

HIGH EFFICIENCY VISIBLE PHOTOCATHODE DEVELOPMENT

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Abstract

The alkali antimonides are of significant interest to the accelerator community, as they have a high quantum efficiency (QE) under illumination by green light. These cathodes are attractive for high-average-current photoinjector applications and understanding their fundamental properties are critical to the production of long lived, reliable cathodes. We report on ongoing work to characterize cathode formation during growth. In-situ X-ray Diffraction (XRD) has been used to compare grain size and texture in antimony layers, and X-ray Photoelectron Spectroscopy (XPS) has been used to investigate the solid-state chemistry of cathode formation.

INTRODUCTION

Brookhaven National Laboratory, Lawrence Berkeley National Laboratory and Stony Brook University have embarked on a collaborative effort to use the tools of modern user facilities to understand and improve the performance of accelerator photocathodes, principally alkali antimonides. Cathodes with 6% quantum efficiency have already been achieved, and methods have been investigated to control the antimony film crystalline properties. The cathodes have been found to be quite robust, operating for weeks at 1 mA/mm² current density, and demonstrating a 50% yield lifetime of 20 hrs at 2 pBar partial pressure of water. An intrinsic normalized emittance of 0.36 $\mu\text{m}/\text{mm}$ rms spot size has been measured [1] for green light.

This report will focus on recent progress in analysis of cathode structure and growth. Cathodes have been studied with *in-situ* x-ray analysis; XRD to understand grain size and texture, and XPS to look at stoichiometry, growth dynamics and contamination.

GROWTH DYNAMICS

Cathode Structure: XRD

In-situ XRD has been used to study Sb growth as a function of substrate material, substrate temperature and deposition method (sputtering & evaporation). Preliminary attempts have also been made to grow K₂CsSb and observe the crystalline structure of the final cathode. This work was performed at National Synchrotron Light Source beamlines X21 and X20C; information on the beamline capabilities is available online [2]. Figures 1 & 2 show the in-plane and out of plane XRD for Sb sputtered on Mo at room temperature

and 150 C, along with the expected peak height assuming a randomly oriented powder distribution.

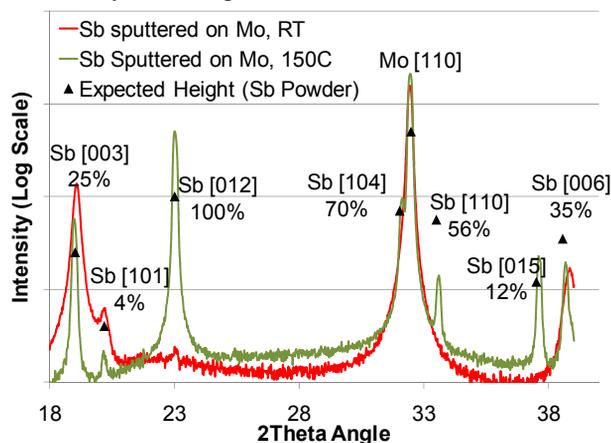


Figure 1: Sb out-of-plane (reflection) diffraction for sputtered Sb films on Mo. The expected peak heights for untextured Sb are shown, along with their relative strengths (percentages). The film grown at room temperature exhibits a clear [003] fiber texture (with a nearly complete absence of [012], [104] & [110]), while the substrate grown at 150 C is less clearly textured but has larger Sb grains (smaller peak widths).

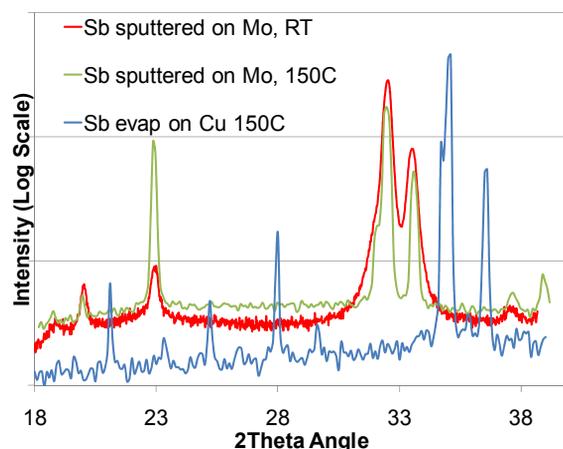


Figure 2: Sb in plane diffraction for Sb sputtered onto polished Mo substrates at room temperature and 150 C. Sb evaporated onto Cu at 150 C is also shown – The XRD-pattern reveals a complete alloying of the Sb-film with the Cu substrate

In the case of low temperature evaporation, the Sb grew in small grains (broad peaks), with a well defined fiber [003] texture, as evidenced by the deviation from the

observed peak heights for the out of plane diffraction as compared to the powder values. The sample grown at 150 C shows sharper peaks (larger grains), but a powder texture. For a Cu substrate, the diffraction data clearly shows the formation of a copper-antimony alloy, thus explaining the very low yield from cathodes formed on this surface. Silicon substrates have also been investigated – these provide more clear definition of the powder orientation (as the Si is near atomically smooth, while the Mo had 100 nm roughness), but no difference in the resulting texture has been observed, suggesting that the texture is not due to lattice matching. For both Si and Mo, films less than ~8 nm thick were amorphous. Above 8 nm, the grain size evolves with thickness. Mapping the grain size and texture evolution with deposition as a function of rate and temperature is one of the next steps in this effort.

Figure 3 shows the out of plane XRD of a cathode on a Mo substrate before and after alkali deposition. The alkalis (K then Cs) were evaporated from Alvac sources with the substrate at ~130 C. A significant amount of unreacted elemental Sb is still present, suggesting that insufficient alkali or diffusion time may have been used for this cathode. No crystalline alkali peaks are observed, but two broad peaks are evidenced which may correspond to an amorphous phase of K_2CsSb .

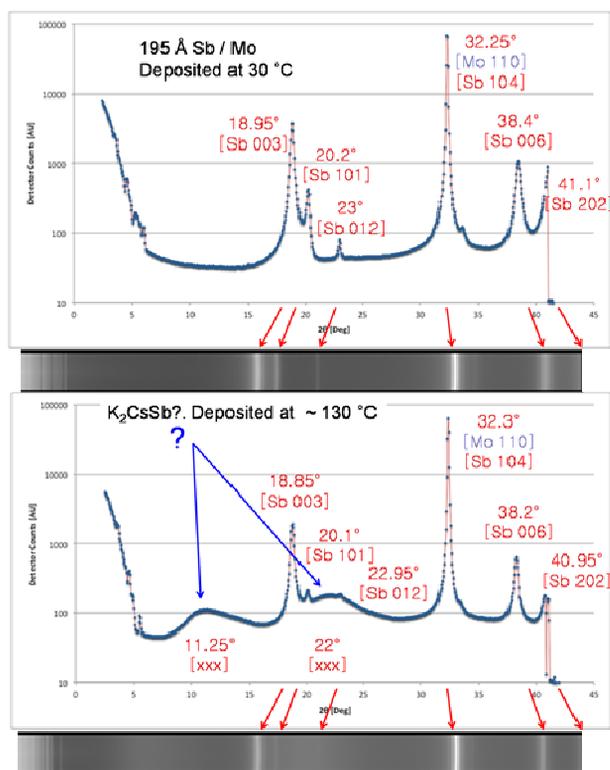


Figure 3: Reflection XRD of cathode before and after alkali deposition. These patterns were taken with a 2D detector; the strips at the bottom show the ring patterns corresponding to the peaks.

Cathode Growth Process: XPS

Two K_2CsSb photocathodes have been grown in a commercial XPS system (RHK) at the Center for Functional Nanomaterials at BNL, with a base pressure of 0.2 nTorr, with a goal of understanding the interdiffusion process which occurs during growth, and observing how the recipe alteration affects the process of growth. This allows comparison of the final phase of the cathodes grown with different substrates or temperatures, and correlation of these differences with QE.

The cathodes were grown on Si [100] substrates with a native oxide layer. The substrate was electrically isolated to perform in-situ measurements of the photocurrent produced by a green laser (532 nm). For the first cathode, the first layer of Sb was evaporated from PtSb beads, with an estimated final thickness of 24 nm. The SiO_2 peak is observable from the substrate (figure 5) initially, but after Sb deposition it disappears, suggesting that the Sb layer is thicker than the 5 nm depth that XPS is sensitive to. For the second cathode, a 10 nm Sb layer was prepared *ex-situ* within a sputter deposition system, with the sample at room temperature (similar to the method used to produce the Sb film in figure 3). For this layer, the thickness was checked via x-ray fluorescent analysis in a scanning electron microscope. The Sb film was exposed to atmosphere prior to insertion into the XPS chamber. XPS was used to investigate the oxide formation on the film during this exposure. Figure 4 shows the O edge XPS spectra of the film initially, and after heating to 200 C, 400 C and 600 C in vacuum. The original XPS spectrum at RT shows four peaks, suggesting the presence of oxides. The 200 C bake doesn't change this significantly, but the 400 C bake yields a strong Sb signal with much smaller oxide peaks. After 600 C heating, pure Sb signature peaks (3d_{3/2} and 3d_{5/2}, with energies of 537.5 eV and 528.1, respectively) are lost, suggesting that most of the Sb has formed Sb_2O_3 (peak at 530.45 eV) and Sb_2O_4 or Sb_2O_5 (peak at 539.8 eV). In addition, the substrate SiO_2 peak is apparent, suggesting that the Sb film may no longer be contiguous.

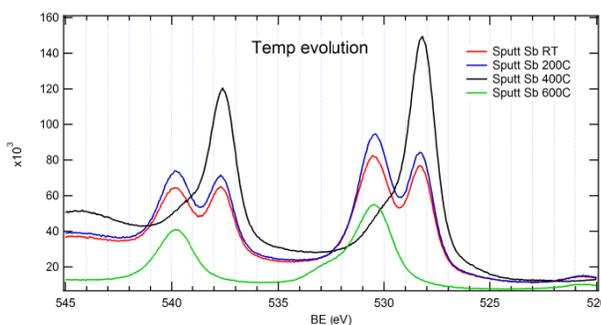


Figure 4: XPS Sb 3d region showing the thermal treatment of Sb sputtered on Si [100] substrate. The substrate was annealed in steps of 200 C, from room temperature to 600 C.

For both cathodes, sequential deposition K and Cs was performed while keeping the substrate temperature between 135 and 145 C in order to favor the alkali

diffusion between layers. The photocurrent generated from the green laser was monitored during deposition; the deposition was halted when the current reached a plateau. Both substances were evaporated from Alvac sources which produce a very constant and reproducible evaporation rate. K was evaporated prior to Cs, leading to the formation of a K-Sb compound, likely K_3Sb [3], apart from the pure K on the surface; this phenomenon can be tracked by the decrease of intensity and the shift in both 3d Sb peaks in the black spectral line of figure 5. Unlike the Sb deposition over Si, the K deposition does not cause a loss of the Sb peaks, suggesting that the K is intermixing with the Sb (as expected). No un-reacted Sb is observed within the interrogation depth (5 nm) of XPS.

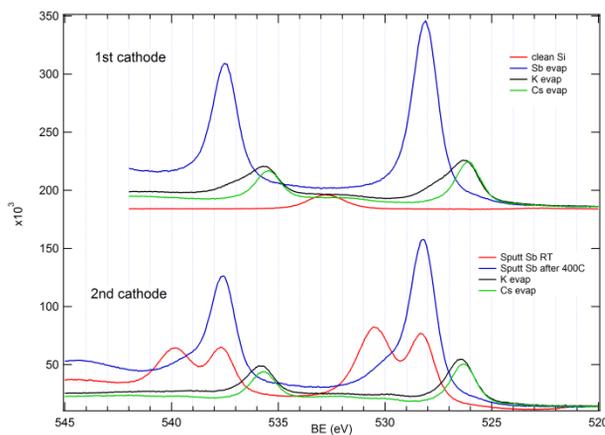


Figure 5: XPS spectra of Sb peaks (3d_{3/2} and 3d_{5/2}) were obtained before and after deposition of K and Cs. Comparison of both spectra shows small differences; both Sb layers present same strong signal from 3d_{3/2} and 3d_{5/2} peaks after the second cathode Sb substrate has been annealed to 400 C, but the shoulder for the ex-situ prepared Sb substrate (bottom blue line) suggests some traces of oxide (Sb_2O_3 and Sb_2O_4 or Sb_2O_5) remain. The Sb signal after K and Cs deposition does not show significant differences among cathodes, suggesting a similar behavior of K and Cs diffusion within the system.

Cs deposition after K also provokes a small shift and intensity decrease in peaks 3d_{3/2} and 3d_{5/2}. This suggests a stoichiometry change in the Sb which is likely to K_2CsSb ; an excess of Cs is expected to be on top of the surface layer, balancing between thermal desorption and chemical reaction to adjacent sites. It is well known that the cubic alkali antimonides, K_3Sb and Cs_3Sb , have a very definite composition and are unstable under alkali excess [4], so the K_2CsSb is the most abundant phase in the final cathode, especially after photocurrent optimization during growth. The final QE in the green was 2.4 % for the first cathode and 0.7 % for the second. From figure 5 it is clear that final composition of both cathodes does not differ

strongly, however the cathodes were of significantly different thickness. Both cathodes were likely too thin for optimum performance at 532 nm, but the first (evaporated Sb) cathode was more than twice as thick as the second (sputtered Sb). It is also possible that the residual Sb oxide present in the *ex-situ* sputtered sample even after 400 C anneal may play a role in its reduced performance.

CONCLUDING REMARKS

The structure and chemistry of multi-alkali cathodes have been investigated via *in-situ* x-ray diagnostics, including XRD and XPS. The initial Sb layer formation was found to have a strong dependence on the substrate temperature during growth, both in grain size and texture. This variation of grain size may affect the rate of reaction with K and Cs and result in different yield. XRD revealed un-reacted Sb on a cathode after alkali deposition, suggesting that either insufficient alkali was deposited or that insufficient time was allowed for intra-diffusion. XPS shows that the Sb film rapidly oxidizes when exposed to air; this oxidation can be largely removed by subsequent heating to 400 C in ultra-high vacuum. K deposition leads to a shift in the Sb binding energies, with no unreacted Sb near the surface.

Looking forward, the recipe development is ongoing, and a wider parameter space will be investigated. In the near future, this program will involve testing cathodes in RF photoinjectors and returning them to the diagnostic tools for post-operational analysis.

ACKNOWLEDGEMENTS

The authors are grateful to John Walsh and Bill Smith for their expert technical assistance and to Priya V Chinta and Jean Jordan-Sweet for their assistance. Research carried out (in whole or in part) at the National Synchrotron Light Source and the Center for Functional Nanomaterials, Brookhaven National Laboratory, supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886. This work was supported by the U. S. Department of Energy, under Contract No. DE-AC02-05CH11231, KC0407-ALSJNT-I0013, DE-AC02-06CH11357 and DE-SC0005713.

REFERENCES

- [1] T. Vecchione et al., *Appl. Phys. Lett.* **99**, 034103 (2011)
- [2] <http://www.bnl.gov/ps/>
- [3] L. Galan and C. Bates, *J. of Phys. D: Appl. Phys.* **14** 293 (1981)
- [4] A. H. Sommer, *Photoemissive Materials*. (John Wiley, 1968).