In situ Heating Studies of Flux Grown Barium Titanate Thin Films

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The crystallization and microstructural evolution of barium titanate (BaTiO_3) thin films were studied by *ex situ* and *in situ* TEM. Previous investigations illustrated that the addition of a boron-based glass flux, $\text{BaO} \cdot \text{B}_2\text{O}_3$ (BBO), improved electrical properties, such as improved tunability, which was hypothesized to be the result of less porosity and larger grains than without BBO addition[1].

To investigate the effects of BBO addition, *ex situ* studies were performed by depositing BaTiO_3 (0% and 5% BBO) via pulsed laser deposition onto sapphire substrates. The thin films were annealed for 1 hr. at 900°C and then thinned mechanically (cross section view) to electron transparency. Materials with 5% BBO addition exhibited highly dense films with moderately sized (121 nm), well-formed grains, as shown in figure 2a. This was contrasted by materials with 0% flux addition, shown in figure 1a, which had smaller grains (56 nm) than the material with 5% BBO and more significant porosity.

In situ heating studies were performed with a custom Protochips Aduro™ TEM holder and Protochips Aduro™ heating “e-chips,” which resistively heat a ceramic membrane topped with a holey carbon film. BaTiO_3 films with 0% and 3% BBO addition were deposited directly on holey carbon films and heated in the TEM. As can be seen in the diffraction patterns of figures 1b and 2b, both samples were amorphous as deposited even though they appear to be nanostructured. Samples were annealed by increasing the temperatures in 20°C intervals. Crystallization events were observed in both samples around 760°C , as in shown figures 1c and 2c. Islands appeared to form in materials with 3% BBO, though it is not yet understood the cause of this behavior. Both 0% and 3% BBO materials were then annealed at 1100°C for 6 and 8 minutes, respectively.

The annealed materials, shown in figures 1d and 2d, had strikingly different microstructures. Grains within 0% BBO samples coarsened significantly, leading to large amounts of porosity. Conversely, the 3% BBO materials remained continuous. This difference in annealing behavior was attributed to flux addition slowing initial grain growth in the 3% sample, which results in the lack of the pores like those seen in the 0% sample. The fact that the film with flux is more continuous than that without flux is consistent with the *ex situ* studies. However, the fact that the grains in the non-fluxed samples grew larger than those in the fluxed samples seems contradictory to the previous *ex situ* studies. This discrepancy is still being investigated and is believed to be the result of different annealing conditions during the *ex situ* and *in situ* studies, as well as the different mechanical boundary conditions of the annealing processes.

To investigate samples similar to materials produced for device applications, studies on FIB prepared thin film cross sections are currently underway. The FIB is utilized to prepare electron transparent cross sections of BaTiO_3 thin films, which are then placed on Protochips Arduro™ heating chips. These experiments will allow for the cross-sectional observation of crystallization mechanisms in the thin films and better understand the effects of the substrate, which may act as a heterogeneous nucleation site for the crystallizing film[2].

References

- [1] Ihlefeld, J. F. "Synthesis and Properties of Barium Titanate Solid Solution Thin Films on Copper Substrates," 2006.
- [2] Project supported by the US DOD MicroElectronics Activity (H94003-10-0-1002).

Figure 1a: 0% BBO BaTiO₃ on Sapphire substrate. Annealed for 1 hr. at 900° C.

Figure 2a: 5% BBO BaTiO₃ on Sapphire substrate. Annealed for 1 hr. at 900° C.

Figure 1b: Amorphous 0% BBO BaTiO₃ on E-chip. With carbon support underneath.

Figure 2b: Amorphous 3% BBO BaTiO₃ on E-chip with carbon support underneath.

Figure 1c: 0% BBO BaTiO₃ immediately after crystallization at 760°C.

Figure 2c: 3% BBO BaTiO₃ immediately after crystallization at 760°C.

Figure 1d: 0% BBO BaTiO₃ after annealing at 1100°C for 6 minutes.

Figure 2d: 3% BBO BaTiO₃ after annealing at 1100°C for 8 minutes.