Atomic Structure of the Initial Nucleation Layer in Hexagonal Perovskite BaRuO$_3$ Thin Films

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Hexagonal perovskites are an attractive family of materials due to their various polymorphs and rich structure–property relationships. BaRuO$_3$ (BRO) is a prototypical hexagonal perovskite, in which the electromagnetic properties are significantly modified depending on its lattice structure. Whereas thin-film synthesis would allow the study of the diverse properties of hexagonal perovskites by epitaxially stabilizing various metastable polymorphs, the epitaxial growth of hexagonal perovskites, especially at the initial growth stage, is yet to be addressed. In this study, it is shown that an intriguing nucleation behavior takes place during the initial stabilization of a hexagonal 9R BRO thin film deposited on a (111) SrTiO$_3$ (STO) substrate. It is found that a nanoscale strained layer composed of different RuO$_6$ octahedral stacking is initially formed at the interface followed by a relaxed single crystal 9R BRO thin film. Within the interface layer, hexagonal BRO is nucleated on the (111) STO substrate by both face- and corner-sharing octahedra. More interestingly, it is found that boundaries between differently stacked nucleation layers (heterostructural boundaries) facilitate strain relaxation, in addition to the formation of conventional misfit dislocations evolved from homostuctural boundaries. The observations reveal an important underlying mechanism to understand the thin-film epitaxy and strain accommodation in hexagonal perovskites.

1. Introduction

Hexagonal perovskites refer to materials with the ABO$_3$ chemical formula, in which the size difference between the A and B cations is large, i.e., the tolerance factor is larger than unity.[1] In hexagonal structures, the structural units, the BO$_6$ octahedra, share either a face or a corner with a neighboring octahedron to release the internal strain induced by the large ionic size of the A-site cation.[1] This leads to a variety of polymorph structures, which can be conventionally categorized by the stacking sequence of AO$_3$ layers (see Figure 1a). For example, a cubic perovskite can be considered as the three-layer cubic (3C) structure within the hexagonal framework because the AO$_3$ planes are connected via corner-sharing with a repeated stacking pattern after three octahedra. The four-layer hexagonal (4H) structure consists of dimers of face-sharing BO$_6$ octahedra, connected to its neighbors along the c-axis by cubic-perovskite-like corner-sharing, with a repeated stacking pattern after four octahedra. The six-layer hexagonal (6H) structure consists of a face-sharing dimer and a single octahedron, connected alternatingly by corner-sharing, with a repeated stacking pattern after six octahedra. The nine-layer rhombohedral (9R) structure consists of trimers of face-sharing BO$_6$ octahedra, connected to each other by corner-sharing, with a repeated stacking pattern after nine octahedra. These hexagonal perovskites can possess other varieties of structures depending on their stacking sequence (either by face- or corner-sharing of the structural units).[2] In this regard, hexagonal perovskites provide an excellent platform for the investigation of a myriad of structure-property relationships.[1-4]

Among hexagonal perovskites, Ba-based ABO$_3$ oxides, such as BaRuO$_3$ (BRO) and BaIrO$_3$ (BIO), have attracted considerable attention as prototypical hexagonal perovskites, because each polymorph exhibits unique electronic and magnetic properties.[7,8] In the case of the BRO system, the cubic phase (3C) \((a = b = c = 4.01 \text{ Å}, \text{space group } 221 (Pm\bar{3}m))\) was found to be a ferromagnetic metal with a transition temperature \(T_c = 60 \text{ K}\), whereas the 4H phase \((a = b = 5.73 \text{ Å}, c = 9.50 \text{ Å}, \text{space group } 194 (P6_3/mmc))\) and 6H phase \((a = b = 5.71 \text{ Å}, c = 14.05 \text{ Å}, \text{space}...\)
group 194 \((P6_3/mmc)\),\(^{11}\) and 9R phase \((a = b = 5.76 \text{ Å}, c = 21.62 \text{ Å},\) space group 166 \((R3m)\))\(^{12}\) are paramagnetic.\(^{8}\) Electronically, the 4H and 6H phases are metallic down to the base temperature while the 9R phase showed a metal-to-semiconductor transition at 150 K with a pseudogap opening.\(^{8,11,13,14}\) On the other hand, the 6H BIO phase is a paramagnetic metal, but the 9R BIO phase undergoes a ferromagnetic transition at \(T_c \approx 180\) K accompanied by a semiconductor-to-insulator transition.\(^7\) The physical properties of the hexagonal perovskite Ba\(_2\)BO\(_3\) \((B = \text{Ru, Ir})\) have been extensively investigated over the last decades, but the exact electromagnetic ground states are still elusive, possibly owing to the strongly correlated electronic nature within the hexagonal structural framework. For example, the electronic transitions in both 9R BRO and BIO phases are thought to be related to the formation of a charge density wave (CDW),\(^{11,13,15}\) and the interaction between molecular orbital states have been suggested as the possible underlying mechanism.\(^{8,16}\) Nevertheless, it is evident that the dissimilar portion of the orbital overlap between the B-site ions within the face-sharing dimers or trimers will greatly affect the physical properties of Ba-based hexagonal perovskites.

As the hexagonal polymorphs are formed by alternate stacking of the hexagonal AO\(_3\) layer along the c-axis, the hexagonal surface symmetry of the \((111)\) cubic-perovskite substrate provides good compatibility for the epitaxial thin film growth. It has been reported that hexagonal perovskite thin films of various polymorph phases are grown with a smoother hexagonal terrace structure on the surface of \((111)\) SrTiO\(_3\) (STO) substrates compared to those on \((001)\) or \((011)\) STO substrates, which are found to have orthogonal textures or plate-like islands, respectively.\(^{17,18}\) While some polycrystalline hexagonal perovskite thin films have been studied using X-ray diffraction and transmission electron microscopy (TEM),\(^{19,20}\) the microstructure of the single-phase thin film has not yet been investigated at the atomic scale, largely owing to the lack of high-quality epitaxial thin films. The formation mechanism of the high-quality hexagonal perovskites at the initial stage of growth on \((111)\) cubic-perovskite substrates would provide crucial information for stabilizing and further strain-engineering the metastable hexagonal perovskite phases through thin-film epitaxy.

In this work, we investigate the interfacial atomic structures of a 9R BRO thin film grown on a \((111)\) STO substrate using high-resolution high-angle annular dark field scanning transmission electron microscopy (HAADF STEM) with geometrical phase analysis (GPA). 9R BRO was chosen as it has the lowest formation energy among the BRO polymorphs \((9R < 4H < 6H < 3C)\),\(^{9,19}\) and, therefore, is the most stable phase. We observe that a thin \((4-6 \text{ nm})\) intermediate layer is formed between the bulk-like 9R BRO thin film and the \((111)\) STO substrate. Interestingly, both the face- as well as the corner-shared layers are observed to coexist as the nucleation layer. Furthermore, we find that the boundaries between the distinctively-stacked nucleation layers act as strain relaxation sites in addition to the conventional misfit dislocations.
2. Results and Discussion

Single-phase 9R BRO thin films (~30 nm) were epitaxially grown on the (111) STO substrate using pulsed laser deposition at the optimal growth temperature of 750 °C and oxygen partial pressure of 300 mTorr. To note, various polymorph BRO phases could be stabilized when grown on (100) STO, depending on the growth parameters of PLD.[28] Cross-sectional STEM specimens were prepared via ion milling at LN₂ temperature after conventional mechanical polishing. High-resolution HAADF STEM experiments were carried out using a Nion UltraSTEM100 operated at 100 kV. The microscope was equipped with a cold field emission gun and a corrector of third- and fifth-order aberration for sub-Å resolution. The nominal convergence angle was 30 mrad, and nominal collection inner and outer half-angles for HAADF STEM were 65 and 240 mrad, respectively. Noise and amorphized surface background arising in the high-resolution HAADF STEM images were reduced with a band-pass filter. GPA and multislice electron-scattering simulation were performed using ER-C GPA[22] and QSTEM[23] code, respectively.

The global lattice structure of an epitaxial 9R BRO thin film on a (111) STO substrate is evidenced via X-ray diffraction $\theta$2$\theta$ scan (Figure 1d). The thin film is found to be composed of the pure relaxed 9R phase without any impurity or other polymorph phases, which has not been previously reported. The full width at half maximum (FWHM) value of the rocking curve (Figure 1e) of the 009 film peak is ~0.057° indicating the high quality of the 9R BRO thin film, which is the best reported compared to FWHM = 0.39° of 4H polymorph.[18] Figure S2 (Supporting Information) presents a low-magnification HAADF STEM image, further demonstrating that the 9R BRO thin film is uniformly grown on (111) STO without any impurities.

Figure 1c shows a high-magnification HAADF STEM image of 9R BRO viewed along the [1120] zone axis. The lattice parameters measured in HAADF STEM are $a = 3.75$ Å and $c = 21.59$ Å, consistent with the XRD result ($c = 21.60$ Å) and the bulk values. Large and small bright dots in the HAADF STEM indicate Ba and Ru atomic columns, respectively, indicating that the STEM image viewed along the [1120] zone axis can be used to directly distinguish the atomic structures of the hexagonal polymorph. The discernability of hexagonal BRO polymorphs in the HAADF STEM image viewed along the [1120] zone axis is further demonstrated in Figure 1b using simulated HAADF STEM images. Note that O atomic columns are not detected in the HAADF STEM images, since the scattering intensity in the HAADF STEM image depends strongly upon atomic number. The local connection between the RuO₆ octahedra in hexagonal perovskites, i.e., face- and corner-sharing, correspond to Ru atomic columns lying aslant from that axis.

Because the growth of epitaxial thin film is predominantly determined at the nucleation stage, it is critical to characterize the atomic structures at the interface between the thin film and substrate.[24,25] Figure 2a shows a typical high-magnification HAADF STEM image for the interfacial region between 9R BRO thin film and (111) STO substrate (several other HAADF STEM images for the interfacial regions are displayed in Figure S1 in the Supporting Information). The image shows that an intermediate layer is formed between the bulk film and substrate denoted by white dashed lines in Figure 2a, where the atomic structure is different from that of nominal 9R BRO. To systematically characterize the atomic structures of the intermediate layer, the interfacial region denoted by the parenthesis in Figure 2a is further magnified in Figure 2b.

![Figure 2](image-url)

**Figure 2.** Microstructure and strain map of the 9R BRO/(111) STO interface. a) High-resolution HAADF STEM image of a 9R BRO/(111) STO interface viewed along the BRO [1120] zone axis. The intermediate layer on (111) STO is marked by the white dashed lines. A low-magnification HAADF STEM image of the 9R BRO thin film is shown in the inset, verifying that the thin film is uniformly grown on a (111) STO substrate without any impurities (here, the scale bar indicates 50 nm). b) Magnified HAADF STEM image of the interfacial region marked by the black parenthesis in Figure 2a. The face- and corner-shared stackings at the nucleation layer are highlighted by the blue and red solid lines, respectively. A few RuO₆ dimer and tetramer formed in the intermediate layer are denoted by the bright and dark grey rectangles, respectively. c) In-plane strain map ($\varepsilon_{xx}$) of the 9R BRO/(111) STO interface obtained via GPA strain analysis. The type-I and II relaxation sites are denoted by the red and blue arrows in the images, respectively. The scale bars indicate 2 nm.
high-magnification image reveals two distinct features of this layer. First, the intermediate layer is composed of dissimilar octahedral face-sharing chain structures other than the nominal trimer, including single octahedron, dimer, and tetramer. The octahedral chains even longer than the tetramer were sometimes observed within the intermediate layer (see Figure S4 in the Supporting Information). Second, the irregular atomic configurations are frequently extended from the film/surface interface to about 4–6 nm above into the intermediate layers (vertical red arrows). Those irregular atomic structures form the type-I relaxation sites, which will be discussed below. Additionally, the image directly demonstrates that the initial RuO$_6$ octahedra in contact with TiO$_6$ octahedra of the STO substrate are both face-sharing as well as corner-sharing. The face- and corner-sharing nucleation layers with the substrate are denoted by the blue and red solid lines in Figure 2b, respectively. Note that the corner-shared nucleation layer occupies the majority of the interface connection, while the face-shared nucleation layers are formed as islands with ~10 nm of lateral size.

To further examine the strain state of the intermediate layer and 9R BRO bulk film, GPA was applied to the HAADF STEM images. Figure 2c shows an in-plane strain ($\varepsilon_{xx}$) map of Figure 2a. This map shows the lattice mismatch between the relaxed 9R BRO and STO is ~4%, consistent with XRD and HAADF STEM results. This map also demonstrates that 9R BRO bulk film is fully relaxed while the intermediate layer is in a partially strained state though the strain relaxes at several specific points. This result further suggests that the formation of nonbulk octahedral chains such as dimers or tetramers in the intermediate layer is related to the metastability of BRO polymorphs in the partially strained state. In addition, the direct comparison of the strain map and the HAADF STEM image reveals that the strain relaxation sites can be classified into two distinctive types depending on the characteristics of the BRO nucleation layer encountered at the relaxation core; type-I and II relaxation sites are denoted in Figure 2 by the red and blue arrows, respectively. The characteristics of each relaxation sites will be discussed in the following paragraph.

The atomic structures denoted by the red arrows in Figure 2b show that the type-I relaxation sites with homostructural boundaries correspond to conventional misfit dislocations formed by a large lattice mismatch. It seems that an atomic-scale core is formed between the face-shared nucleation layers, and the dislocation structures extend from the interfacial core to about 4–6 nm above in distance. The strain map in Figure 2b additionally shows that the epitaxial strain is relaxed in the type-I relaxation sites via a two-step process. The strain is partly relaxed at the atomic-scale core within the nucleation layer and finally fully relaxed at the other end-point of the dislocation structure. These type-I relaxation sites are important because they define the thickness of the intermediate (strain relaxation) layer. Meanwhile, the atomic structures denoted by the blue arrows in Figure 2b show that the type-II relaxation sites are the line segments where the face- and corner-shared nucleation layers meet. In other words, the type-II relaxation sites are the stacking disorder boundary (heterostructural boundary) occurring at the nucleation layer of the hexagonal 9R BRO thin film. The core structure was blurred and not clearly resolved in the HAADF STEM images, suggesting that the boundaries are not perfectly aligned along the [110] STO || [1120] BRO direction. The sites where the epitaxial strain is relaxed are presented in the schematic of the nucleation layer in Figure 3.

The atomic-scale characterization of the 9R BRO thin film grown on the (111) STO substrate provides important insights into the thin film epitaxy of hexagonal perovskites. First, the (111) cubic-perovskite substrate is verified as an ideal choice for hexagonal perovskite growth in terms of chemical compatibility and lattice symmetry; a pure 9R BRO epitaxial film was formed without any impurities or polymorphs. Second, nanoscale intermediate layers composed of nonbulk octahedral chains are observed at the interface, which is attributed
to the partially strained state imposed on the hexagonal BRO. This observation suggests that various metastable BRO polymorphs with similar hexagonal structural framework might be stabilized in the thin-film form owing to their small formation energy difference, of which the growth could be further controlled by the epitaxial strain. Moreover, our results reveal that the epitaxial strain is relaxed at the boundaries where the face-shared and corner-shared nucleation layers meet, as well as the conventional misfit dislocations. This is a clear distinction between strain relaxations in cubic and hexagonal perovskites. While the lattice mismatch and strain susceptibility are the dominant factors to be considered for strain-engineering of cubic perovskite, the stacking of nucleation layers also needs to be considered and controlled for hexagonal perovskite to be epitaxially strained.

3. Conclusion

In summary, we investigated the atomic structure of a hexagonal 9R BRO thin film grown on a (111) STO substrate using high-resolution HAADF STEM imaging with GPA strain mapping. Nanoscale intermediate layers composed of different RuO$_6$ octahedral stacking were formed between the relaxed 9R BRO bulk film and the STO substrate. The formation of the intermediate layers can be attributed to the partial strain imposed on the interfacial region. The BRO thin film was observed to be nucleated on the (111) STO substrate by face-sharing as well as corner-sharing. The stacking disorder boundaries were found to act as the relaxation sites in addition to the conventional misfit dislocations. This study demonstrates that thin-film epitaxy can be used as a promising way to stabilize metastable or artificial BRO polymorphs. Furthermore, our study suggests that the control of nucleation stacking is critical for growing epitaxial thin films of hexagonal perovskites.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data openly available in a public repository that issues datasets with DOIs.

Keywords

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