

XPS AND UHV-AFM ANALYSIS OF THE K_2CsSb -PHOTOCATHODE GROWTH *

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Abstract

Alkali-Antimonide growth was examined at the Center of Functional Nanomaterials (CFN) at Brookhaven National Laboratory (BNL). The materials were grown in a UHV chamber and analyzed by means of core-level x-ray electron spectroscopy (XPS) and UHV-atomic-force microscopy (UHV-AFM). We were able to grow CsK_2Sb cathodes with an average quantum efficiency around 1-2.5 % under good vacuum conditions. The findings will be compared to materials grown under less favorable conditions with water partial pressures of up to $1 \cdot 10^{-7}$ Torr during evaporation. It appears that cathodes grown within a high water partial pressure environment can show up to 1% quantum efficiency but usually showed none.

INTRODUCTION

The next generation of light sources will require photocathodes with low intrinsic emittance and weeks of operational lifetime at 100 mA average current, short response time and high quantum efficiency at 532 nm wavelength [1, 2, 3].

To fulfill these criteria semiconductor cathodes with a uniform surface are needed. Bi-Alkali antimonides are a prime candidate due to their high quantum efficiency in the green. These materials are known since the 1960s and investigated by the photo-multiplier-tube (PMT) community but with passing interest on the materials science [4].

For the performance of the cathode the chemical composition in the surface region and morphology of the film are of great interest. Therefore XPS and UHV-AFM measurements were performed to complement our XRD and XRR study on the growth of CsK_2Sb [5].

As a starting point we followed the long known recipe by Sommer [6] under various vacuum conditions and analyzed the chemical composition and measured the quantum efficiency of these materials.

EXPERIMENTAL SETUP

A UHV chamber with a base pressure of $3 \cdot 10^{-10}$ Torr, with a water partial pressure in the 10^{-7} Torr to 10^{-9} Torr

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range during evaporation was used for the experiments. The XPS measurements were carried out with $Al-K\alpha$ x-ray radiation (1486 eV photon energy) and an x-ray photoelectron spectrometer (Specs Phoibos 100 MCD analyzer). The XPS study was performed in the constant analyzer energy mode (CAE) at 20 eV pass energy, resulting in an accuracy of ± 0.25 eV for the binding energy and 10 % for composition determination. For morphology determination the chamber was directly connected to a commercial RHK UHV-750 variable temperature scanning-tunneling and atomic force microscopy (STM/AFM) and the samples could be moved there without exposure to air. AFM images were obtained in contact mode with a silicon cantilever. The evaporation rates were recorded with a film thickness monitor. The photocurrent measurements were carried out with a class-III green laser of 532 nm and 6 mW and a negative bias of -10 V was applied to the sample. As substrates HF dipped Si(100) p-type wafers were used. The HF dipping was performed to remove the natural oxide layer. After HF treatment the wafer was rinsed with deionized water and dried with dry Nitrogen prior to mounting inside the vacuum chamber.

The Antimony layer was either evaporated in-situ from SbPt beads at 100°C substrate temperature or sputter deposited ex-situ at room temperature in a Kurt Lesker LAB 18 modular PVD system. Sputtered films consisted sometimes up to 50 % of oxidized Antimony. Heating these films to 400°C for about 4 min removes most of the oxide in the surface region.

Cesium and Potassium were evaporated from commercial Alvac sources at a substrate temperature of 135°C. After the Antimony, the Alkalis were evaporated in sequence, following the recipe from Sommer [6]. During alkalis deposition at a rate of 0.2 Å/s, the photocurrent was monitored. The deposition was stopped once a plateau in quantum efficiency was reached. After each growth step the photoelectron spectrum was taken. Cathodes prepared at the CFN user facility showed a quantum efficiency of 0-2.5 % at 532 nm.

From the ratios of the area of the PE emission peaks the composition of the surface layer (3-6 nm) can be determined. For ratio determination atomic sensitivity factors were taken into account [7]. For evaluation we considered the following regions (B.E.): Sb 3d/O 1s (542-520 eV), Cs 3d (775705 eV), K 2p (320-275 eV), Si 2p (110-92 eV), survey spectra were taken after each deposition before the region spectra.

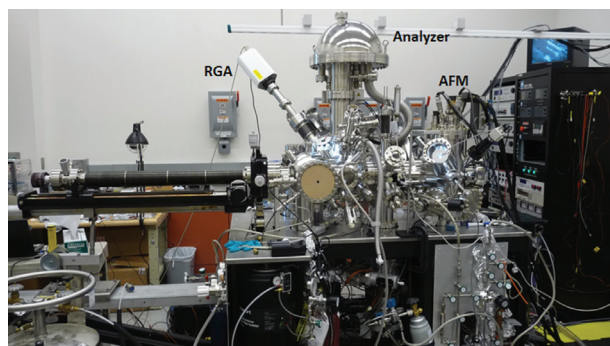


Figure 1: UHV chamber at CFN equipped with an electron energy analyzer, RGA and UHV-AFM.

RESULTS

After mounting the atomically flat Si(100) wafers in the UHV system, the wafer was heated to 100°C. The in air mounting of the substrate took usually longer than 30 min after HF dipping and resulted in the formation of a new oxide layer which is evident through the appearance of the Oxygen 1s peak at 532.7 eV in the XP spectra of the bare substrate, figure 2a.

Antimony Layer

Following the PMT recipe, as a first growth step Antimony was deposited. The Si substrate was heated to 100°C for several minutes prior to Sb deposition and kept during Sb growth. Usually upon Antimony deposition, with a thickness in the range of 10 - 20 nm, the Oxygen signal at 532.7 eV could not be resolved, see figure 2b. Sputtered Antimony films are much smoother than evaporated Sb-layers, therefore growth from sputtered Sb films was also examined. Sometimes these films showed a large amount of oxidized Sb, about 50 % of the Antimony in the surface area is oxidized. After heating these films to 400°C for 4 min most of the Sb in the surface area is metallic, but about 10 % remain oxidized, see figure 2c.

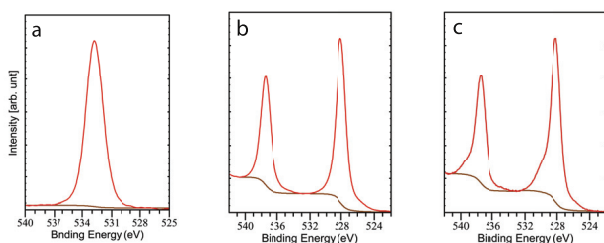


Figure 2: XP spectra of the O1s region (red: signal, brown: Shirley background). a: substrate after heating to 100°C; b: evaporated Antimony layer [9]; c: sputtered Antimony layer after heating for 2 min to 400°C.

The K-Sb Compound

Figure 3 shows two examples of K-Sb cathodes grown in different vacuum conditions. In 3a the Sb region of a good

cathode is presented, most of the Antimony is reduced and reacted with Potassium, Sb 3d_{5/2} 3d_{3/2} are found at 526.2 eV and 535.6 eV, respectively. About 17 % of the Antimony in the surface region remains in the metallic state and is not reacted with Potassium.

Figure 3b shows an example of a cathode grown with a high water partial pressure in the UHV system, p_{water} of up to 10⁻⁷ Torr were recorded. The 3d doublet of oxidized Antimony, Sb 3d_{5/2}, 3d_{3/2} at 529.8 eV and 539.6 eV, respectively, shows the highest intensity.

Both cathodes have some intensity in the oxygen region around 531.5 eV, showing that oxygen is incorporated in both cathodes in the surface region.

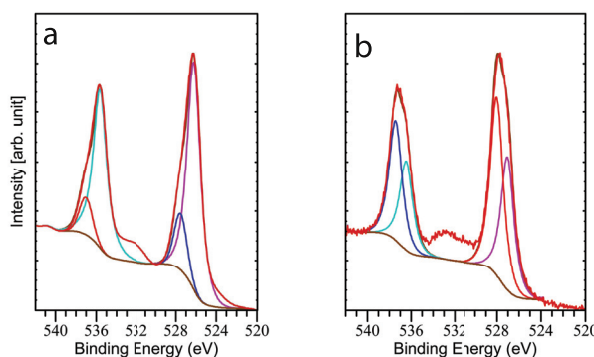


Figure 3: XP spectra of the O1s region (red: signal, brown: Shirley background, add lines: components). a: good cathode with low oxygen content and 83 % of the Antimony reduced [9]; b: bad cathode with high oxygen content and most of the Antimony oxidized

The Cs-K-Sb Compound

As a last step, Cesium was evaporated at 135°C substrate temperature. Usually, upon Cesium deposition all of the Antimony in the surface region is reduced, see figure 4a. Nevertheless, even under good vacuum conditions Oxygen contamination is found, O 1s peak at 531.3 eV. This suggests that some Oxide is formed in the surface region. The position of the Oxygen 1s peak suggests Potassium- and Cesiumoxide formation [8].

The shifts in the Alkali-spectra are very small and within the experimental error. Identification of alkali-oxide and alkali-antimonide is therefore not possible.

Figure 4b shows the Sb region of the K-Sb compound shown in figure 3b after Cs deposition. Some of the Antimony is metallic and the Sb 3d doublet is found at 3d_{5/2} 527.9 eV and 3d_{3/2} 537.4 eV, these values are about 1.5 eV higher than the reduced Sb 3d peaks found for the good cathode - figure 4a, the Antimony in the figure 4b is not in the same chemical surrounding than in 4a.

The surface layer composition of cathodes grown under good vacuum conditions is Cs_{2.1}K_{1.1}Sb. For the cathode shown in figure 4a a quantum efficiency of 2.4 % at 532 nm was measured. The composition of the surface

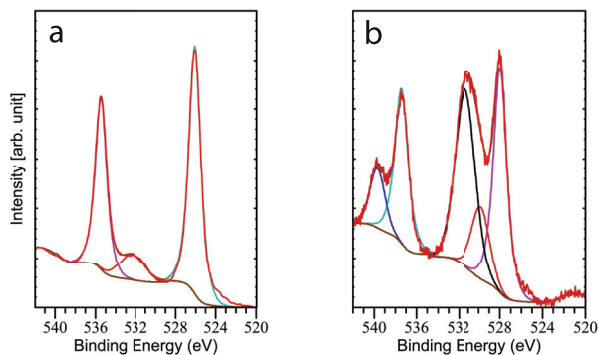


Figure 4: XP spectra of the O1s region (red: signal, brown: Shirley background, add lines: components). a: good cathode with low oxygen content and all of the Antimony in the surface region reduced [9]; b: bad cathode with high oxygen content and most of the Antimony reduced, but some still oxidized and a high amount of oxygen

region happens to be reverse with respect to XRD results [5]. From X-ray diffraction it is known that the bulk of the material grown under similar conditions shows the CsK₂Sb lattice parameters. No evidence is found for a Cs₂KSb system, suggesting that the surface region is not crystalline.

The cathode in 4b showed no quantum efficiency at 532 nm. That confirms that the high water partial pressure present during growth prevents the formation of cathode material in favor of Oxides built up.

UHV-AFM

After a full cathode growth, UHV-AFM measurements were performed. The cathode was moved into the AFM-setup without exposure to air. The material grows in pillars which are less than 100 nm apart. This morphology results in a rather high surface roughness of 25 nm (root mean square value). In-situ XRR measurements support this finding, see [5] for further details.

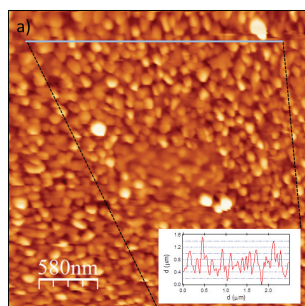


Figure 5: AFM topography image of a full cathode, picture taken from [9].

The cathode shown in figure 5 showed a quantum efficiency of 1.1 % at 532 nm. The XP spectra exhibited oxygen contamination.

CONCLUSION

XPS and UHV-AFM measurements were performed in different vacuum conditions. A high water partial pressure ($p_{water}=10^{-7}$ Torr) during evaporation results in the formation of Oxides and the materials exhibits no quantum efficiency at 532 nm. Compounds grown under good vacuum conditions still show some Oxygen contamination, but exhibit quantum efficiencies around 1 - 2.4 % at 532 nm. The material does not form a smooth film, but grows in pillars as shown by AFM.

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