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Investigation of Chalcogenide Perovskite Thin Films Using Scanning Transmission Electron Microscopy (STEM)

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Perovskite sulfides, with tunable and direct bandgaps in the visible regime and excellent physical properties comparable to existing oxide perovskites, show promise as future optoelectronic and solar applications [1, 2, 3]. With the recent success of epitaxial thin film growth of $BaZrS_3$ (BZS) via molecular beam epitaxy [4], new opportunities are available to engineer material properties through interface and defect engineering. As such, characterizing the film structure, defects, and the film-substrate interface at the atomic scale is essential for establishing growth behavior and improving film quality and functionality.

In this presentation, we will report the interface between orthorhombic BZS thin films and rhombohedral $LaAlO_3$ substrates using scanning transmission electron microscopy (STEM), including atomic resolution imaging, energy dispersive X-ray spectroscopy (EDS), and electron energy loss spectroscopy (EELS). First, we confirm that the films exhibit an atomically and chemically sharp interface even though there is significant lattice mismatch. Specifically, cube-on-cube epitaxy would yield a near 30% mismatch given the pseudocubic lattice constants of the $LaAlO_3$ substrate (3.8114 Å) and BZS (4.975 Å), reduced to 8% mismatch if the BZS was rotated 45-degrees. Even so, as shown in Figure 1, we identify the presence of two competing growth modes based on these rotated structures: Mode 1 (M1) consisting of a self-assembled epitaxial interface without 45-degree rotation, and Mode 2 (M2) consisting of the predicted 45-degree rotated direct epitaxy. We will show that the M1 growth is fully relaxed throughout the film thickness, relieving the substrate-film lattice mismatch and residual strain associated with both lattice parameter mismatch as well as the M2 growth. Additionally, we will highlight the film-substrate interface to better understand these two growth modes, along with other rich features within the BZS thin film, such as rotation variants (Figure 2) and anti-phase boundaries, as well as the influence of step edges in the $LaAlO_3$ substrate. Finally, we will use atom column-based image analysis along with local EDS and EELS measurements to determine the relationship of these defects to structural distortions and composition [5].

References:

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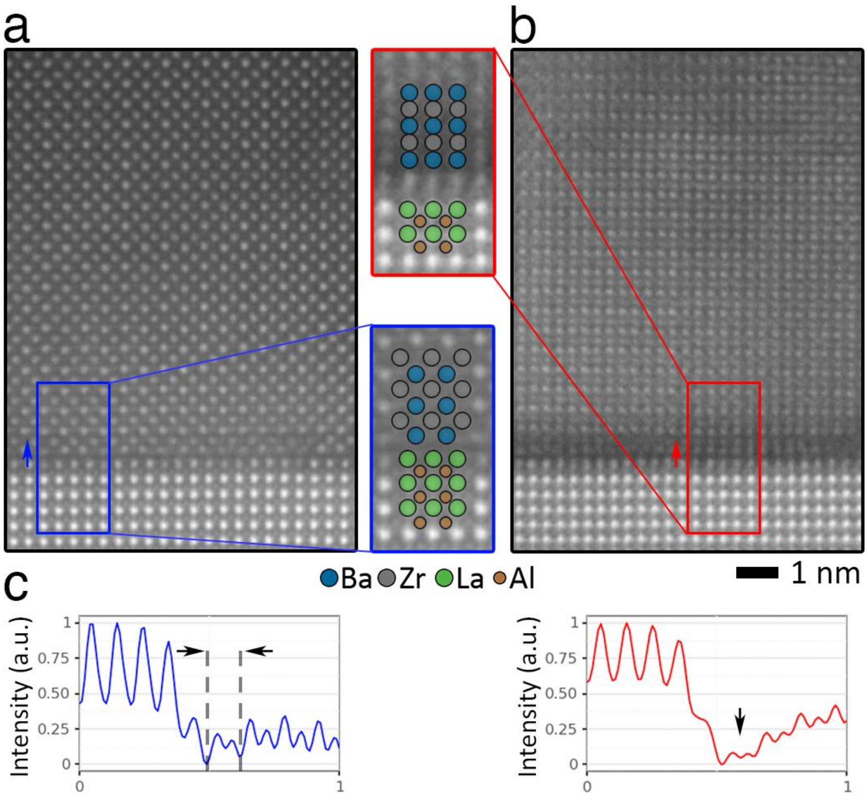

Figure 1. HAADF STEM images of (a) M1 growth and (b) M2 direct epitaxy, with insets showing atom column species corresponding with the structure of BaZrS3 and LaAlO3 film and substrate. Line profiles in (c) show the decrease in HAADF contrast for the interface layers in each growth type.

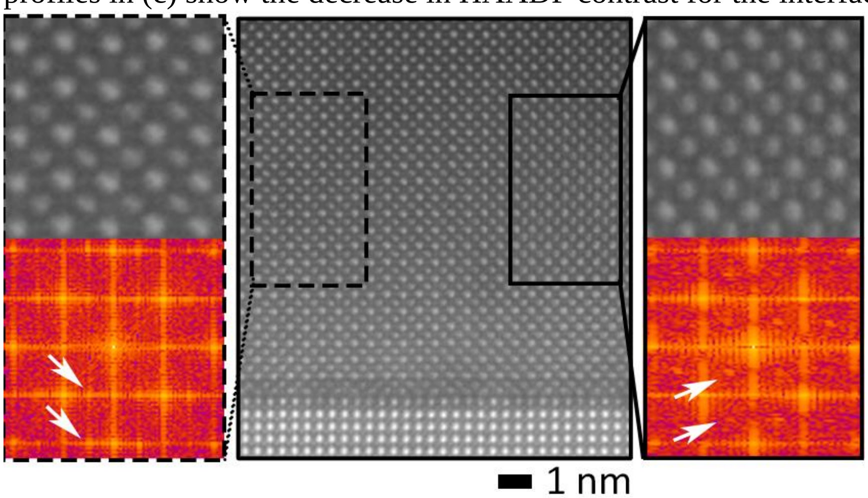

Figure 2. HAADF STEM image of film-substrate interface showing M1 growth. Two rotation variants are shown, given by differing atom column arrangement and corresponding FFTs in insets.