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SYNTHESIS OF ORDERED SODIUM POTASSIUM ANTIMONIDE PHOTOCATHODES VIA MOLECULAR BEAM EPITAXY*

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Abstract

Alkali antimonide photocathodes are recognized for their efficacy as photoemissive materials in electron sources. This study explores the fabrication of thin, ordered films of sodium potassium antimonide via Molecular-Beam Epitaxy (MBE) at the **PHO**tocathode **E**pitaxy **B**eam **E**xperiments (PHOEBE) laboratory at Cornell University. We utilized a co-deposition technique to reduce the Mean Transverse Energy (MTE) while maintaining high quantum efficiency (QE). The synthesized photocathodes were characterized in terms of their QE and crystal structure. QE measurements across the 400- to 700-nm wavelength range demonstrated oscillations correlated to optimized optical interference effects on silicon nitride (SiN) substrates. Reflection high-energy electron diffraction (RHEED) patterns confirmed the successful growth of ordered crystal structures for the first time. Additionally, we investigated the photocathode's sensitivity to oxidation, revealing their relative robustness. In particular, incorporating higher partial pressures of oxygen during growth improved the QE and extended the operational lifetime of the photocathodes grown on Si substrates.

INTRODUCTION

The **PHO**tocathode **E**pitaxy **B**eam **E**xperiments (PHOEBE) lab looks to improve beam brightness through photocathode improvements, including increasing QE and targeting single- or ordered-crystal growth to limit the momentum spread of outgoing electrons.

Using Molecular-Beam Epitaxy (MBE), the alkali and antimony solid sources are evaporated, forming a molecular beam that deposits thin layers – down to single monolayers onto a crystalline substrate. Depositing on lattice-matched substrates allows the formation of single-crystal photocathodes.

Due to their high QE, alkali-antimonide photocathodes are ideal candidates for creating bright beams, but with current growth techniques, the crystal structure is likely disordered. Growing on a substrate with a good lattice match to the desired photocathode stoichiometry can induce ordered growth and lower the Mean Transverse Energy (MTE) of the resulting electron beam, for example, by reducing surface roughness. Na-K-Sb photocathodes have been widely utilized as electron sources as they produce a high QE, 16% at 400 nm and 7.5% at 500 nm [1], at a thickness in the range of 120 nm [2]. However, by focusing on the crystal structure of the photocathode during growth, the roughness properties and crystallinity can be controlled while maintaining QE.

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EXPERIMENTAL DETAILS

All Na-K-Sb samples were grown on Si(111), Si(100), or SiN(100) substrates, each undergoing the same cleaning process: each substrate and substrate/sample holder is sonicated for 15 minutes in the following solutions: deionized water with a 2-3 of drops of Mirco-90, deionized water, methanol, and isopropyl alcohol. The PHOEBE MBE system uses effusion cells to control material fluxes via the source temperature. Fluxes are measured by a Quartz Micro-Balance (QMB). A 2:1:1 ratio between fluxes is used to target Na_2KSb synthesis. This stoichiometry is chosen because the lattice match for Na_2KSb is superior to the NaK_2Sb match for all three substrates. Minimized strain and lower matching ratios can stimulate smoother and ordered crystal growth. A matching ratio in this context is defined to be the ratio of unit cells of the materials of interest that create the lowest strain. Na_2KSb has a cubic crystal structure with a lattice parameter of 7.70 Å. NaK_2Sb also has a cubic structure but a lattice parameter of 8.304 Å [3]. Growths were started on Si, a cubic crystal with a lattice parameter of 5.40 Å [4]. Stoichiometry was decided based on minimized strain and matching ratio between unit cells, with a maximum ratio of 1:10 or 10:1 (Si:Na_xK_ySb). Na_2KSb has an optimized strain of 1.29% with a matching ratio of 7:5. Whereas, NaK_2Sb has an optimized strain of 1.95% with a matching ratio of 9:6. This process was also utilized in determining the desired stoichiometry for the growth on the hexagonal Si_3N_4 substrate. Na_2KSb has an optimized strain of 1.32% with a 1:1 ratio, and NaK_2Sb has an optimized strain of 2.88% with a ratio of 9:8 (Si_3N_4:NaK_2Sb). The SiN substrate consists of a 300 nm thick Si_3N_4 layer on top of a Si substrate. Additionally, this substrate is polycrystalline and rough compared to the single-crystal Si substrates.

Before growth, the substrate is annealed at a range of temperatures between 450-1200 °C to remove organics from the cleaning and oxides from the surface. After annealing, with the substrate at growth temperatures, a Residual Gas Analyzer (RGA) is used to determine the background partial pressures of the system before growth. Fluctuations in alkali metal partial pressures are common due to successive growth, which contributes to additional, unaccounted-for

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fluxes during depositions. Additionally, residual oxygen background pressure is present in close temporal proximity to oxidation studies.

During growth, Reflection High-Energy Electron Diffraction (RHEED) is observed to identify the crystal structure of the cathode surface. The RHEED includes an electron gun positioned such that electrons reflect off the cathode surface and hit a phosphor screen. The pattern visible on this screen can provide qualitative, and in some cases, quantitative information on surface ordering/crystallinity. Streaks indicate layer-by-layer or step-flow, while rings indicate polycrystalline growth. The modulation of streak intensity and transition to a transmission pattern, characterized by spots, indicates roughening and 3D island growth. To determine if the sample is single-oriented, it must exhibit the correct periodicity upon azimuthal rotation. QE can also be measured during growth by illuminating the sample with a specific wavelength laser, the resulting photocurrent can be determined by measuring the drain current from the electrically floated sample holder, which is biased at −40 V.

Following growth, the samples are moved to a separate storage chamber for spectral response measurements. For these 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 sample and is biased at 120 V. QE measurements are taken from 400 nm to 700 nm.

Oxidation studies can be performed in the growth chamber using a leak value to dose oxygen of 99.999% purity. Oxygen partial pressures are monitored throughout using the RGA, and the photocurrent is measured at 402 nm.

RESULTS

Each photocathode was grown using a co-deposition method, where Na, K, and Sb are simultaneously evaporated. For certain growths, QE is measured during deposition. Film thickness ranges from 8.64 nm to 135 nm.

Si(100) and Si(111)

Focusing on five samples (Table 1), differences between spectral response measurements can be identified (Fig. 1(f)). Although these samples are grown on different substrates, there is no clear correlation between spectral response trends and Si(111) or Si(100). RHEED images taken after the growth indicate two distinct crystal structures, including ordered growths [Figs. 1(c-e)] and polycrystalline growths, Fi. 1(b). Figure 1(a) also shows a RHEED indicating both ordered and polycrystalline structure. The RHEED taken from Sample 022 indicates the surface is rough; this can be attributed to the large mismatch between the substrate and film, as discussed above.

High QE at WLs higher than 540 nm are seen for samples 005 and 023. These samples both show a polycrystalline structure, not shown by the lower QE sample (Samples 019, 006, 022). The development of a polycrystalline structure

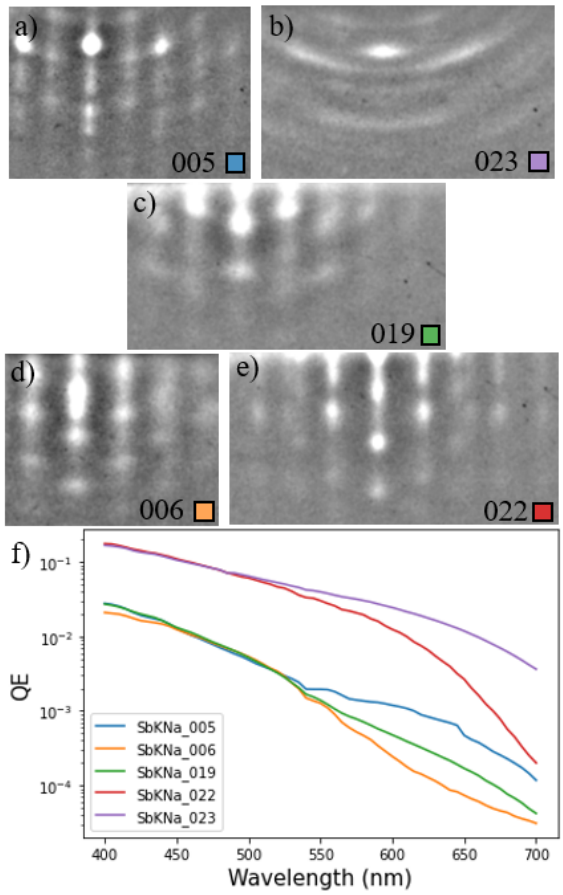

Figure 1: All RHEED images in these figure have a bandpass filter a) RHEED image from sample 005, spotty streaks and rings equally visible b) RHEED image from sample 022, rings visible c) RHEED image from sample 019, spotty streaks with faint ring pattern visible d) RHEED image from sample 006, spotty streaks visible e) RHEED image from sample 023, spotty streaks visible f) Spectral response of cathodes grown on Si substrate from 400 to 700 nm.

can likely be attributed to the quality of the substrate surface, material flux, or other uncontrolled factors. Although the RHEED images are still 3D-like and angle dependence is not yet seen, sample 022 provides proof of some crystalline alignment and therefore an ordered growth. Continued observation of the spectral response results evinces another distinct separation between samples. High-QE samples are characterized by a QE >10% at 400 nm, while the low-QE ones have a QE close to 2% at the same wavelength. This behavior can be linked to the oxygen partial pressure during growth, which was in the range of 1×10^{-10} Torr for the high-QE samples.

Enhanced QE was seen when cathodes remained in the growth chamber with similar oxygen partial pressure. Sample 022 was left in the growth chamber overnight, with an oxygen background of the order of 1×10^{-10} Torr, and QE increased from 17.6% to 18.1%. Meanwhile, Sample 023, which was left in the storage chamber, displayed a QE decrease from 16.7% to 9.45%.

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Table 1: Na-K-Sb Sample Data on Si Substrate

#	Si Substrate	Sample Holder Temp (°C)	Na/K/Sb Temp (°C)	Thickness (nm)	Crystallinity	Oxygen BG (10^{-10} Torr)	QE @ 400 nm (%)
#005	100	110	260/265/380	20.7	mixed	0	2.78
#006	111	120	260/265/380	8.64	ordered	0	2.09
#019	100	100	260/255/380	30.5	mixed	0	2.72
#021	100	100	260/255/380	71.3	ordered	3.36	13.8
#022	111	100	257/244/386	124	ordered	8.64	17.6
#023	111	100	257/244/386	113	poly	6.43	16.7

Si_3N_4

All samples grown on SiN substrates were prepared using the same source temperatures: Sb at 380 °C, K at 255 °C, and Na at 260 °C. Samples of different thicknesses were deposited by varying the deposition duration. RHEED images from these films indicate ordered behavior, albeit a rough surface texture, which is expected from the substrate quality, Figs. 2(a, b). The spectral response of these cathodes exhibits a peak around 500 nm. The thickness of the cathode is related to the size of this peak, which is due to an optical interference phenomenon from the substrate. Similar results are seen for Cs_3Sb samples grown on SiC [5]. Figure 2(c) shows the spectral response results normalized at 400 nm. The 90 min cathode was grown on top of the 45 min cathode, and the 135 min cathode was grown on top of the 15 min cathode. The QE values observed for samples at 400 nm ranged from 1% to 5%, increasing from the first to the second deposition both times. The thickness of these samples is directly proportional to the time of growth, with an average monolayer time of 1 min/monolayer.

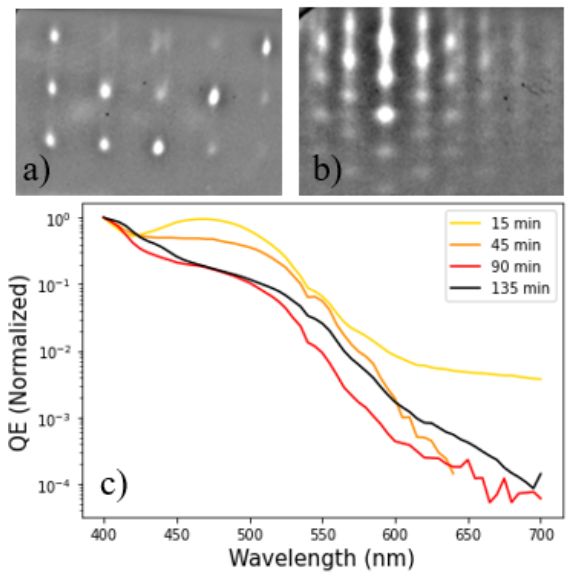

Figure 2: a) RHEED image of SiN substrate with bandpass filter b) RHEED image from 135 min sample with bandpass filter c) Normalized Spectral Response: Na-K-Sb on SiN.

Si Oxidations

Photocathodes grown on Si were used for oxidation experiments. Approximately 40 Langmuir of oxygen is slowly released into the system for each oxidation. During oxidation, only the sample photocurrent is measured as opposed to QE. At the beginning of the oxygen exposure, the samples' photocurrent increases, followed by a rapid decrease. This can be seen in Figure 3 as the normalization was performed about the photocurrent when the dose was equal to 0 L. Films grown with higher oxygen background pressure had smaller magnitude peaks. After closing the oxygen source, the photocurrent showed a small recovery. For example, sample 023 was still photoemitting the day after oxidation at 2% of the pre-oxidation values. The reasoning behind the two different oxidation trends needs to be further explored. Na-K-Sb photocathodes are more robust to oxygen than Cs_3Sb, and some Na-K-Sb samples showed a similar robustness to CsSb (Fig. 3).

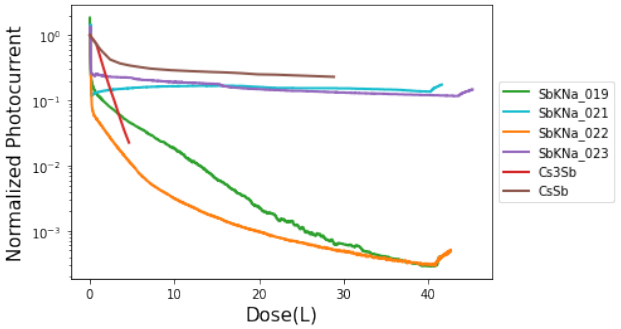

Figure 3: Oxidation of Na-K-Sb on Si compared to Cs_iSb_j.

CONCLUSION

Ordered Na-K-Sb growths have been synthesized on Si(111), Si(100), and Si_3N4 substrates, with QE values consistent with previous studies. Na-K-Sb has exhibited resilience to oxygen, remaining photoemitting for up to 40 Langmuir.

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