

Interface Evolution of Flux-Grown BaTiO₃ Thin Films on Sapphire Substrates

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The crystallinity and microstructure of BaTiO₃ (BTO) thin films deposited on sapphire substrates can be enhanced dramatically by the addition of a high-temperature liquid phase; a small volume fraction of BaO-B₂O₃ (BBO) flux provides a mass transport mechanism that enhances crystal perfection and homogenizes the grain structure [1]. But, with increasing BBO flux, a secondary phase, BaAl₂O₄, develops at BTO/sapphire interface [2]. In this work, we report the structural evolution of the BTO/sapphire interface region as a function of BBO flux. The penetration depth and amount of the BaAl₂O₄ secondary phase present correlates with the amount of BBO present.

Thin films were prepared from BaTiO₃ targets containing 0, 1, 3, and 5% BBO flux (869 °C eutectic composition) on c-oriented sapphire substrates using pulsed laser deposition at 450°C. A post-anneal in air at 900 °C was used to crystallize the films. A secondary phase of BaAl₂O₄ was found at the BTO/sapphire interface. Figure 1 shows the structural evolution of the sapphire interface region (the region adjacent to BTO/sapphire interface). The 0% BBO sample shows a thin, continuous, single crystal BaAl₂O₄ layer (3-5 nm) at the interface with ordered sapphire directly beneath the interface (Figure 1a). The thin films that contain the flux show pockets of BaAl₂O₄, which lie at the interface and increase in size as flux concentration increases (10-20 nm for 1%, 40-190 nm for 3%, and 50-200 nm for 5% sample, respectively). Also, it is observed that as the flux concentration increases a layer of γ -Al₂O₃ forms directly beneath the interface (Figure 1b). SAED diffraction (Figure 1c) and electron energy loss spectroscopy (EELS) were used to identify the location and volume of the secondary phase with respect to the interface (Figure 1d).

The formation of the secondary phase BaAl₂O₄ is predicted by the BaO-Al₂O₃ phase diagram [3]. The formation of the BaAl₂O₄ phase appears to result from the diffusion of Al-O out of the sapphire substrate, as evidenced by a large number of point defects and their ordering in the sapphire of the 0% BBO BaTiO₃ sample (Figure 1a). The flux does introduce excess BaO to the system, but the amount added does not account for the increased volume of BaAl₂O₄ that is observed in the samples with flux. We surmise that the flux not only provides BaO for the reaction but that the transient liquid phase provides a mechanism for fast Al and O diffusion. As the diffusion of Al and O is enhanced by the addition of the flux, the vacancy concentration in the substrate becomes so large that a phase transition occurs, resulting in areas of γ -Al₂O₃, which has a much lower density than sapphire and accommodates the loss of Al and O [4].

References:

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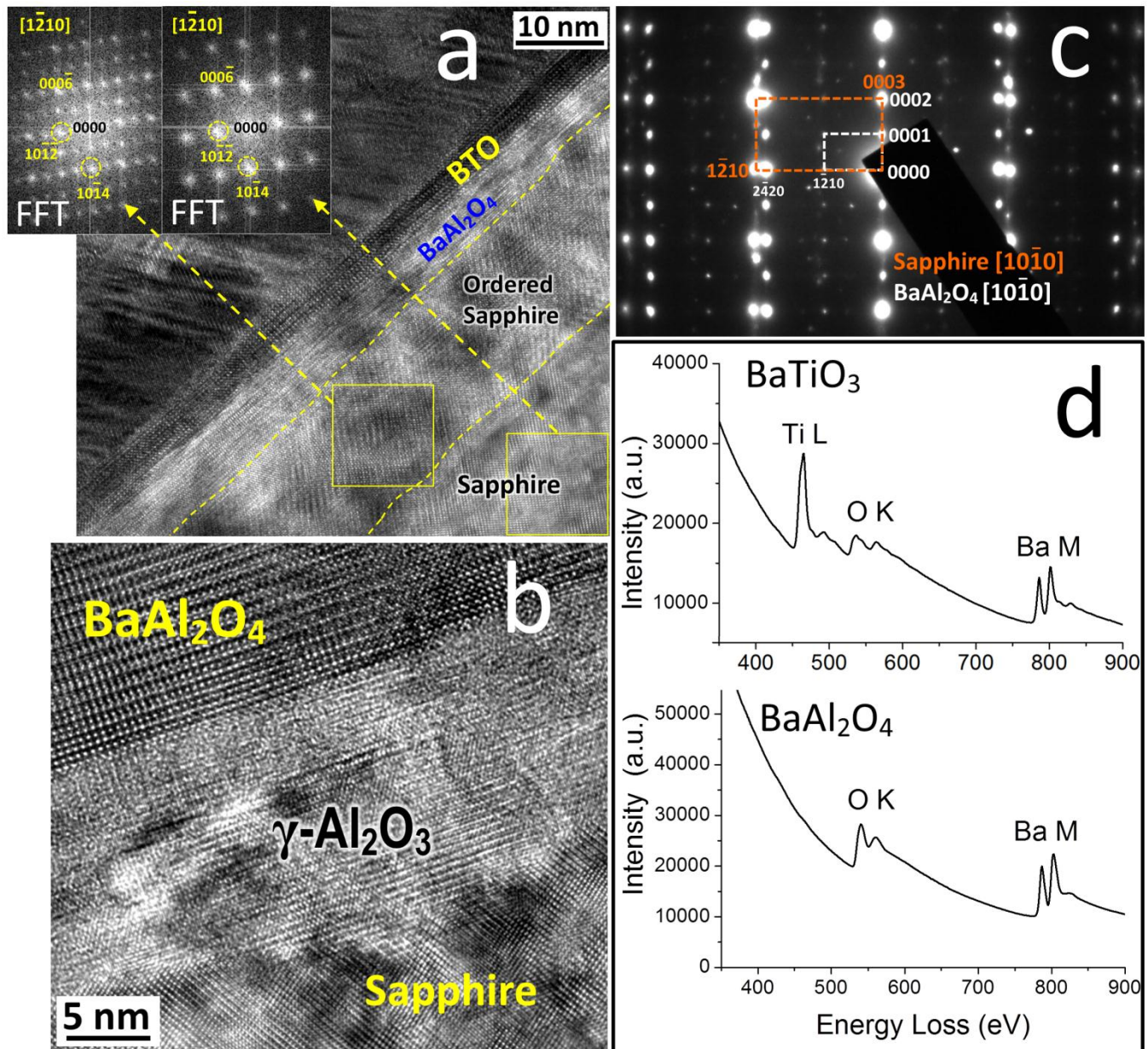


Figure 1. (a) The interface of 0% BBO BaTiO₃ thin film showing the interface layer of BaAl₂O₄ with respect to the sapphire substrate. (b) The interface of 5% BBO BaTiO₃ thin film showing a layer of γ -Al₂O₃ between the sapphire substrate and a pocket of BaAl₂O₄. (c) A SAED pattern that shows the presence of BaAl₂O₄ and its epitaxial relationship to the sapphire substrate (3% sample). (d) EELS spectrum showing the Ti-L, O-K, and Ba-M edges in BaTiO₃ and another spectrum showing the O-K and Ba-M edges in BaAl₂O₄, notice the lack of the Ti peak.