Antiperovskite Thin Films Grown by Plasma-Assisted Molecular Beam Epitaxy

Madison Miller

Materials Science and Engineering, University of Florida

2022 Cornell NanoScale Science & Technology Facility International Research Experiences for Undergraduates (CNF iREU) Program

CNF iREU Principal Investigator: Dr. Takeo Ohsawa, Electroceramics Group, Research Center for Functional Materials, National Institute of Material Science (NIMS), Tsukuba, Ibaraki, Japan

Primary Source(s) of Research Funding: 2022 CNF iREU Program via NSF grant NNCI-2025233

Contact: madison.miller@ufl.edu, ohsawa.takeo@nims.go.jp

Website: https://cnf.cornell.edu/education/reu/2022

Abstract:

Antiperovskite crystals are of increasing interest in the semiconductor industry because of their narrow bandgap and potential to be used for near infrared applications. These crystals have the same structure as perovskites, but the positions of the cations and anions are switched; this results in a stoichiometry of R_3MO where R is an alkali earth element and M is a metal [1]. Current material options for near-infrared semiconductor devices are all toxic, which is not ideal for potential biomedical applications. Ca_3SiO is a nontoxic antiperovskite that has a narrow, direct bandgap and is a near infrared semiconductor that could replace current toxic options. However, thin film fabrication of this material must be improved before the use of Ca_3SiO in near infrared devices can be realized.

Introduction:

The goal of this project was to use plasma-assisted molecular beam epitaxy (PA-MBE) to grow Ca_3SiO thin films, determine ways to control the Ca/Si composition of the films, and determine the crystal orientation and crystallinity of the Ca-Si-O thin films grown using PA-MBE. Twenty thin films were deposited on $SrTiO_3$ (100) substrates over a range of Ca temperatures, and each film was capped using Al_2O_3 that was also deposited using PA-MBE. The films were then characterized using X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and X-ray fluorescence (XRF). It was found that the Ca/Si beam equivalent pressure (BEP) ratio could be used to tune which Ca-Si-O phase was deposited, and CaO is preferentially formed due to the high concentration of Ca. One of the samples had the desired Ca_3SiO composition, while the rest of the films contained other phases such as $CaSiO_3$ and Ca_2SiO_4. The Al_2O_3 capping layer was found to be effective in protecting the Ca_3SiO from reacting with air. Future goals include improving the reproducibility of Ca_3SiO formation as well as optical and electrical transport characterization of these films.

Summary of Research:

First, the $SrTiO_3$ (100) substrates were annealed at 1100°C in air to create an atomically flat surface for the film to be deposited on. Atomic force microscopy was used to verify that the substrate surface was atomically smooth. Then, PA-MBE of Ca and Si was conducted for two hours with the substrate temperature set at 900°C. The silicon cell temperature was kept constant for all samples, while a range of temperatures between 400 and 600°C were tested for the calcium cell. The BEP ratios for the range of Ca temperatures tested are shown in Figure 1. Oxygen was flowed in the chamber and the partial pressure ranged between 0.5 and 3.0 × 10^{-5} torr during the deposition process for each sample. After this deposition, the substrate temperature was lowered to approximately 100°C and Al deposition was conducted for two hours to form an Al_2O_3 capping layer. The temperature of the Al cell was 850°C. Each sample was then characterized using XRD, XRF, and XPS to determine the composition and structure of the films.

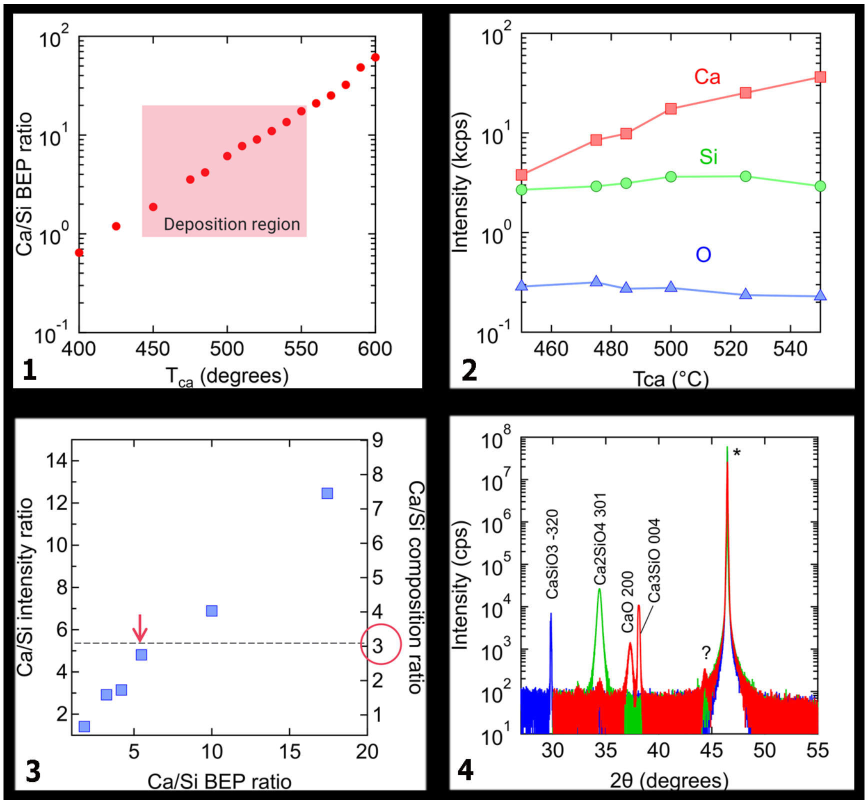

*Figure 1, top left: A plot showing the Ca/Si beam equivalent pressure (BEP) ratios for the Ca temperature range used for deposition, which is indicated by the red box. The Si temperature remained constant. Figure 2, top right: Intensity vs calcium deposition temperature for Ca, Si, and O, taken using XRF. Figure 3, bottom left: A plot showing the Ca/Si composition ratios for each Ca/Si BEP ratio used for sample deposition. The ideal Ca/Si composition ratio is 3, and the sample closest to this ratio is indicated by the red arrow. Figure 4, bottom right: A high-resolution XRD scan of three samples deposited at different Ca/Si BEP ratios. The peak labeled with * is a characteristic peak of the $SrTiO_3$ substrate.*

Conclusions and Future Steps:

The XRF measurements collected for the samples confirmed that the calcium intensity increases as the Ca temperature increases, which is shown in Figure 2. The Si and O intensity was relatively constant across all samples since the growth parameters for these two materials were kept constant. For the desired Ca_3SiO film, the ideal Ca/Si composition ratio should be 3. A wide range of Ca/Si ratios were measured for the samples as can be seen in Figure 3. By looking at this data it can be seen that the composition ratio changes as the Ca/Si BEP ratio changes. A Ca/Si BEP ratio of 5.5 resulted in a sample with a nearly ideal composition ratio of 3. This film was also the only sample that had a Ca_3SiO peak in its XRD spectrum. The characteristic peaks for the Ca-Si-O compounds present in the films are within the 25° to 55° region of the XRD spectrum; a high-resolution scan of this region for three different samples is shown in Figure 4. The three samples shown in this spectrum are characteristic of all of the films, as they show the three primary stoichiometries found in the samples: $CaSiO_3$, Ca_2SiO_4, and Ca_3SiO. There were also CaO peaks present in most of the sample spectra, which is due to a high concentration of Ca in the sample.

The presence of different Ca-Si-O phases for different deposition conditions indicates the Ca/Si BEP ratio could be used to tune the phase of the final film. However, this relationship will need to be further studied since only one film had the desired Ca_3SiO structure despite multiple samples being deposited at the ideal 5.5 Ca/Si BEP ratio. In addition, Ca_3SiO is known to be reactive in air, so the effectiveness of the Al_2O_3 capping layer was tested by conducting XRD again one month after depositing the film. There were no changes in the XRD spectrum, which indicates that aluminum oxide is effective at protecting the Ca_3SiO phase in air.

The relationship between the Ca/Si BEP ratio and Ca/Si composition needs to be further investigated to improve the reproducibility of Ca_3SiO formation. Future deposition processes can be conducted at different substrate temperatures, Si flux, or different oxygen content to better tune the composition of the final films. Another area of interest is optical and electrical transport characterization for these films.

References:

[1] Quintela et al., Sci. Adv. 2020; 6 : eaba4017.