Atomic Scale Understanding of the Epitaxy of Perovskite Oxides on Flexible Mica Substrate

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The excellent functionalities of perovskite oxides and the growing demands for flexible devices lead to great interests on epitaxial growth of functional oxide films on flexible mica substrates. Understanding the film epitaxy on the substrate with a very different crystal structure is a key issue for the optimization of the film growth and hence properties. Such understanding largely depends on knowing the atomic structure of the interfaces between the films and the substrates. Here, the interface between the epitaxial films of SrTiO₃ on the fluorophlogopite mica substrate is studied in detail. Two types of interfaces, clean or with secondary phase, exist in this system, leading to two types of crystallographic orientation relationships. Atomic-resolution scanning transmission electron microscopy images reveal that at the clean interface the (111) Sr–O₃ atomic plane of SrTiO₃ interacts with the (001) (SiAl)₂–O₃ plane of mica. This interface structure and thus the epitaxy of the film are understood in light of the strong similarity of the oxygen sublattices in these two atomic planes. First-principles calculations demonstrate strong bonding of the atoms at the interface, which is also corroborated by the observation of misfit dislocations at the interfaces.

1. Introduction

Nowadays, rapid progress is being made in applications of flexible smart electronics, such as rollable displays, robots, wearable and implantable devices.[1–3] These flexible devices depend strongly on the functionality of bendable and stretchable materials, which can be realized by freestanding thin films and/or growing films on flexible substrates.[4–6] Several approaches have been developed to obtain such flexible thin films, including the releasing-and-transferring technique[7–9] and the direct growth of thin films on flexible substrates, such as polymer materials[10] and metal foils.[11,12]

Mica, phyllosilicate mineral, has drawn much attention as substrates among layered materials due to its superior properties. As shown in Figure S1 of the Supporting Information, mica possesses monoclinic structure with the space group C2/m, and the (001) basal plane exhibits a pseudohexagonal atomic configuration.[13,14] They can be cleaved into thin sheets along the (001) basal plane between the K-atom plane and the structural block of (SiAl)O₄ tetrahedron/Mg(OF)₆ octahedron/(SiAl)O₄ tetrahedron (TOT), where the connection has a weak interaction nature. The cleaved sheets show the atomically smooth surfaces and are chemically inert, electrically insulating and thermally stable, and thus provide a perfect platform for growth of heteromaterials. Most importantly, the mechanical flexibility makes mica a favorable substrate for fabricating flexible thin films of various materials, especially functional oxides. The growth of these oxides has been discussed in light of (quasi) van der Waals (vdW) epitaxy.[15,16]

Very recently, intensive research has been devoted to such epitaxial growth of functional perovskite and spinel oxides films on mica for flexible devices.[17–24] For perovskite SrRuO₃ film system, the crystallographic orientation relationship between films and mica substrate was determined as [111]films || [001]mica and [011]films || [010]mica by X-ray diffraction (XRD).[21] The similar orientation relationships have also been observed for spinel oxide films on mica.[18–20] Electron microscopy imaging and electron diffraction analysis confirmed the orientation relationships. In addition, an ultrathin interdiffused layer within 1 nm was considered to be present at the interface between CoFe₂O₄ and mica.[19] Some crystal defects like vacancies or dislocations at this interdiffused layer might release the large lattice misfit stress in this system. In contrast to the undoubted vdW integration in 2D material system,[16–21] there are still fascinating questions, which need to be answered, on the mechanism regarding the heteroepitaxy of these oxides on mica. Clearly, details of atomic structure at the interfaces are the key issues for answering the questions. Up to now, no atomic scale evidences have been reported yet concerning the interface structure.
In this work, we report on a detailed study of the interface structure between perovskite oxide films and fluorophlogopite mica (F-Mica) substrates by high-resolution scanning transmission electron microscopy (HRSTEM). Two types of crystallographic orientation relationships are determined corresponding to two types of interfaces depending on the growth conditions of the film system. The interfacial atomic structure, interfacial defects, and strain are characterized. Based on the experimental results, structural model of the interface is proposed to interpret the observed orientation relationships and the epitaxy mechanism.

2. Results and Discussion

XRD analysis of θ–2θ scans and ϕ-scans was applied to the samples for investigating the epitaxial quality of the films. In the diffraction spectrum obtained by θ–2θ scans, shown in Figure S2a of the Supporting Information, only the (00l) peaks of F-Mica substrate and (111) peaks of the La0.8Sr0.2MnO3 (LSMO) or SrTiO3 (STO) layer, which overlap with each other, are observed, providing the evidence for the crystallographic relation of [111]STO||[001]F-Mica. Here and in the following, the lattice plane index for LSMO is referring to a basic pseudo-cubic perovskite structure for easy reference to the cubic STO. The in-plane crystallographic orientation relationships between the LSMO/STO two-layer films and the F-Mica substrate were characterized by ϕ-scans with the (002)STO/LSMO and the (202)F-Mica peaks. As shown in Figure S2b of the Supporting Information, for the films grown at 800 °C, six sharp (002)STO/LSMO peaks for the LSMO/STO layers and three peaks for the F-Mica substrate are seen. Considering the threefold symmetry of the cubic perovskite structure, the observed sixfold peaks in ϕ scan might be the results of in-plane orientation domains, which have in-plane rotation of 60°. For F-Mica structure (C2/m), there is a threefold symmetry, the observed three peaks in ϕ scan are (202)F-Mica, (133)F-Mica, and (133)F-Mica, which have similar plane spacing and distribution and thus lead to a pseudo threefold symmetry. An important feature for the ϕ scan of the film and the substrate is the shift of 30° existing between the (002)STO/LSMO and (202)F-Mica peaks, resulting in the in-plane orientation relationships between the film and the substrate of (110)STO||[100]F-Mica and (112)STO||[010]F-Mica. This type of relation is denoted as OR-I. XRD reciprocal space mapping measurements were taken around the (111)STO, (312)STO, (004)F-Mica, and (208)F-Mica peaks for the determination of plane spacing of (111)STO, (110)STO. The spacing of the (111)STO and the (110)STO planes was measured as 0.2254 and 0.2755 nm, respectively, almost identical with the parameters of bulk STO. The plane spacing of (004)F-Mica was measured as 0.25 nm, fitting well to the parameters of F-Mica bulk. These data provide evidences for a fully relaxed STO film.

For the films grown at higher temperature (950–1050 °C), a different in-plane orientation relationship was determined between the STO films and the F-Mica substrate based on XRD data (Figure S3a, Supporting Information), i.e., (110)STO||[010]F-Mica and (112)STO||[010]F-Mica. This type of relation is denoted as OR-II. TEM results show that an interface layer of secondary phase forms (Figure S3b, Supporting Information), which exhibits different structure from the film and the substrate. Therefore, such relation does not represent direct relationship between the STO film and the F-Mica substrate, and will not be discussed in this work.

Figure 1a shows a low magnification image of the STO film layer on F-Mica substrate with OR-I. The interface between the film and the substrate looks sharp. The substrate in this area is evidenced by the lattice fringes of the (001) plane. The STO film exhibits a microstructure feature of columnar domains, which have an averaged in-plane dimension of about 20 nm. The domain boundaries start from the interface and penetrate the entire thickness of the film layer. Figure 1b shows an electron diffraction pattern (EDP) obtained by a selected area aperture covering both film and part of F-Mica substrate. The EDP includes multiple EDP from the STO film and the substrate. The EDP of the F-Mica substrate is identified as the [100] zone axis pattern and the corresponding basic diffraction spots are noted by a yellow rectangular. The rest diffraction spots can be indexed as belonging to the (110) zone axes of STO crystals with two orientations corresponding to two types of domains, as denoted by the blue and purple rectangular.
and the F-Mica substrate are clearly seen, and the interface is clean without secondary phase. Based on this image, the lattice configuration across interface or in-plane strain was investigated by a geometric phase analysis (GPA). Figure 2b shows the GPA result along the in-plane direction, the strain map Exx representing the relative change of lattice plane spacing in the in-plane direction. The color scale below the map scales the changes, taking the lattice of F-Mica as reference. The averaged change of about 4% for the lattice plane spacing across the interface was obtained from the map, which fits well with the lattice mismatch between STO and F-Mica under the condition of the determined orientation relationship. From the Exx map, the interface looks very sharp also with respect to the lattice change as well. In the Exx map, an apparent feature can be observed along the interface as marked by an array of arrows, where big changes concentrate at very small regions, predicting the possibility for either strong abruption of lattice registration or existence of interfacial dislocations. Figure 3 shows a magnified and denoised ABF image, showing details of the lattice registration across the interface. Under the ABF imaging condition, the dark dots represent the atomic column positions. The interface position is marked by a horizontal yellow dashed line, which is identified by checking the stacking atomic planes and plane spacing of both the film and the substrate. It is evident that at interface position, the (001) (SiAl)₂O₃ plane of F-Mica meets the (111) Sr–O₃ plane of STO, as shown by the attached structural models. A group of vertical dashed lines traces the registration of the two compound lattices across the interface, which reveals a structure feature of a misfit dislocation.

Figure 4a shows an STEM high angle angular dark field (HAADF) image of the interface area, recorded along the [001] direction of F-Mica (the [011] direction of STO), which is orthogonal to the viewing direction of the image in Figure 3. By combination of the image, i.e., Figure 4 with Figure 3, the 3D information of the interface structure can be obtained. Again, the investigation on the stacking sequences of the atomic planes from the two compound sides results in the same conclusion on the interface structure as that obtained from the image in Figure 3. The two compounds terminate at the interface with the (001) (SiAl)₂O₃ plane of F-Mica meeting the (111) Sr–O₃ plane of STO. The detailed information on the structure of the interface can be inferred from the details of the image contrast across the interface. The termination at the interface of the Sr
atomic columns of the STO film is evidenced by their image contrast and the separation spacing along the interface, which follows the translation period along the [11 \_2] direction of STO. It is noted that the contrast is weaker than that of film intra. The contrast is also clear for the Mg–(OF) octahedrons layer below the interface. At the interface, the contrast of the (SiAl)\_2–O\_3 plane is very weak and confused in the HAADF image of Figure 4a. However, clear contrast is visible directly below the Sr–O\_3 starting plane of the STO film, as denoted by a yellow arrow in the ABF image shown in Figure 4b, which was simultaneously recorded with the HAADF image shown in Figure 4a. The positions of the contrast fit to the (SiAl)\_2–O\_3 plane of the F-Mica substrate. However, the contrast is lower than that of the regular columns. From the images of Figure 4, a distance of 0.86 nm was measured between the last K atom plane of the F-Mica substrate and the first Sr–O\_3 plane of the STO film. This distance value is evidently smaller than the distance value between two K atom planes (1.02 nm), but very close to that.

Figure 4. a) An HAADF image of an STO/mica interface area, recorded along the [100] direction of F-Mica (parallel to the [110] direction of STO). b) The ABF image recorded simultaneously with the HAADF image in (a). The interface position is marked by horizontal yellow dashed lines. Corresponding projected structures of STO and F-Mica are attached on both images, showing the termination of the STO film and the F-Mica substrate at the interface.
between the K atom plane and the second (SiAl)$_2$O$_3$ plane, indicating a strong interaction between the Sr–O$_3$ plane and the (SiAl)$_2$O$_3$ plane. According to the images viewed in the two orthogonal directions, it is evident that no so-called vdW gap could be observed along the interface in this film/mica system.

Due to the lattice mismatch and the formation of the interfacial dislocations, the interface is not an ideally coherent interface. As a result, the structure of the interface changes from the defect-free parts to the parts around the dislocations. We are especially interested in the structure at the defect-free parts of the interface. This part of interface represents the most possible combination of the two materials at nucleation stage of the film growth, and thus is responsible for the epitaxy of the STO film on mica substrate. A primary model for the interface structure was suggested by carefully examining the atom arrangements of the two compounds across the interface, i.e., the oxygen arrangements in the SrO$_3$ plane and in the (SiAl)$_2$O$_3$ plane, as shown in Figure 5a,b. The oxygen hexagonal network belonging to the (SiAl)$_2$O$_3$ plane is slightly distorted (Figure 5a), while the oxygen network belonging to the Sr–O$_3$ plane of STO in Figure 5b is undistorted. It can be found that disregarding the lattice mismatch and distortion, the arrangements of the oxygen atoms in the two planes are almost identical. In particular, under the observed orientation relationship, the two oxygen networks fit to each other perfectly. This nearly identical oxygen network is an essential bridge to accommodate both the Sr and Si/Al atoms, connecting the two compounds with OR-I. The suggested primary structure model, in which the oxygen network of the (SiAl)$_2$O$_3$ plane is adopted, is shown in Figure 5c viewed along both the [112]$_{\text{STO}}$ and the [110]$_{\text{STO}}$ directions. It is clear that the [112]$_{\text{STO}}$ projection of the structure model fits well to experimental image shown in Figure 3, where the Sr atomic columns of STO join the (Si,Al)–O columns of F-Mica. However, the [110]$_{\text{STO}}$ projection deviates from that part shown in Figure 4. Since the interfacial dislocation lines are along the [112]$_{\text{STO}}$ direction (look in edge-on direction in the image of Figure 3), the dislocation lines incline with the [110]$_{\text{STO}}$ view direction of the image in Figure 4. Therefore, the incline of the dislocation lines leads to that the projected structure of the interface looks gradual change from place to place. If we extend the view area of the image in Figure 4, we can observe the interface part that fit well to the structure model.

To understand the interface stability and the atomic structure of (111) STO and (001) F-Mica, we carried out first-principles investigations to cross check with experimental results. Several interface models have been presented and compared to experimental results. Among them, the most compatible interface models (see Figure 5) representing the observed interface structure (Figures 3 and 4) lay the basis for ab initio studies. The interfacial energy per unit cell (with 72 atoms) for the (111) Sr–O$_3$ plane of STO stacked with (001) (SiAl)$_2$O$_3$ terminated F-Mica is ~2.27 eV (favored by 1.14 eV over Ti plane STO stacked with F-Mica) indicating strong bonding.

Based on the valencies of the ions, the charges at the interface are investigated, as shown in Figure S4 of the Supporting Information. The TOT structural block in F-Mica is natively charged with 1−, while the K-atom layer is positively charged with 1+, leading to charge neutral compound. At the interface, where two compounds meet, a charge neutral state would be favorable. Parallel to the (001) plane of F-Mica, STO (111) has two types of stacking atomic planes, a Ti atomic plane with charge of 4+ and a Sr–O$_3$ atomic plane with charge of 4−. For the interface model shown in Figure 5 and Figure S4 (Supporting Information), if the atomic positions of lattice are fully occupied, the interface is expected to be positively charged due to the joining of the Sr atomic plane, as denoted in Figure S4 of the Supporting Information. Calculations showed that the excess of positive charges (charge imbalance) at the interface (as shown in Figure S4, Supporting Information) causes distortions of the oxygen octahedra in STO due to charge–charge repulsion. A possibility to make the interface charge neutral is to reduce the occupancy at the positions of the Sr and (SiAl) atoms in the interfacial layer marked by green in Figure S4 of the Supporting Information. If 40% of the positions are vacant, the interface becomes charge neutral. Indeed, from the STEM images in Figure 4 the weaker contrast can be observed for the interfacial Sr layer and the (SiAl)$_2$O$_3$ plane than those in the parts away from the interface, which can be interpreted by the existence of vacancies.

In order to predict possible ion vacancies, we have also calculated the binding energy of each cation (i.e., Sr$^{2+}$ and Si$^{4+}$) at the interface. It is found that the energy required to remove one Si$^{4+}$ (0.67 eV) from the interface is 0.08 eV lesser than Sr$^{2+}$ (0.75 eV). Moreover, in the proximity of Si$^{4+}$ vacancy, the oxygen sublattices [initially in (SiAl)$_2$O$_3$ form] arrange themselves similar to the bulk Sr–O$_3$, indicating a more likely vacancy of Si or Al. Based on these results, several different structural models with vacancies have been proposed (as shown in Figure 6: Figure S5, Supporting Information) to reduce interfacial charge imbalance. The lowest energy model (Figure 6) is favored by 2.37 eV over the second lowest energy configuration (Figure S5a, Supporting Information).

The calculation results also show an increase in Si–O ideal distance in TOT block at interface (as shown in Figure 6), which indicates charge transfer (i.e., STO has pulled the (SiAl)$_2$O$_3$ layer toward itself to achieve its bulk oxygen sublattice configuration mainly due to strong tendency of Sr to bond with O), which is not the characteristic of vdW epitaxy, supporting the presence of chemical bonding. The Sr–O bond length at interface is 0.274 nm, which is very close to its bulk bond length of 0.276 nm in (111) plane. The Sr–K distance in computational model (Figure 6) is in close agreement to the experimentally observed distance (Figure 4). Therefore, the first-principles calculations fit well with the experimental results.

For the 3D oxide materials grown on flexible mica substrates quasi-vdW epitaxy has been introduced to interpret the growth mechanism. In our specific case of perovskite STO on F-Mica substrate, we have observed an interface with very close contact of the two compounds without vdW gap that was reported in the system of the BiSbTe film on α-Al$_2$O$_3$ substrate. In that work, a Te layer was observed to passivate the dangling bonds of the surface atoms of the α-Al$_2$O$_3$ substrate, providing a saturated surface for vdW epitaxy of the film. The passivating layer of Te is recognized by its same in-plane periodicity of the atoms as the substrate, instead of that of the film. This is a very good and representative example for quasi-vdW epitaxy based on the previous discussion. Our experimental investigations revealed misfit dislocations at the interface area of F-Mica side
(Figure 2). The experimental results provide the evidence that the strain due to the lattice mismatch is accommodated in a very narrow layer in the F-Mica side (Figure S6, Supporting Information), resulting in almost stain-free state of the grown STO film. From Figure S6 of the Supporting Information it is seen that the existence of the dislocations leads to a good match between the strained and unstrained O-planes, preserving the octahedral arrangement across the Mg plane. In addition, the existence of the dislocations at the interface implies that across the interface the interfacial atoms, Sr and O have strong bonding, which is not the characteristic of vdW epitaxy. Indeed, simulations based on first-principles have confirmed the bonding state at the interface.

3. Conclusion

The interfaces between perovskite STO and F-Mica have been characterized in detail to understand the epitaxy mechanism.
of perovskite oxides on mica, by means of TEM and high-resolution STEM. Two types of crystallographic orientation relationships exist depending on the temperature used for the film growth. The clean interfaces without secondary phases are intensively studied. It is found that the interfaces show a structure with strong mixing or interacting between the (111) Sr–O₃ atomic plane of STO and the (001) (SiAl)₂–O₃ atomic plane of F-Mica, due to the strong similarity of the oxygen network. This similarity provides excellent atomic environment for the film epitaxy in the determined orientation relationship. In addition, dislocations are found at the interfaces, which show stand-off behavior in the F-Mica side. The lattice mismatch is accommodated within a very narrow layer with a thickness of stand-off distance of the dislocations, resulting in almost stain-free state of the grown STO film.

4. Experimental Section

Fabrication of Epitaxial Films: The samples used for investigations of interface structure are the LaSrMnO₃/SrTiO₃ (LSMO/STO) two layer films on (001) F-Mica substrates, which were prepared by means of a KrF excimer pulsed laser deposition system with a wavelength of 248 nm. In the deposition process, the energy density of the used laser beam was about 1.5 J cm⁻². The STO film layers were grown at 800, 900, and 1000 °C with an oxygen pressure of 5 Pa, and then annealed in the growth chamber at 700 °C for 15 min under an oxygen of 5 × 10⁶ Pa followed by cooling down to room temperature at the rate of 30 °C min⁻¹. The lattice parameters, crystalline quality, and crystallographic orientation relationships of the two-layer films were investigated by high-resolution X-ray diffraction (XRD) using PANalyticalX'Pert MRD.

Electron Microscopy and Analysis: Cross-sectional specimens with the viewing direction parallel to the crystallographic (110) and (121) directions of the STO film were prepared by focused ion beam (FIB) using a lift-out technique on FEI Helios 600i Dualbeam system. The FIB-prepared samples were then polished by Ar-ion milling. High-resolution STEM and conventional TEM investigations including electron diffraction analysis and diffraction contrast imaging were carried out on a spherical-aberration corrected JEOL ARM 200F scanning transmission electron microscope with a resolution of 0.08 nm at an operating voltage of 200 kV. During STEM investigations a probe size of 0.1 nm was used with a semiconvergence angle of α = 22 mrad. The angular detector collecting the electrons with scattering angles in a range of 70–175 mrad was used for HAADF imaging. The detector for ABF imaging covered the angular range of 10–18 mrad. The samples were also investigated at 80 kV on an FEI Titan G2 80-200 ChemiSTEM microscope equipped with a high-brightness Schottky field emission electron gun and a probe Cs corrector. The beam semiconvergence angle α = 18 mrad and a collection semiangle range of 6–15 mrad were used for the ABF imaging. Noise reduction of the images was made by a nonlinear filtering algorithm.[32] GPA analysis was carried out using the developed software package,[33] which is free available via http://www.er-c.org/centre/software/gpa.htm.

First-Principles Calculations: First-principles calculations were performed using projector augmented wave (PAW) method as implemented in the GPAW software package.[34] The PBE functional of generalized gradient approximation with an energy cut-off of 700 eV was used for convergence. Brillouin zone was sampled using an appropriate 2 × 1 × 2 k-point grid. Only the interfacial atoms were allowed to relax until the atomic forces were <0.01 eV Å⁻¹ while the rest of the atoms were constrained to replicate the bulk as observed in HRSTEM images. A sufficient vacuum of 1 nm was employed for all the calculations. Interface energy was calculated by separating the crystal structures to a large distance of 1.2 nm where the structures were free from each other’s influence using \( E_i = E_1 - E_2 \) where \( E_i \) is interface energy, \( E_1 \) is energy when STO and mica are binding strongly, and \( E_2 \) is energy when STO and mica have no binding (i.e., separated by a large distance).[35] Energy required to remove each cation was calculated by separating single cation (Si⁴⁺ or Sr²⁺) from the interface to a very large distance and comparing it with ideal structure (when cation sits in interfacial site). All the proposed structural models with vacancies have equal number and same type of atoms, therefore, the energies of their relaxed structures were used to draw comparison amongst their stability. All the structure models were created in ASE[36] and visualized in VESTA.[37]

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.

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[1] A. Nathan, A. Ahnood, M. T. Cole, S. Lee, Y. Suzuki, P. Hiralal, F. Bonaccorso, T. Hasan, L. Garcia-Gancedo, A. Dyadyusha, S. Haque, P. Andrew, S. Hofmann, J. Moultrie, D. P. Chu, A. J. Flewitt, A. C. Ferrari, M. J. Kelly, J. Robertson, G. A. J. Amararatunga, W. I. Milne, Proc. IEEE 2012, 100, 1486.
[2] M. Kaltenbrunner, T. Sekitani, J. Reeder, T. Yokota, K. Kuribara, T. Tokuhashi, M. Drack, R. Schwödiauer, I. Graz, S. Bauer-Gogonea, S. Bauer, T. Someya, Nature 2013, 499, 458.
[3] Y. Khan, A. E. Ostfeld, C. M. Lochner, A. Pierre, A. C. Arias, Adv. Mater. 2016, 28, 4373.
[4] M. Koo, K. I. Park, S. H. Lee, M. Suh, D. Y. Jeon, J. W. Choi, K. Kang, K. J. Lee, Nano Lett. 2012, 12, 4810.
[5] Y. Fujisaki, H. Koga, Y. Nakajima, M. Nakata, H. Tusui, T. Yamamoto, T. Kurita, M. Nogi, N. Shimizu, Adv. Funct. Mater. 2014, 24, 1657.
[6] T. Cheng, Y. Z. Zhang, W. Y. Lai, W. Huang, Adv. Mater. 2015, 27, 3349.
[7] S. R. Bakaual, C. R. Serrao, M. Lee, C. W. Yeung, A. Sarker, S.-L. Hsu, A. K. Yadav, L. Dedon, L. You, A. I. Khan, J. D. Clarkson, C. Hu, R. Ramesh, S. Salahuddin, Nat. Commun. 2016, 7, 10547.
[8] D. Lu, D. J. Baek, S. S. Hong, L. F. Kourkoutis, Y. Hikita, H. Y. Hwang, Nat. Mater. 2016, 15, 1255.
[9] L. Shen, L. Wu, Q. Sheng, C. Ma, Y. Zhang, L. Lu, J. Ma, J. Ma, J. Bian, Y. Yang, A. Chen, X. Lu, M. Liu, H. Wang, C. L. Jia, Adv. Mater. 2017, 29, 1702411.
[10] P. Docampo, J. M. Ball, M. Darwin, G. E. Eperon, H. J. Snaith, Nat. Commun. 2013, 4, 2761.
[11] A. I. Kingon, S. Srinivasan, Nat. Mater. 2005, 4, 233.
[12] H. Palmeedi, H. G. Yeo, G. T. Hwang, V. Annareddy, J. W. Kim, J. J. Choi, S. Trolier-Mckinstry, J. Ryu, APL Mater. 2017, 5, 096111.
[13] J. W. McCauley, R. E. Newham, G. V. Gibbs, Am. Mineral. 1973, 58, 249.
[14] R. M. Hazen, C. W. Burnham, Am. Mineral. 1973, 58, 889.
[15] Y. Bitla, Y. H. Chu, FlatChem 2017, 3, 26.
[16] P. C. Wu, Y. H. Chu, J. Mater. Chem. C 2018, 6, 6102.
[17] Y. Yang, C. Yuan, Z. Yan, Y. Wang, X. Lu, J.-M. Liu, Adv. Mater. 2017, 29, 1700425.
[18] J. Jiang, Y. Bitla, C.-W. Huang, T. H. Do, H.-J. Liu, Y.-H. Hsieh, C.-H. Ma, C.-Y. Jang, Y.-H. Lai, P.-W. Chiu, W.-W. Wu, Y.-C. Chen, Y.-C. Zhou, Y.-H. Chu, Sci. Adv. 2017, 3, e1700121.
[19] H. J. Liu, C. C. Wang, D. Su, T. Amrillahl, Y. H. Hsieh, K. H. Wu, Y. C. Chen, J. Y. Juang, L. M. Eng, S. U. Jen, Y. H. Chu, ACS Appl. Mater. Interfaces 2017, 9, 7297.
[20] T. Amrillahl, Y. Bitla, K. Shin, T. Yang, Y. H. Hsieh, Y. Chiou, H. J. Liu, T. H. Do, D. Su, Y. C. Chen, S. U. Jen, L. Q. Chen, K. H. Kim, J. Y. Juang, Y. H. Chu, ACS Nano 2017, 11, 6122.
[21] J. D. Liu, Y. Feng, R. J. Tang, R. Zhao, J. Gao, D. N. Shi, H. Yang, Adv. Electron. Mater. 2018, 4, 1700522.
[22] C. H. Ma, J. Jiang, P. W. Shao, Q. X. Peng, C. W. Huang, P. C. Wu, J. T. Lee, Y. H. Lai, D. P. Tsai, J. M. Wu, S. C. Lo, W. W. Wu, Y. C. Zhou, P. W. Chiu, Y. H. Chu, ACS Appl. Mater. Interfaces 2018, 10, 30574.
[23] W. Liu, M. Liu, R. Ma, R. Zhang, W. Zhang, D. Yu, Q. Wang, J. Wang, H. Wang, Adv. Funct. Mater. 2018, 28, 1705928.
[24] L. Shen, M. Liu, C. Ma, L. M. Liu, H. Fu, C. You, X. Lu, C.-L. Jia, Mater. Horiz. 2018, 5, 230.
[25] A. K. Geim, I. V. Grigorieva, Nature 2013, 499, 419.
[26] K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. C. Neto, Science 2016, 353, aac9439.
[27] L. A. Walsh, C. L. Hinkel, Appl. Mater. Today 2017, 9, 504.
[28] C. L. Jia, B. Kabiuss, K. Urban, K. Herrmenn, J. Schubert, W. Zander, A. I. Braginski, Phys. C 1992, 196, 211.
[29] J. Y. Hwang, Y.-M. Kim, K. H. Lee, H. Ohta, S. W. Kim, Nano Lett. 2017, 17, 6140.
[30] A. Koma, K. Ueno, K. Saiki, J. Cryst. Growth 1991, 111, 1029.
[31] A. Koma, J. Cryst. Growth 1999, 201–202, 236.
[32] H. Du, Ultramicroscopy 2015, 151, 62.
[33] H. Du, C. L. Jia, L. Houwen, V. Mettenko, R. A. De Souza, R. Waser, J. Mayer, Acta Mater. 2015, 89, 344.
[34] J. Enkovaara, C. Rostgaard, J. J. Mortensen, J. Chen, M. Dulak, L. Ferrighi, J. Gavnholm, G. Hahn, G. A. J. Amaratunga, W. I. Milne, Acta Mater. 2010, 17, 485301.
[35] A. H. Larsen, J. J. Mortensen, J. Blomqvist, I. E. Castelli, R. Christensen, M. Dulak, J. Friis, M. N. Groves, B. Hammer, C. Hargus, J. Phys. Condens. Matter 2017, 29, 273002.
[36] K. Momma, F. Izumi, J. Appl. Crystallogr. 2008, 41, 653.