CsK$_2$Sb GROWTH STUDIES, TOWARDS HIGH QUANTUM EFFICIENCY AND SMOOTH SURFACES*

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Abstract

The properties of CsK$_2$Sb, make this material an ideal candidate as photocathode for electron injector use. Producing photocathodes with quantum efficiencies of 5 % and greater at 532 nm poses no challenge, nevertheless the traditional growth mechanisms, which are based on a sequential deposition of Antimony, Potassium and Cesium at a range of temperatures up to 150°C yield a rough surface with a rms roughness in the range of 25 nm, determined by AFM [1]. Surface roughness in this region impacts the emittance. Whereas thermal sequential deposition gives a roughness on the order of the film thickness, for high gradient accelerators, we need a roughness on the order of 1 nm in order to preserve low emittance.

Studies are performed to optimize roughness. Various growth procedures are exploited and the resulting samples' surface roughness compared.

INTRODUCTION

Within the last years multi-alkali-antimonides have been a targeted material for use as photocathode for high brightness, high repetition rate and low emittance injector applications.

Their high quantum efficiency (q.e.) in the visible region and fast response time make alkali-antimonies prime candidates. The group of interest includes K$_3$Sb, Cs$_3$Sb and a number of multi-alkali antimonide materials like CsK$_2$Sb and (Cs)Na$_2$KSb, which exhibit q.e. of >5% at 532 nm wavelength.

These materials have been used in photomultiplier tubes for several decades [2], but little is known about the detailed chemistry of these materials during synthesis. Therefore adapting this technology and transfer it into production of reproducible and reliable photocathodes for the use in photoinjectors are still ongoing.

In an effort to understand the growth procedure and reaction mechanism and finally it's influence on the photocathode behavior, in-situ growth measurements are undertaken.

Nondestructive X-ray measurements are utilized to analyze the growth and morphology of alkali-antimonies. A number of experimental techniques are being used simultaneously. Information about film thickness, roughness, crystallinity and composition are being recorded and complimented by photocurrent (phc) measurements during deposition and spectral response measurements after growth. This paper will give a short comparative analysis on tested growth methods and their resulting surface roughnesses as determined by X-ray reflectivity (XRR) for CsK$_2$Sb photocathodes.

EXPERIMENTAL

Wide angle X-ray diffraction (WAXD), X-ray scattering measurements and X-ray fluorescence (XRF) are performed in-situ during growth. After growth measurements include spectral response curves in the range from 200 - 800 nm and X-ray diffraction (XRD) measurement to verify crystallinity and composition of the crystalline phases.

Experiments are carried out at the Cornell High Energy Synchrotron Source (CHESS) at beam line G3, measurements are conducted at photon energies in the range of 9.8 keV to 11.26 keV. Two Pilatus 100K detectors are used to record the X-ray data. A Vortex-detector is positioned approx. 18 cm from the sample recording the fluorescence data. The active range of the detector starts at 2.5 keV, allowing for a reasonable detection of the K signal at 3.3 keV.

The materials are grown in a UHV system with a base pressure of $2 \cdot 10^{-10}$ Torr or below. Water and Oxygen partial pressures are in the low 10^{-12} Torr range.

Sb is deposited from PtSb beads and Alkali metals from Alvatec or SAES getter sources. The deposition rate is held around 0.2 Å/s.

The photocurrent is monitored during the growth, a bias voltage of 20 V is applied and using a 5 mW green laser to illuminate the sample.

Further information about the setup can be found elsewhere [3].

The roughness and thickness data presented here are determined by Parratt's recursion, after extracting the XRR intensity from the raw images [4].

Si(100) and MgO(001) are used as substrates. The Si substrates are cleaned in aceton, followed by isopropyl-alcohol and as a last step dipped in HF and stored in DI water until transferred to the UHV system, which could take 10 min - 2 days.

MgO substrates were dipped in DI water. Both materials are blown dry with Nitrogen prior to mounting in the UHV chamber. Then the substrates are heated to 500°C for 1- 5h, after which they are cooled down to the respected deposition temperature.

During deposition the substrate is usually held at 100°C.

Sample 1 is prepared following the sequential growth mode. Starting with a 15 nm Sb layer, followed by K deposition and monitoring of the photocurrent (phc). K deposition is stopped once the phc plateaus. Finally, Cs is deposited as long as the phc keeps increasing.

Sample 2 is a variation of the sequential growth method. The deposition sequence with respect to sample 1 is slightly changed. The deposition of Sb and K is alternated. Until a final combined Sb thickness of 10 nm was reached. As a final step the photocurrent is maximized by Cs deposition.

Sample 3 is an example of a co-deposition sample. This sample is grown following a method developed by Gosh and Varma [5]. Onto the bare substrate Sb and K are co-deposited, followed by co-deposition of Cs and Sb until the photocurrent stops increasing.

The 4th sample is the first sputtered CsK_2Sb film. The full cathode thickness of 50 nm is sputtered in one step. Further information about the sputter experiment can be found here [6].

Results

Figure 1 shows XRR scans of each step within the sequentially grown cathode, sample 1. The material is grown on Si(100), black fit. The Si substrate is relatively smooth with a surface roughness around 0.4 nm, determined from XRR. Surface roughnesses determined by AFM on Si substrates prepared in the same way, yielded a value of 0.3 nm rms roughness, which is in good agreement with the value obtained by XRR. In some cases it was found that the Si substrates exhibit a thin SiO_2 layer even though they are dipped in HF to remove the native oxide layer in advance to mounting in the UHV chamber.

Sb grows in (003) preferred orientation, as shown previously [7], and layer thicknesses determined by XRR usually agree very well with thicknesses measured with the film thickness monitor (FTM) during deposition. The thickness of the Sb layer, green curve, is 13 nm with an out of plane roughness of 0.9 nm.

The influence of the Sb layer towards the final cathode roughness are believed to be minor, since the Sb crystal structure dissolves and before the K-Sb crystalline phases appear the mixture on the surface undergoes an amorphous state [3].

A variety of crystal structures are to be found in the K-Sb system [8]. Once enough K is present on the surface the mixture starts to crystallize suddenly and the photocurrent starts to increase. The pink curve in fig. 1 shows an XRR scan of the sequentially grown K-Sb phase. From the corresponding XRD scan, not shown, it is known that cubic K_3Sb is the main component. It is apparent that the slope of the scan is already drastically different from the Sb curve, pointing to a much rougher surface. Pointing towards a much rougher surface. The light blue curve in fig. 1 was taken after Cs deposition. Here the intensity drops off even faster than for the K-Sb phase scan and almost no intensity changes are found after 1.5° incidence angle. The surface roughness as determined by XRR for this cathode, sample 1, is 3.5 nm.
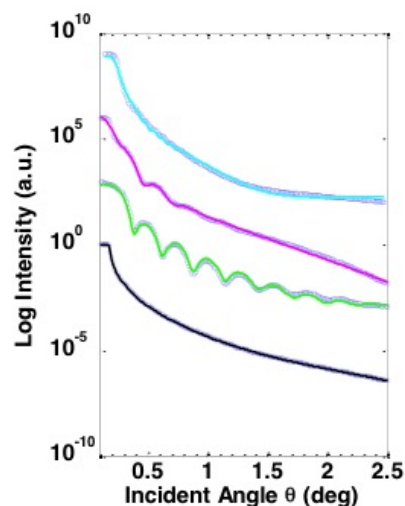

Figure 1: Sample 1: XRR scans (open circles) and fits (colored lines) of a sequentially grown cathode. Substrate (black), Sb (green), K-Sb (pink) and Cs-K-Sb (light blue). The scans are offset for clarity.

Table 1: Thickness and Roughness values in nm of various CsK_2Sb cathodes as determined by XRR in nm and the corresponding quantum efficiency at 532 nm wavelength

sample	thickness	roughness	q.e. at 532 nm [%]
1	83	3.5	6.5
2	51	0.8	0.5
3	49	5.5	6
4	51	0.6	2

In fig. 2 XRR data from an Sb and K alternating growth, sample 2, are shown. Again the scans are offset for clarity. The first scan, dark blue, is the substrate Si(100). The fit of the first Sb layer, red curve, yields a thickness of 5 nm and 0.2 nm roughness. After K deposition, green curve, the layer is 16 nm thick and the roughness has increased to 0.5 nm. The corresponding XRD scan, not shown, shows that the layer is amorphous. Subsequent Sb deposition, pink curve, does not increase the roughness. After adding K until the phc plateaus, the film is predominantly cubic K_3Sb, with a small amount of hexagonal K_3Sb, as determined by XRD. Additional Cs deposition, yellow curve, doe not increase the roughness of the K_3Sb layer and it remains at 0.8 nm.

Figure 3 shows XRR data obtained during a sample growth sequence as described by Ghosh and Varma [5]. The black curve, shows the experimental data and simulation for the Si(100) substrate scan. The first layer is grown by simultaneous deposition of Sb and K, the final layer consists of mainly hexagonal K_3Sb. This layer is approx. 32 nm thick and exhibits a surface roughness of 4.8 nm, red curve. After another layer of Cs and Sb, deposited at the same time, is grown on top of the K-Sb phase, with a thickness of approx. 50 nm, exhibits a out of plane roughness of 5.5 nm, green curve in fig. 3.
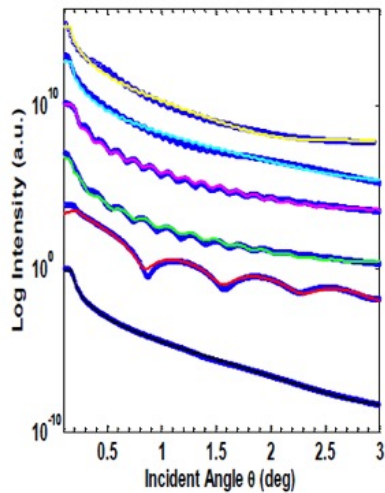
Figure 2: Sample 2: XRR scans (open circles) and fits (colored lines) of an alternating growth mode sample in which K and Sb were deposited alternative. From bottom to top: substrate (dark blue), Sb (pink), K-Sb (green), Sb-K-Sb (pink), K-Sb-K-Sb (light blue), Cs-K-Sb-K-Sb (yellow).
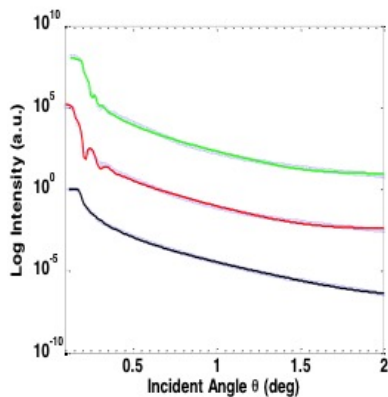

Figure 3: Sample 3: XRR measurements (open circles) and data simulation (colored lines) of a co-deposition cathode. The fit for the Si substrate (black), the K-Sb phase (red) and the Cs-K-Sb phase (green). For this cathode K and Sb were first co-deposited, followed by Cs-Sb co-deposition, similar to the growth mode described by [5]

First experiments are conducted to sputter CsK_2Sb to yield repeatedly smooth surfaces below 1 nm surface roughness. The material is grown on Si and MgO substrates and showed a sub nanometer roughness in both cases with a q.e. of about 2 % at 532 nm. For further information see [6].

CONCLUSION AND OUTLOOK

It is shown that sequentially grown samples as well as samples grown by following the growth mode described by Ghosh and Varma exhibit very rough surfaces. Nevertheless these cathodes also show the higher quantum efficiency. The alteration of the sequential growth mode, by growing

thin layers of K-Sb and final conversion to CsK_2Sb yields smoother surfaces but a much lower quantum efficiency.

Surface roughnesses below 1 nm for a full cathode are also reached by sputter deposition.

Table 1 shows some representative examples of cathode thicknesses and surface roughnesses as determined by XRR and their corresponding quantum efficiencies at 532 nm wavelength. The values give an idea on the surface roughness after growth. Nevertheless the final values determined by XRR might be misleading.

The nano structure of the cathodes surface itself might be responsible to distort simulations of the XRR scan and can lead to big differences in the roughness determined by AFM and XRR [9], as we have shown to be the case for the sequentially grown sample. In addition, XRR only measured the out of plane roughness component, whereas to understand field dependent increase in emittance, we need both the in plane and out of plane roughness. As well it is known that for samples with a huge degree of roughness the diffuse scattering cannot be excluded from calculations as done in traditional XRR simulation [10]. All in all a complimentary method to determine the surface roughness is necessary and UHV-AFM measurements are planned for the future.

ACKNOWLEDGMENT

REFERENCES

[1] S. Schubert et al., APL Materials 1, 032119 (2013).

[2] H. Kume et al., IEEE Trans. Nucl. Sci. 32, 448 (1985).

[3] M. Ruiz-Osés et al., APL Materials 2, 121101 (2014).

[4] L.G. Parratt, Phys. Rev. 95, 359 (1954).

[5] C. Ghosh et al., Journal of Appl. Phys. 49, 4549 (1978).

[6] J. Smedley et al., "Sputter growth of alkali antimonide photocathodes: an in operandi materials analysis", TUPHA003, *These Proceedings*, IPAC'15, Richmond, USA (2015).

[7] S. Schubert et al., "Influence of growth method on K_3Sb photocathode structure and performance", MOPRI018, *Proceedings*, IPAC'14, Dresden, Germany (2014).

[8] J. Sangster et al., Journal of Phase Equilibria 4, 510 (1993).

[9] O. Filies et al., Apple. Surf. Sic. 141, 357 (1999).

[10] Y. Fujii, Material Science and Engineering 24, 012008 (2011).