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FIRST STEPS TOWARD MOLECULAR BEAM EPITAXIAL GROWTH OF POTASSIUM ANTIMONIDE PHOTOCATHODES *

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Abstract

Molecular-beam epitaxy (MBE) growth with lattice-matched substrates can lead to the synthesis of single-crystal alkali antimonide photocathodes. Single-crystal photocathodes are expected to have not only high quantum efficiencies (QE) but also low mean transverse energy since they are usually grown as thin films. In this proceeding, we report the synthesis of potassium antimonide photocathodes at the PHOtocathode Epitaxy Beam Experiments (PHOEBE) laboratory at Cornell via MBE by using a sequence of shuttered growth of different unit cells. These cathodes are characterized in terms of spectral response and crystalline structure. The reflection high energy electron diffraction (RHEED) pattern acquired while synthesizing these photocathodes indicates epitaxial growth occurring on both SiC and Si(100) substrates. Oxidation studies were also performed to better understand the robustness of these materials under non-ideal ultra-high vacuum (UHV) conditions.

INTRODUCTION

The Center for Bright Beams (CBB) [1], a National Science Foundation Science & Technology Center, has been working on ways to increase the brightness of electron beams which is a central figure of merit for applications in science, medicine, and industry [2]. One of the center's objectives is to improve the photoemission performance of photocathodes, given that the maximum brightness obtained from an electron beam in a linear accelerator is determined by its source [3, 4].

A natural way in this direction is to look for materials with high quantum efficiencies (QE) and low mean transverse energy (MTE) of photoelectrons. Alkali antimonides semiconductors are already known because of their high QEs [5], however, depending on how these semiconductors are grown, their surfaces are typically rough and films are polycrystalline, which increases the emitted momentum spread and therefore the MTE.

Consequently, growth methods that lead to smooth, thin, and ordered photocathodes are the target of many researchers. In this proceeding, we report on the first steps toward epitaxial growth of potassium antimonide photocathodes. Different growth techniques were studied and compared in terms of the quality of the film, as indicated by the reflection high energy electron diffraction (RHEED) pattern, the photocathode spectral response, and the robustness to controlled oxygen exposure.

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EXPERIMENTAL DETAILS

All samples have been grown and characterized at the PHOtocathode Epitaxy Beam Experiments (PHOEBE) laboratory at Cornell [6]. All substrates have been cleaned by cycles of 15 min sonication in the following solutions: deionized water with a few drops of Micro 90, deionized water, methanol, and isopropyl alcohol. The substrates are then annealed in vacuum at temperatures between 450 C and 650 C. For SiC, substrates are annealed until a clear RHEED pattern is observed, about 15 to 30 min. The beam energy for RHEED was 15 keV.

During the growth, the sample is constantly illuminated with green light at 532 nm and the photocurrent of the sample is collected by measuring the drain current from the electrically floated sample holder, which is biased at -40 V. Then the QE is calculated with respect to the incident light source. RHEED images are taken at different stages of the growth to monitor the crystallinity of the formed film. RHEED images were processed using an FFT-Bandpass filter with ImageJ software. This filter enhances the discernibility of features against background noise, thereby improving overall contrast [7].

Once the growth is completed, samples are moved to a storage chamber for spectral response measurements [6]. During spectral response measurements, the sample is illuminated with an Oriel Apex Monochromator light source, and the photocurrent of the photocathode is collected with a Keithley picoammeter 6487 from a metallic coil placed 5 cm from the samples and biased at +120 V. For oxidation studies, the photocathodes are moved back to the growth chamber and dosed with oxygen of purity 99.999% through a leak valve. The partial pressure of oxygen is monitored with an RGA while the QE at 455 nm is measured.

RESULTS

Deposition Method

Two deposition methods were studied for these cathodes: sequential deposition and coevaporation. For sequential deposition (Sample SbK_001), a thin layer of Sb (~ 4 nm) is deposited first on a SiC substrate at 120 C, then the temperature of the substrate is decreased to 100 C followed by K deposition. The total thickness of the K layer is estimated to be 17 nm based on previously obtained QMB flux measurements. For coevaporation (Sample SbK_002), a two-step deposition/crystallization process, as described in [8], is performed using K source instead of Cs. Briefly, a sequence of shuttered growth of two unit cells (u.c.) are deposited on

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a SiC substrate at a substrate temperature of 80 C. Then, the sample is heated to the crystallization temperature of 130 C. The sample is left to this temperature for 15 minutes and finally cooled back to the growth temperature. Crystallization and cooling are done under K flux. This cycle is repeated three times for a total of 6 u.c. (~ 6 nm).

The lattice parameter of the SiC is a_{SiC} = 4.36 Å, which is close to that for cubic K_3Sb ($a_{K_3Sb}/2$ = 4.23 Å) [9] with a strain of ~ -3 %. Therefore, SiC is a natural choice for growing epitaxial K_3Sb photocathodes.

The RHEED images of the SiC substrate and samples SbK_001 and SbK_002 are shown in Fig. 1. The substrate was annealed at 650 C for 30 minutes, then cooled down to the growth temp. Figures 1a and 1b show the two orientations of the SiC substrate, SiC[10] and SiC[11] respectively, right before the deposition started. For the case of sample SbK_001 grown by sequential deposition, a ring pattern is observed (Fig. 1c), while the two-step method led to a partial streaks pattern (Fig. 1d). The fact that the RHEED pattern is different for each sample shows that the deposition method plays a crucial role in the crystallization of the photocathodes. In this system, sequential deposition leads to a polycrystalline cathode, whereas the two-step method allows the formation of a more ordered film and, therefore promotes epitaxial growth.

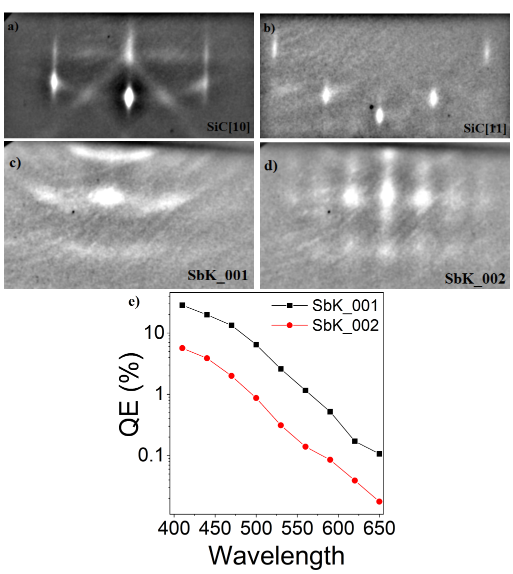

Figure 1: RHEED Images of: Annealed SiC a) orientation [10], b) orientation [11], Samples c) SbK_001 grown by sequential deposition and d) SbK_002 grown by coevaporation. e) Spectral Response.

Although RHEED partial streaks pattern from sample SbK_002 indicates an epitaxial growth of potassium antimonide, further analysis is needed to confirm the stoichiometric of the photocathode and is beyond the scope of this proceeding. However, some additional information about the quality of the film can be inferred from Fig. 1d. First, the fact that the streaks are wide indicates small domain formation, additionally, the modulation on the streaks shows that the film is not flat but rough. Better growth conditions are needed to improve the film's quality, nevertheless, this work shows that the epitaxial growth of potassium antimonide is within reach.

The spectral response of each sample was also measured, and results are shown in Fig. 1e. Although the sample grown by sequential deposition seems to perform better, i.e., QEs are higher for this sample, it is important to note that the thickness is different for each film. SbK_001 film is thicker than SbK_002, which may explain the higher QEs. Nevertheless, the peak in QE in the visible exceeds 1% as expected for these materials [5].

Oxidation Experiments

New samples were grown using the two-step shuttered method for oxidation experiments, SbK_007 and SbK_008. The growth and crystallization temperatures for these samples were 70 C and 120 C respectively, and the thickness of each sample is ~6 nm. Figures 2a and 2b show the RHEED patterns for each sample. In both cases, RHEED images show spotty streaks, which indicates that films are grown ordered but rough. Although these photocathodes were grown under similar parameters, the RHEED pattern for sample SbK_008 is more intense. This is because this sample was grown on a new substrate, which may account for the better quality of the film.

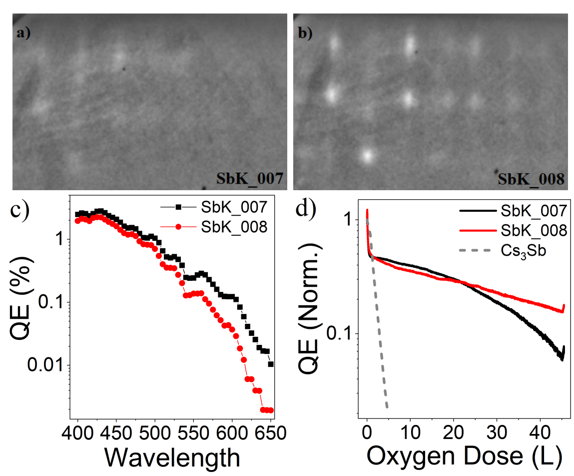

Figure 2: RHEED Images of films a) SbK_007 and b) SbK_008. c) Spectral response, and d) oxidation response.

The spectral response of these samples is shown in Fig. 2c. Similar QEs are seen for both samples at wavelengths lower than 535 nm, but for high wavelengths, there is a decrease in QE of one order of magnitude. The difference in QE can be due to higher partial pressures in the system at the time of the growth, leading to different oxidation species or contamination at the surface. Sample SbK_007 was grown at a pressure of 8.8x10^{-8} Torr, while the pressure for sample SbK_008 was 1.0x10^{-7} Torr.

Oxidation studies were done on both samples. Each sample was exposed to controlled levels of oxygen and the photocurrent at 455 nm was recorded. The normalized QE as

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Table 1: Sample's Growth Specifications

Sample	Growth Method	Substrate	Sources Temperature Sb / K (C)	Thickness (nm)	QE at 530 nm (%)
SbK_009	Shuttered	SiC	375 / 265	6	0.38
SbK_014	Codep.	SiC	368 / 253	7.5	1.82
SbK_015	Codep.	SiC	366 / 253	3.5	0.88
SbK_017	Codep.	Si(100)	366 / 253	5	0.22

a function of the oxygen dose for both samples is shown in Fig. 2d. The oxygen dose is measured in Langmuir (L) equivalent to 1x10^{-6} Torr x 1 s. These results show that although the QE of both samples goes down quickly with little oxidation, the degradation is not as fast as the case of Cs_3Sb (gray dashed line), therefore, these photocathodes can live in an oxygen environment for longer times.

The degradation of sample SbK_007 is faster after 20 L than for sample SbK_008, which indicates that although the samples were grown with the same substrate temperatures and source fluxes, the partial pressure of the system at the time of the growth plays a significant role on the surface of the samples. Further studies are needed to understand and characterize this observation.

Different Growth Parameters

To improve the roughness of the photocathodes, four more samples were studied with different growth parameters, a summary of the growth parameters of each sample is presented in Table 1 along with their final QE at 530 nm. All samples were grown at a single substrate temperature of 100 C. RHEED images for all samples are shown in Fig. 3. Sample SbK_009 was grown using the shuttered technique mentioned before but at a single temperature. The other three samples (SbK_014, SbK_015 and SbK_017) were grown by codepositing both sources, K and Sb, instead of the shuttered method.

RHEED images in Fig. 3 not only demonstrate some ordering formation but also show less vertical modulation on the intensity of the streaks, which indicates less rough films. These results also indicate that potassium antimonide photocathodes tend to prefer single-temperature growth, unlike cesium antimonide [8], which could be attributed to the fact that the lattice mismatch strain between SiC and cubic K_3Sb is smaller than in the case of Cs_3Sb which facilitate the epitaxial formation and therefore no crystallization step is needed.

The spectral response of these photocathodes varies significantly, as shown in Fig. 3e. The differences in the thicknesses of the samples may account for this discrepancy, but the formation of different species at the surface cannot be ruled out, in particular for the case of sample SbK_015 which is the thinner sample and has QEs similar to the thicker sample SbK_009. X-ray photoemission spectroscopy studies are suggested to better understand and characterize the surface formation of these cathodes.

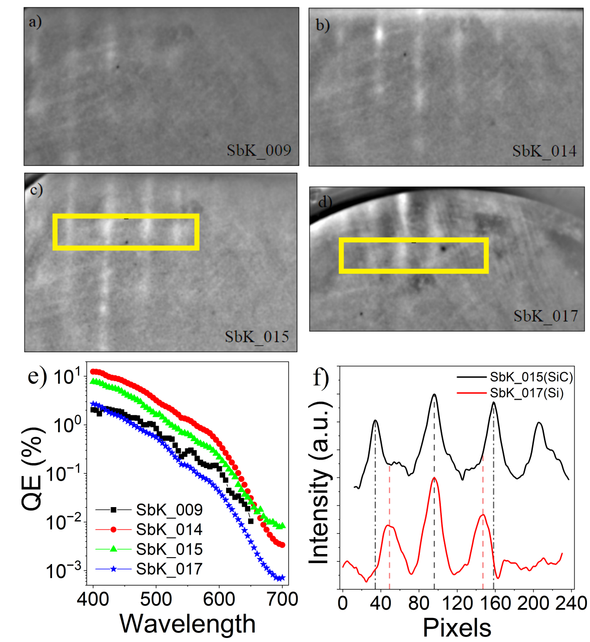

Figure 3: RHEED Images of films a) SbK_009, b) SbK_014, c) SbK_015 and d) SbK_017. e) Spectral Response, f) RHEED profiles.

Finally, Fig. 3d shows the domain formation of potassium antimonide on a Si(100) substrate. In this case, the formation of cubic K_3Sb is ruled out since the Si(100) has a lattice parameter of 5.43 Å(strain ∼ −28%). Yet, the formation of hexagonal KSb_3 (lattice parameter 5.55 Å) is expected due to a smaller strain (∼ 2%). Line profiles of samples SbK_015 and SbK_017 from the area marked with a yellow rectangle in Figs. 3c and 3d are shown in Fig. 3f. These profiles demonstrate that the grown samples have different lattice parameters.

CONCLUSION

First steps toward epitaxial growth of potassium antimonide have been demonstrated. These photocathodes not only exhibit high QE compared to metals but also are robust under oxygen environments which makes them interesting in applications where ultra-high vacuum (UHV) conditions are not obtainable. X-ray photoemission spectroscopy studies are suggested to characterize the stoichiometry of these cathodes and the oxidation states at the surface.

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