Understanding how to incorporate single crystal BTO (111) on 6H-SiC (0001) for next-generation electric devices

Sue-Jonnathane Celestin, Katherine S. Ziemer
Chemical Engineering Department, Northeastern University, Boston MA, 02115, USA

October 5th, 2016
11:45am, in 105 Shillman Hall

Barium titanate ($BaTiO_3$ or BTO) has attracted a great deal of interest because of its potential use in applications that range from thin-film capacitors to ferroelectric and piezoelectric devices [1]. However, there is less research exploring BTO as a thermoelectric material in devices. Other oxides have recently been shown to possess a high Seebeck coefficient (100 μV/K) defined as the resulting voltage in response to a temperature gradient, and a low resistivity (200 μΩ cm) [2], suggesting that BTO may also be a good candidate for thermoelectric application. This work investigates the growth mechanisms and processing windows that are anticipated to promote high quality, stoichiometric epitaxial BTO -single crystal (111)-oriented films on semiconductor substrates to explore BTO's potential as a thermoelectric material.

Many of the physical properties of complex oxides, including BTO, are directional and are strongly dependent on the details of the cationic and oxygen stoichiometry. Complex oxides often have multiple structures for a given stoichiometry, therefore small changes in stoichiometry within the unit cell can affect the structure and resulting properties. Moreover, as the substrate surface controls both crystal quality and orientation, it is necessary to understand the physical mechanisms involved in the nucleation and growth of thin films on solid surfaces. For BTO, we have shown in previous work that it is necessary to use a thin crystalline MgO (111) film as a template layer or interlayer to minimize the strain between BTO and a 6H-SiC substrate [3]. However, the nucleation and growth mechanism for controlling BTO desired film properties are still unknown.

Molecular beam epitaxy (MBE), which provides control of crystal growth at the atomic level, was used to grow the MgO (111) thin film layers and the BTO (111) thin films. The impact of atomic flux on the crystalline quality of the BTO films was then studied by Reflection high energy electron diffraction (RHEED), a technique used to characterize and monitor the surface and crystal orientation of growing films in real time. X-ray photoelectron spectroscopy (XPS) was used to characterize the atomic chemistry, bonding states in the films and the cationic (Ba/Ti) ratio.

6H-SiC(0001) substrates were cleaned in an *ex-situ* hydrogen furnace which produces an atomically smooth, stepped surface with a $\sqrt{3}\times\sqrt{3}$ R30° surface reconstruction, verified by RHEED and XPS. The XPS scans of hydrogen-cleaned 6H-SiC surface repeatedly show 10 at% or less oxygen contamination on the surface. This aspect, along with the sharp non-diffusive spots known as intermediate Laue rings observed in the RHEED pattern, confirm attainment of the $\sqrt{3}\times\sqrt{3}$ R30° surface reconstruction of the substrate.

The barium flux was controlled by changing the temperature of the effusion cell and the titanium flux was controlled by varying the power supply current of the titanium source. The Ti flux was held constant and the Ba flux varied and the Ba/Ti ratio in the film measured. To enable effective comparison between samples, the substrate temperature and the oxygen flux was held constant. Figure 1 shows the effect of increasing the barium flux on the crystal structure of the

film, where it can be seen that while the Ba/Ti flux ratio is approaching the desired value of 1, the crystallinity is decreasing.

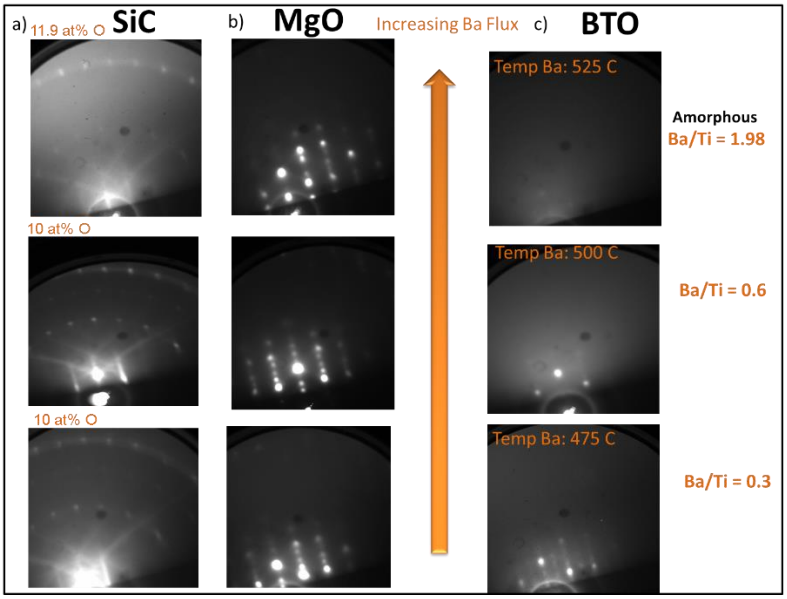

Figure 1: RHEED patterns of a) hydrogen cleaned 6H-SiC with 10 at% oxygen contamination (b) MgO film grown on hydrogen-cleaned 6H-SiC showing 3D growth features. c) BTO film grown at using different barium flux

The XPS results of the MgO (111) films grown on 6H-SiC indicate that the quality of the starting surface has great impact on surface chemistry and structure of the subsequent-layers. Figure 1 shows the RHEED patterns of the hydrogen-cleaned 6H-SiC substrate, the MgO (111) layer and the BTO (111) films. The spotty RHEED patterns of the MgO (111) films suggest that the films follow a 3-D growth mechanism. For the BTO films, the RHEED patterns corresponding to the BTO (111) surface indicate that changing the Ba/Ti flux ratio does impact both the crystallinity and the stoichiometry. XPS results show that the Ti atoms are in the desired TiO_2 environment and the Ba atoms are in a BaO environment, however none of the films are stoichiometric BTO. These results indicate that it is necessary to find a balance between the three (Ba, Ti, O) independent flux variables in order to obtain stoichiometric BTO (111) films.

We thank the chemical engineering department of Northeastern University for support.

References:

1. Hongtao X., Pervez N.K., York R.A. *Tunable microwave integrated circuits BST thin film capacitors with device structure optimization*. *Integr. Ferroelectr.* 2005, 77: 27–3535
2. I. Terasaki, Y. Sasago, K. Uchinokura *Large thermoelectric power in $NaCo_2O_4$ single crystals.* Physical Review B, 56, 1997
3. T. L. Goodrich, Z. Cai, M. D. Losego, J.-P. Maria, L. F. Kourkoutis, D. A.Muller, and K. S. Ziemer, "Improved epitaxy of barium titanate by molecularbeam epitaxy," *Journal of Vacuum Science Technology B*, vol. 26, p. 024803, 2008.