DEPOSITION AND IN-SITU CHARACTERIZATION OF ALKALI ANTIMONIDE PHOTOCATHODES

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Abstract
Alkali antimonide cathodes have the potential to provide high quantum efficiency for visible light and are significantly more tolerant of vacuum contaminants than GaAs, so they are attractive for use in high-average-current photoinjectors to generate high quality electron beams. We have grown multi-alkali cathodes on [100] silicon substrates, simultaneously acquiring in-situ X-ray diffraction (XRD) and X-ray reflection (XRR) data throughout the growth process. Correlations between cathode structure and growth parameters and the resulting quantum efficiency (QE) have been explored.

INTRODUCTION
Cathode growth has traditionally been performed based on iteration and variation of recipes developed over the years. This trial-and-error style approach, while modestly successful, does not take advantage of the tools of modern materials science. Recent work [1] by a collaboration between Stony Brook University, Brookhaven National Laboratory, and Lawrence Berkeley National Laboratory aims to improve performance of alkali antimonide photocathodes by observing changes in the photocathode structure and chemical composition during growth using XRR, XRD, X-ray photoemission spectroscopy (XPS) and X-ray fluorescence (XRF). Understanding the mechanism of growth and how the final crystalline structure can affect the overall quantum efficiency is critical to methodically developing a good recipe for robust high QE photocathodes.

This report will focus on recent progress in the analysis of observed in-situ crystalline transitions related to simultaneous changes observed in QE response.

EXPERIMENTAL DETAILS

In-situ film growth and real-time X-ray scattering measurements were performed at the X21 beamline of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). Approximately 2x10^{12} ph/sec of 10 keV (\lambda = 0.12 nm) X-rays were used. The incident x-ray beam was 1 mm wide and 0.5 mm high.

Figure 1: The experimental set up at the X21 beamline at NSLS. A 4 axis diffractometer with a UHV chamber allows the in-situ x-ray diffraction characterization of cathode growth. Inset: Position of the two Pilatus cameras placed after the beryllium X-ray exit window of the chamber.

The experiment was performed using a 4 axis diffractometer with two Pilatus 100 K X-ray cameras. One of the cameras was situated in small angle scattering/reflection mode while the other simultaneously recorded wide angle diffraction data during the deposition. The first camera is at 78.5 cm from the sample normal to the X-ray beam, and the second camera at 19.7 cm with an angle of 25° vertically out of plane. The base pressure of the ultra-high vacuum growth chamber was 3x10^{-10} Torr throughout the experiment; a residual gas analyzer (RGA) was used to monitored contaminants during growth. Values of H\textsubscript{2}O, CO and CO\textsubscript{2} partial pressures never exceeded 2x10^{-10} Torr during deposition, and were typically >5x10^{-11} Torr.

Substrates were electrically isolated during cathode growth and photocurrent was monitored by applying a negative bias. Deposition rates were monitored using a quartz crystal film thickness monitor (FTM). During growth, the X-ray incidence angle was kept at 1.8 degrees onto the sample (grazing incidence), and nu was set to 5 degrees (resolving the in-plane diffraction structure). This resulted in the beam spot overfilling the 2 cm wide sample. After each growth step, out-of-plane scans were taken by rotating nu and zeta.
GROWTH DYNAMICS

In-situ XRR and XRD has been used to study the growth of each basic element (component) of the cathode. The substrate was Si (100), which had been treated with HF to remove the native oxide. Antimony was evaporated from PtSb beads onto the substrate. For the first sample this was done with the substrate at room temperature; for the second it was done at 100°C. The substrate temperature has previously been shown to affect the crystalline texture of the Sb film [2]. For both cathodes, the alkalis were evaporated sequentially (potassium then cesium) from Alvatec® sources; the substrate temperature was 140°C for K evaporation and 130°C for Cs evaporation. The quantum efficiency (@ 532 nm) was monitored during alkali deposition. The peak QE was 2.7% for the first cathode and 3.7% for the second. Both cathodes displayed a crystalline structure evolution, with the initial Sb crystal structure disappearing and being replaced by an alkali-antimonide structure.

The surface evolution was also monitored during deposition with XRR. Figure 2 shows an example of XRR results during evaporation of Sb and K. Fringes appear due to interference of X-rays scattered from the two interfaces (Si-cathode and cathode-vacuum); the Fourier transform (FT) of these fringes yields the film thickness. If the film is uniform, the FT will give a definite peak, while a rough film will have a smaller or non-existent peak. In general, the thicker films have increased roughness. The addition of potassium roughens the surface (and dissolves the Sb crystal structure); once sufficient potassium is added, the cathode recrystallizes and the XRR peak reappears (left hand progression of figure 2).

Figure 2: Left: XRR evolution during Sb growth. The FT allows determination of the deposited Sb thickness. Right: The same procedure was followed for tracking the K thickness during deposition. For an in-situ sputtered Sb film (18 nm), fringes appear around 3 nm. The roughness increases as K-evaporation starts; the presence of a single peak shows that K instantaneously (within 1 second) reacts and intermixes. As K-evaporation continues, the peak disappears, indicating significant roughness. For the final film (at 37 nm), the roughness decreases and the peak reappears.

Figure 3 shows XRD results for a fixed angular position ($\nu = 5$ degrees) of the detector where Sb and K peaks are detected. Initially, Sb peaks are clearly visible after deposition at room temperature (RT) onto a Si(100) substrate (Fig. 3, frame 1). There is an initial bump in the photocurrent (frame 2) while the Sb structure persists - this is thought to be the result of reduction of the material workfunction due to alkali coverage. As the K deposition continues (frames 3-4), changes in the photocurrent are monitored (right column) during growth. These changes are correlated with modifications in the crystalline structure of the cathode - the initial steep rise corresponds to the loss of Sb structure. It should be noted that the Sb crystal structure is observed to completely disappear, to be replaced 60 second later by an potassium antimonide structure. Comparison between two cathodes grown with different starting points (RT and 100°C Si(100) substrate) has been performed. Differences between these two cathodes suggest that different reaction rates between K and Sb give rise to different final performances of the cathodes. Previous studies have shown that Sb has a very clear [003] surface texture when deposited at RT; the film deposited at 100°C, while still crystalline, lacks this texture [2]. It seems feasible that differences in the original Sb configuration over the Si(100) leads to a different sticking of K, though further analysis of this effect is in progress.

Figure 3: Time evolution of the intensity of the antimony diffraction rings during potassium deposition at 140°C. The XRD data (left) is correlated with the changes in photocurrent recorded during evaporation (right). In frames 1 and 2, Sb rings are perfectly visible. Over time, these peaks diffuse and new peaks related to new crystalline structures from K appear. The rise in photocurrent shown in frame 3 corresponds to the disappearance of the Sb peaks and the formation of potassium antimonide. Top right graph shows the photocurrent evolution reaching a maximum QE value of 0.1%.
Similar sets of data were obtained for each layer evaporated while growing the cathodes. The final QE values in the range of 2.5-3.7% were obtained. The very low partial pressure of H$_2$O, CO and CO$_2$ (maintained below 2e-10 Torr) during the growth process has been recognized to play a key role in the successful performance of the final cathode. Previous studies with two orders of magnitude worse vacuum (H$_2$O partial pressure of 20 nTorr) demonstrated the same structure of the Sb film, but the evolution during K deposition in this case was very different. The Sb crystal structure dissolved, but the cathode never recrystallized, and the photocurrent rise was never observed.

After the XRR and XRD measurements were performed, SEM images of the cathodes were obtained (after brief air exposure). Figure 4 shows scanning electron microscope (SEM) and energy dispersive X-ray (EDX) images for cathode 1 and cathode 2. EDX allows measurement of the final Sb thickness - 36 nm for cathode 1, 40 nm for cathode 2, in line with expected totals based on the FTM values during deposition. Both cathodes show a segregation of K, but a relatively uniform coverage of Cs and Sb, suggesting either that K forms islands during deposition or that air exposure preferentially removes K. Sb and Cs were found in the correct stoichiometric ratio (~1:1), however a dearth of K was observed.

![Figure 4: SEM images of two different K$_2$CsSb cathodes.](image)

**CONCLUDING REMARKS**

The evolution of the crystalline structure of multi-alkali cathodes has been investigated via *in-situ* X-ray diagnostics, including XRD and XRR. The initial Sb layer formation was found to have important implications in the final performance of the cathodes. The final roughness of this initial monolayer of Sb was found to play a key role in the way the subsequent depositions of alkalis (specially the K) diffused and finally crystallized, affecting the final yield. XRD evolution over time revealed complete reaction of K with the Sb at a faster rate when the first Sb layer was grown at 100 C. However, in both cases, all of the Sb was converted to potassium antimonide eventually. Photocurrent measurements during cathode growth allow us to correlate structural crystalline changes with modifications in the yield. 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.

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