

Structural and Electromechanical Properties of Epitaxial BiFeO₃ Thin Films

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BiFeO₃ has coupled ferroelectric and antiferromagnetic properties. Before this multiferroic coupling can be exploited or even completely understood, it is necessary to characterize the structure and electromechanical properties. We used x-ray diffraction to study the structure of thin films of BiFeO₃ on SrRuO₃ conducting layers epitaxially deposited on a SrTiO₃ substrate. For 400 nm (001) oriented BiFeO₃ thin films, we found a rotation of the atomic planes in the entire film caused by anisotropic relaxation on the miscut substrate. Mosaic blocks several microns in size had additional small, random rotations caused by the relaxation process. Within each mosaic block we found x-ray scattering signatures of a striped ferroelectric domain structure consistent with a strained rhombohedral phase.

Time resolved synchrotron x-ray microdiffraction was used to probe the piezoelectric response of the film within a single mosaic block. We found that the out of plane d_{33} piezoelectric coefficient was uniform across the entire film ($d_{33} = 53$ pm/V). The local in-plane response varied widely, however. We believe the variation in the apparent d_{31} is an effect of differences in mechanical constraints for each ferroelectric domain. The variation related to the proximity of the domain to a defect, dislocation, or edge of a mosaic block as well as the neighboring polarization domains.

Forbidden x-ray diffraction reflections were observed which are incompatible with the accepted R3c symmetry of BiFeO₃. These reflections were characterized to determine their origin and improve our understanding of the structure. The intensity of the forbidden reflections is larger in films that are relaxed, but are present in bulk crystals of BiFeO₃ as well. The pseudocubic $\frac{1}{2}(111)$ reflection exhibits a resonant enhancement near the Fe K-edge on top of a non-resonant signal. The observed intensities were compared to structure factor calculations in which Fe cations are displaced from their positions in published structural refinements of BiFeO₃. A model in which neighboring Fe cations are displaced in antiparallel directions matches the intensities and wavevectors of the observed reflections. An ordered redistribution of charge on the Fe cations, similar to charge disproportionation, is a potential driving force for these Fe displacements.