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Critical Thickness of Epitaxial $CH_3NH_3Pb(IBr)_3$ Thin Films Formed on $CH_3NH_3PbBr_3$ Single Crystal Substrates

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Abstract

We have grown pseudomorphic and fully-relaxed epitaxial lead halide $CH_3NH_3Pb(BrI)_3$ alloy thin films on $CH_3NH_3PbBr_3$ single crystalline substrate, and have estimated critical thickness. The obtained critical thickness is consistent with conventional theoretical models.

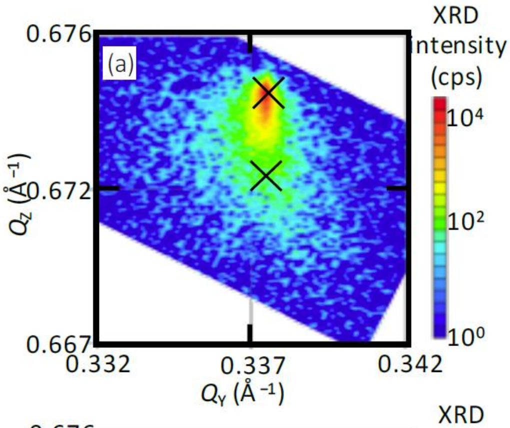
1. Introduction

Lead halide perovskite semiconductors are expected to play a crucial role to realize 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. We have successfully fabricated pseudomorphic epitaxial $CH_3NH_3Pb(BrI)_3$ alloy thin films on $CH_3NH_3PbBr_3$ single crystalline substrates by using vacuum deposition technique [1]. For realizing high-quality epitaxial lead halide perovskite thin films without threading/misfit dislocations, it is indispensable to investigate critical thickness (thickness from pseudomorphic to relaxed epitaxial thin films). In this paper, we report on the epitaxial growth of pseudomorphic and relaxed lead halide perovskite alloy thin films and on the investigation of the critical thickness by using X-ray diffraction (XRD) reciprocal space mapping (RSM) technique and spectroscopic ellipsometry technique.

2. Experimental and discussion

We prepared five epitaxial $CH_3NH_3Pb(BrI)_3$ alloy thin films with different thicknesses by irradiating CH_3NH_3I and PbI_2 molecules on fabricated (001) $CH_3NH_3PbBr_3$ single crystalline substrates in vacuum evaporation system. The film thicknesses of the samples are 85, 110, 196, 208, and 254 nm, which were measured by using ellipsometry as described lately. The fluxes of supplied materials were kept constant by tuning materials temperatures with PID feedback. We set the rate of PbI_2 to 0.4 Å/s and total pressure of CH_3NH_3I to 0.015 Pa, respectively. The substrate temperature was kept at 21°C using cooled water. Details of the fabrication of $CH_3NH_3PbBr_3$ single crystalline substrates are described in our previous paper [1].

We measured RSM of symmetric and asymmetric reflections by using high-resolution X-ray diffractometer equipped with a Ge (220) two-crystal monochromator. Figure 1 (a) shows the RMS from asymmetric (024) reflection of a 196-nm-thick epitaxial thin film sample. Broad diffraction spots



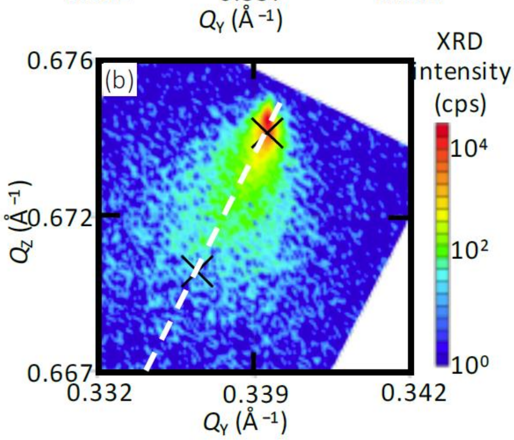


Fig. 1 Reciprocal space mappings of (024) reflection of epitaxial heterostructure samples with the film thickness of 196 nm (a) and 254 nm (b). The white dotted line is parallel to the straight line connecting (000) and (024) reflections of the substrate.

of the thin film are observed right under the intense diffraction peaks of the substrate. This clearly shows that the 196-nm-thick epitaxial thin film is pseudomorphic. From the obtained RSM of the (002) symmetric reflection and the (024) asymmetric reflection and by using Poisson's ratio of 0.29 [2], we estimated the unstrained bulk lattice constants of the film ($a_{\text{thin-film}}$) to be 5.943 Å. By using the pseudo-cubic lattice constant (6.276 Å) of $CH_3NH_3PbI_3$ [3] and by assuming Vegard's law, we also calculated corresponding iodide composition to be 2.3%. Lattice mismatch ($|a_{\text{thin-film}} - a_{\text{sub}}|/a_{\text{sub}}$), where a_{sub} represents the lattice constant of a $CH_3NH_3PbBr_3$ substrate, is 0.0019. On the other hand, the diffraction spot of a 254-nm-thick epitaxial thin film sample is observed on a straight line connecting diffraction points (000) and (024) of the substrate. This shows that the 254-nm-thick epitaxial film is fully relaxed. We obtained the unstrained bulk lattice constants and the corresponding iodide composition of the film to be 5.969 Å and 10 %, respectively. By increasing the film thickness larger than 208 nm, we obtained not pseudomorphic but fully-relaxed $CH_3NH_3Pb(BrI)_3$ epitaxial thin films.

We estimated thicknesses of the epitaxial thin films using ellipsometric characterization. Figure 2 shows ellipsometric spectra of the fabricated sample with the film thickness of 196 nm. Interference fringes observed in the wavelength range from 650 to 1600 nm are due to multiple reflections in the perovskite alloy thin film layer. To fit theoretical curves to experimental data, we used an optical model composing 175-nm-thick surface roughness layer/82-nm-thick perovskite alloy layer/$CH_3NH_3PbBr_3$ substrate. The optical constants of the perovskite alloy are described by using effective medium approximation (EMA) based on optical constants of $CH_3NH_3PbI_3$ and $CH_3NH_3PbBr_3$ [4]. Those of the roughness layer are the EMA mixture of those of the perovskite alloy and air. The composition of iodine in the perovskite alloy is 2.4%, while that of air in the roughness layer is 35%. The agreement of the fitting with experimental data indicates that the obtained thickness is reliable. By summing up the thickness of the perovskite alloy and an effective thickness of the perovskite alloy in the roughness layer, we estimated typical thickness of the perovskite alloy to be 196 nm (= 82 nm + 175 nm × (1−0.35)).

To investigate critical thickness of $CH_3NH_3Pb(BrI)_3$ epitaxial thin films on $CH_3NH_3PbBr_3$ single crystalline substrates, we plot obtained typical thicknesses dependent on lattice mismatches of the samples (Fig. 3). The critical thickness exists in the region sandwiched between two theoretical critical thickness based on energy valance model [5] and force valance model [6]. This phenomenon frequently observed in inorganic semiconductor epitaxial growth indicates the critical thickness of perovskite epitaxial thin films is consistent with those of inorganic semiconductors.

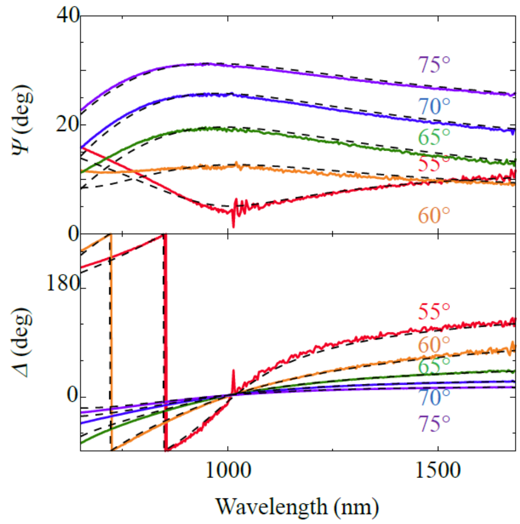


Fig. 2 Ellipsometric spectra of the 196-nm-thick epitaxial film sample. The colored solid and black dotted lines represent experimental and fitted curves, respectively. The numbers indicate incident angles.

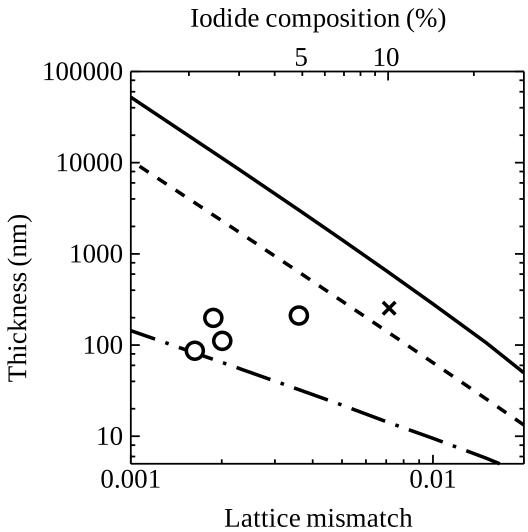


Fig. 3 Thickness vs. lattice mismatch of the fabricated epitaxial hetero-structure samples. Circle and cross marks represent that obtained epitaxial thin films are pseudomorphic and fully relaxed, respectively. Solid and dashed-and-dotted lines are theoretical curves based on energy valance model [5] and force valance model [6], respectively. The dotted line is a tentative guide for critical thickness.

3. Conclusions

We have investigated critical thickness of the fabricated epitaxial heterostructures. The critical thickness is consistent with conventional theoretical models. This result will give a guideline to the epitaxial growth of lead halide perovskite alloys without threading/misfit dislocations.

Acknowledgements

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