsewhere [9].

The Auger analysis was performed in a UHV system connected to the growth chamber by an UHV transfer device. During the transfer and Auger analysis operations, the total pressure does not exceed $3 \cdot 10^{-10}$ mbar. Auger spectra were taken using a single pass Cylindrical Mirror Analyser (CMA) operating in the first derivative mode. The modulation voltage was 6 V peak-to-peak. The exciting electron beam was coaxial to the CMA cylinders, the beam energy was 3 keV and the beam current was 600 nA over a 100 μm × 100 μm area. We considered the following Auger lines: Mo MNN (186 eV), K LMM (252 eV), Sb MNN (454 eV), O KLL (503 eV), Cs MNN (563 eV) and Fe LMM (703 eV).

Depth profiling was accomplished by an Ar^+ ion gun operating at 0.8 keV and a current density of 40 μA/cm² over a 2 mm × 2 mm area. Ar^+ beam at 4 keV, 250 μA/cm² over a 4 mm × 4 mm area was also used to prepare the substrates in a different way.

RESULTS AND DISCUSSION

In fig. 1 are reported the Auger spectra taken at each growth step, i.e. on the substrate (stainless steel AISI 304),
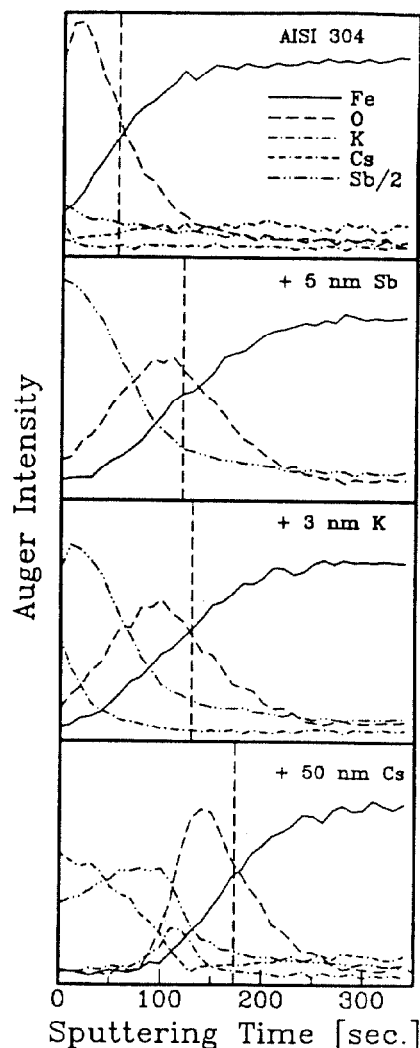

Fig. 2. Auger depth profiles after each step of photocathode growth. The vertical dashed line indicates the position of the substrate-cathode interface, arbitrarily assumed to correspond to the 60 % of the final substrate signal.

after heating at 723 K for 30 minutes; after the Sb deposition; after the K deposition; on the completed photocathode. The presence of Sb and Cs at the initial stage, shows that the re-generating procedure at 723 K does not recover completely the substrate. Furthermore, a large oxygen contamination is present at the surface. The Sb signal is clearly visible also after the deposition of several nm of K and Cs, indicating that a chemical reaction between Sb and the alkali metals takes place.

The Auger signal comes from a depth of the order of the electron inelastic mean free path, i.e. 1-2 nm for the Auger lines we considered. Therefore, the Auger spectra gives information about the stoichiometry of the topmost layers.

To have great insight into the in-depth distribution of the photocathode components, we carried out depth profiling. This procedure consists of Ar^+ bombardment of the sample to remove progressively the surface layers and collecting the
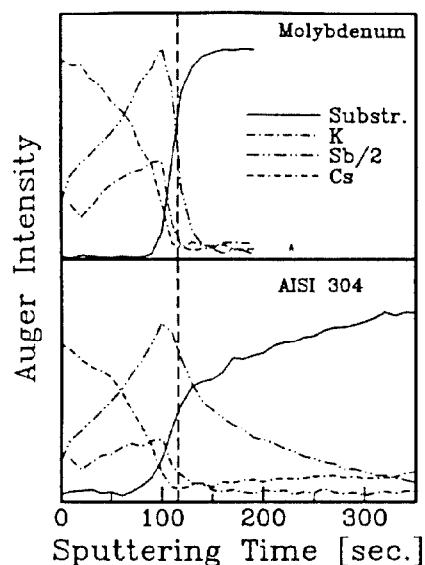
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Fig. 3. Auger depth profiles of the two parts of the composite Mo-AISI 304 substrate, taken after the following procedure: i) sputter cleaning to remove completely the C and O at the surface; ii) a first photocathode growth; iii) heating to 723 K for 30 minutes; iv) a new photocathode growth.

Auger signals as a function of time. The sputtering time can be converted to a depth scale if the sputtering rate is known. This parameter can be estimated from the data available for the pure elements as 0.1 - 0.2 nm/s. In fig. 2 are shown the results of such analysis for each step of the photocathode growth which has been already considered in fig. 1. After the Sb deposition, the oxygen places between the overlayer and the substrate, living a pure Sb surface. Can be inferred from the similar behaviour of the K and Sb depth profiles, that the subsequent K evaporation leads to the formation of a K - Sb compound at the surface of the cathode.

The depth-profile taken after the final Cs deposition shows that a quite complex interdiffusion process takes place in the overlayer. We observe the formation of a Cs-Sb compound at the surface, and the segregation of almost all the K at the substrate interface. Thus the formation of a "true" multialkali photocathode on this substrate may be questioned.

The effect of the presence of contaminants like C and O on the substrate before the heating procedure at 723 K as well as the effect of different kinds of substrates play a primary role on the physical properties of the photocathode. To investigate this point a Mo - AISI 304 composite substrate has been cleaned by Ar^+ sputter etching at 4 keV. After this procedure no traces of C and O has been detected on the surface, and a photocathode has been grown on it with the aforementioned procedure. After that, the substrate has been regenerated by heating at 723 K for 30 minutes and a new photocathode has been deposited.

By comparison between the lower panels of figs. 2 and 3, we note that the different cleaning procedure on the AISI 304 substrate leads to different in-depth distributions of the cathode components. In absence of surface contamination, two effects can be observed. First, no segregation of K at the substrate interface is observed. Sb, K and Cs are present in the whole deposited layer, pointing out that the photoemissive overlayer is a homogeneous compound. The second effect is a strong Sb diffusion in the substrate which takes place during the high temperature regeneration process.

This effect is a peculiar property of the sputter-cleaned AISI 304 substrate, and constitutes the main difference between the two kinds of substrates we considered (fig. 3). On the other hand, it does not seem to affect the in-depth distribution of the photocathode components.

CONCLUSIONS

We have grown multialkali photocathodes under UHV conditions, monitoring the intermediate phases of the deposition process by means of Auger analysis and ion sputtering depth-profiling. Different cleaning procedures and substrates have been employed for the construction of the photoemissive material. Auger analysis pointed out that after the heating process at 723 K, a large amount of C and O contamination, as well as traces of the elements of the preceding depositions are detectable on the surface of the substrate. On the AISI 304 substrate a strong diffusion of Sb several tens of nm below the surface has been observed after the regenerating procedure. The presence of contaminants seems to prevent the formation of a K_2CsSb photocathode, and most of the K is segregated at the substrate interface. If the substrates are cleaned by sputter etching before the photocathode growth, a true multialkali photocathode can be obtained.

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