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Epitaxial Nature of $CH_3NH_3Pb(BrI)_3$ Thin Films Formed on $CH_3NH_3PbBr_3$ Single Crystal Substrates

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Abstract

We have successfully fabricated epitaxial lead halide perovskite alloy ($CH_3NH_3Pb(BrI)_3$) thin films on $CH_3NH_3PbBr_3$ single crystal substrates by co-evaporating CH_3NH_3I and PbI_2. The epitaxial nature of the fabricated thin films has been confirmed by using X-ray diffraction reciprocal space mapping technique.

1. Introduction

Lead halide perovskite semiconductors are attractive materials for efficient solar cells, light emitting devices, and photodetectors. Most of these devices have been fabricated using polycrystalline thin films sandwiched between other materials such as metal oxides, organic compounds and metal electrodes. However, perovskite hetero-epitaxial thin films formed on lead halide perovskite single crystal substrates will, if realized, open up new possibilities of these materials. Hetero-epitaxial perovskites will lead to single-crystalline heterostructures and/or all-perovskite devices. We have tried to fabricate $CH_3NH_3Pb(BrI)_3$ thin films on $CH_3NH_3PbBr_3$ single crystal substrates by using vacuum deposition technique. Our previous attempts resulted only in PbI_2 film formation containing a small amount of $CH_3NH_3Pb(BrI)_3$ as a minor component, and epitaxial nature was not confirmed [1]. In this paper, we report on fabrication of pure lead halide perovskite thin films without PbI_2 impurity and epitaxial nature of the fabricated films characterized by using X-ray diffraction (XRD) reciprocal space mapping (RSM) technique.

2. Experimental

We prepared $CH_3NH_3PbBr_3$ single-crystal substrates by inverse temperature crystallization method [2]. 1.0 mol/L solution containing equimolar CH_3NH_3Br and $PbBr_2$ in N,N-dimethylformamide was percolated, and then heated at 80°C in an oil bath for 3 hours. We obtained cubic-shaped single crystals with 2 × 2-mm^2 square areas and 1-mm thicknesses. The topfaces of the single crystals were confirmed to be parallel to (001).

We deposited lead halide perovskite thin films by irradiating CH_3NH_3I and PbI_2 molecules on the fabricated (001) $CH_3NH_3PbBr_3$ single crystalline substrates in a vacuum evaporation system for 67.5 min. The supply rates of CH_3NH_3I and PbI_2 were kept 1.6 Å/s (chamber pressure: 0.015 Pa) and 0.4 Å/s, respectively. We kept substrate temperature at 21°C using circulating water.

We measured XRD pattern ($2\theta/\omega$ scan) of a thin film on a $CH_3NH_3PbBr_3$ single crystal substrate from 5° to 95° and the result is shown in Fig. 1. Only five peaks corresponding to (001) of the single crystal substrate were observed, and other polycrystalline signals including PbI_2 (12.7°) were not detected.

We measured RSM of symmetric and asymmetric reflections by using high-resolution X-ray diffractometer equipped with a Ge (220) two-crystal monochromator. Figures 2 and 3 show the RMS from symmetric (002) reflection and asymmetric (024) reflection of the sample, respectively. Broad diffraction spots of the thin film are observed right under the intense diffraction peaks of the substrate in both RSM. This clearly shows that the fabricated thin film is (001)-orientated and the film is not relaxed but is pseudomorphic. We measured XRD ϕ scan profiles of {024} asymmetric diffractions from the substrate and the thin film depicted as cross points shown in Fig. 3. Both {024} diffractions shown in Fig. 4 exhibit four peaks separated by 90° intervals. This is consistent with four-fold symmetry around [001] of $CH_3NH_3Pb(Br_{1-x}I_x)_3$ ($0 \leq x < 0.8$) [3]. The in-plane ϕ angles are exactly the same for the substrate and the thin film indicating that the thin film is perfectly epitaxial with its [100] and [010] axes parallel to those of the substrate. These measurements clearly show that the fabricated thin film is of epitaxial nature.

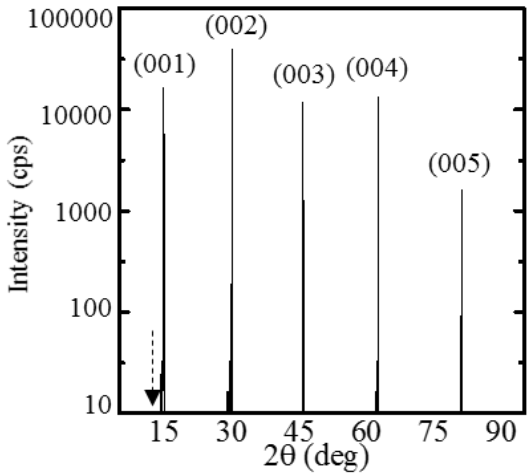

Fig. 1 $2\theta/\omega$ XRD pattern of a thin film on a $CH_3NH_3PbBr_3$ single crystal substrate from 5° to 95°. Indexes are determined by lattice constant of a cubic $CH_3NH_3PbBr_3$.single crystal. Dashed arrow represents the diffraction angle of PbI_2 (0001).

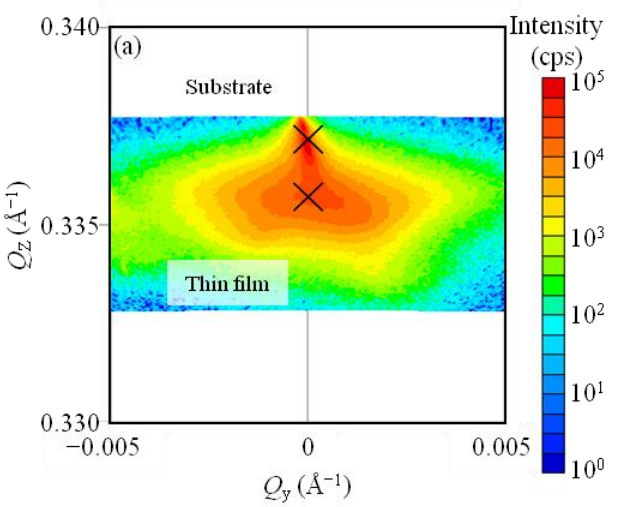

Fig. 2 Reciprocal space mapping of (002) reflection of a thin film on a $CH_3NH_3PbBr_3$ single crystal substrate.

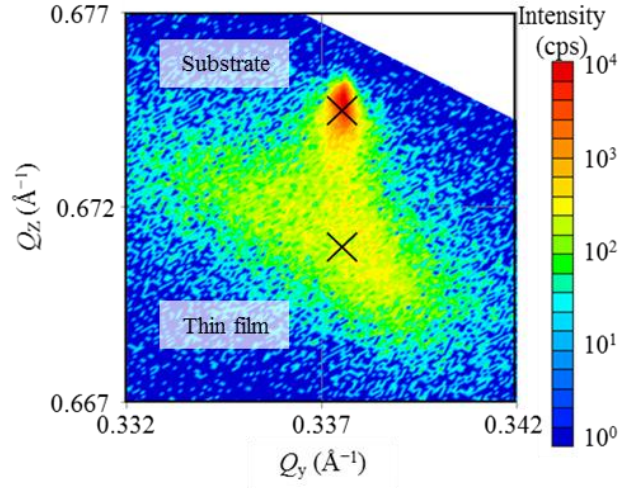

Fig. 3 Reciprocal space mapping of (024) reflection of a thin film on a $CH_3NH_3PbBr_3$ single crystal substrate. Cross marks show the top of each peak where ϕ scan profiles are measured.

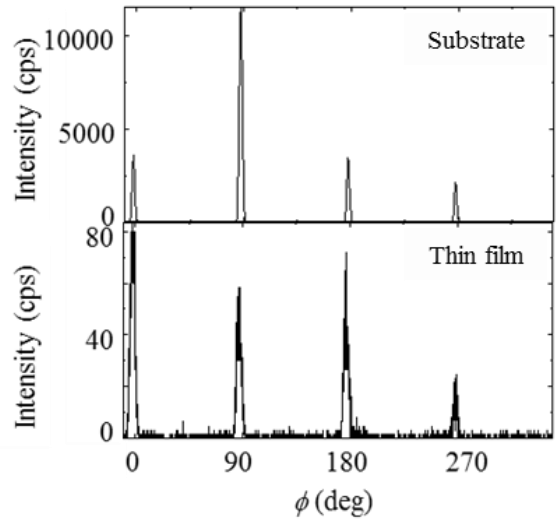

Fig. 4 XRD ϕ scan profiles of a thin film on a $CH_3NH_3PbBr_3$ single crystal substrate for {024} diffractions from the substrate (top) and from the thin film (bottom).

3. Discussion

We analyzed RSM to evaluate real space lattice of the formed thin film. From the obtained RSM of the (002) symmetric reflection, we estimated the lattice constants of the film and the substrate along [001] (vertical direction) to be 5.967 Å and 5.935 Å, respectively. By using the RSM of the (024) asymmetric reflection, the lateral lattice constants of the film and the substrate along [010] were calculated to be 5.935 Å. The obtained lattice constant of the substrate is consistent with that of cubic $CH_3NH_3PbBr_3$ reported in the literature [4]. By using Poisson's ratio of 0.29 [5] and the pseudo-cubic lattice constant (6.276 Å) of $CH_3NH_3PbI_3$ [6] and assuming Vegard's law, we obtained the bulk lattice constant of the epitaxial thin film to be 5.947 Å. The corresponding iodide composition of the epitaxial film is 0.03 ($CH_3NH_3Pb(Br_{0.97}I_{0.03})_3$). The epitaxial thin film exhibits in-plane 0.2 % compressive strain and 0.16 % tensile strain along [001] axis. The formation of the mixed halide thin film with a relatively low iodide composition is probably caused by the interdiffusion of halide ions (Br^- and I^-). The small iodide concentration with smaller lattice mismatch of 0.2 % (compare with large mismatch of pure $CH_3NH_3PbI_3$,6 %) is presumably beneficial for epitaxial film formation. The mosaicity of the epitaxial thin film was estimated to be 0.5°.

4. Conclusions

We have succeeded in fabricating a hetero-epitaxial pseudomorphic thin film of lead halide perovskite semiconductor alloy $CH_3NH_3Pb(Br_{0.97}I_{0.03})_3$ on a (001) $CH_3NH_3PbBr_3$ single crystal substrate by vacuum co-evaporation. This is a great milestone toward next-generation single-crystal perovskite devices.

References

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