Epitaxial growth of organolead-halide perovskite on rubrene single crystals

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Abstract

We attempted hetero-epitaxial growth of organolead-halide perovskite on single-crystal organic semiconductors by vapor deposition for the purpose of preparing a perovskite film with high crystallinity and flatness. The CH₃NH₃PbI₃ was epitaxially grown on rubrene single crystals. It was also observed that the CH₃NH₃PbI₃ epitaxial film had high flatness with clear step and terrace structure where the step height was corresponding to the lattice constant of CH₃NH₃PbI₃ (6.2 Å). Crystal orientation of CH₃NH₃PbI₃ changed and larger grain was obtained with the increase of the substrate temperature under growth. we can see several types of orientation in CH₃NH₃PbI₃ film deposited alternatively.

1. Introduction

In recent years, organolead-halide perovskite solar cells have been studied actively due to remarkable progress of their power conversion efficiency.

Controlling crystal growth of perovskite is important research subject from the both standpoint of fundamental research and device application. Many research of preparing high quality perovskite films have been reported. However, elucidation of preparing high quality perovskite films and the clear mechanism of film formation is still under development. Controlling perovskite crystal growth lead to the construction of ideal film structures and performance improvement of perovskite solar cells can be expected as well.

In this study, we attempted hetero-epitaxial growth of CH₃NH₃PbI₃ on single-crystal organic semiconductors by vapor deposition for the purpose of preparing a perovskite film with high crystallinity.

2. Results and discussion

Fabrication process

Rubrene single crystals were fabricated by physical vapor deposition. The (001) orientation of the rubrene single crystal was verified by out-of plane X-ray diffraction (XRD, RIGAKU Smart lab., CuKα1 for X-ray source) and step and terrace structure was observed by atomic force microscope (AFM). The rubrene single crystal thin plates were mounted on a glass substrate and transferred to the vacuum chamber. PbI₂ and CH₃NH₃I were co-evaporated on the rubrene single crystal thin plate by IR laser deposition method [1] to form CH₃NH₃PbI₃ film.

The three dimensional crystal orientation of CH₃NH₃PbI₃ on rubrene single crystals was investigated by grazing incident X-ray diffraction (GIXD), at SPring-8, BL46XU.

Orientation of CH₃NH₃PbI₃ on rubrene single crystal

The GIXD was observed by rotating the sample with φ-axis (perpendicular to the substrate). The results were converted to reciprocal space and mapped as shown in Fig.1.

In this result, it revealed that CH₃NH₃PbI₃ crystal was epitaxially grown along the crystal orientation of rubrene single crystals.

Fig.1 Reciprocal space mapping (kz = 0) figured with sample-rotated GIXD measurement of CH₃NH₃PbI₃ grown on rubrene single crystals at 80°C.
Morphology of CH$_3$NH$_3$PbI$_3$ on rubrene single crystals

Figure 2 shows morphology of CH$_3$NH$_3$PbI$_3$ epitaxial film on a rubrene single crystal. Clear step-and-terrace structure was observed which can be an evidence for high flatness. Moreover, since a step of about 6.2 Å corresponding to the lattice constant of CH$_3$NH$_3$PbI$_3$ was observed (Fig.2 (b) and (c)), the growth mode can be layer-by-layer.

![Fig.2 AFM image of CH$_3$NH$_3$PbI$_3$ epitaxial film.](image)

Influence of Growth temperature to CH$_3$NH$_3$PbI$_3$ film

Figure 3 shows reciprocal space mapping of CH$_3$NH$_3$PbI$_3$ grown on rubrene single crystals at each temperature. We can see several types of orientation in the film deposited at room temperature. In the film deposited at room temperature, 7 orientation patterns were observed, on the other hand, it was decreased to 3 orientation patterns in the films deposited at elevated temperature.

![Fig.3 Reciprocal space mapping ($k_z = 0$) figured with sample-rotated GIXD measurement of CH$_3$NH$_3$PbI$_3$ grown on rubrene single crystals at (a) Room Temp. (b) 80°C (c) 120°C.](image)

Figure 4 shows the surface morphology of the perovskite film at each growth temperature (room temperature, 80°C, 120°C). As the growth temperature increased, crystal grains became larger. This can be due to the enhancement of the diffusion of molecule, which decreases the number of crystal nuclei and crystals per one can grow larger.

![Fig.4 surface morphology of CH$_3$NH$_3$PbI$_3$ film of each growth temperature (a) Room Temp. (b) 80°C (c) 120°C.](image)

Changes in orientation of CH$_3$NH$_3$PbI$_3$ film by alternative deposition

Next then, we attempted alternative deposition of PbI$_2$ and CH$_3$NH$_3$I on rubrene single crystals. Figure 5 shows reciprocal space mapping CH$_3$NH$_3$PbI$_3$. In the result, we can see several types of orientation in the film deposited alternatively.

![Fig. 5 Reciprocal space mapping ($k_z = 0$) figured with sample-rotated GIXD measurement of CH$_3$NH$_3$PbI$_3$ grown on rubrene single crystals by alternative deposition.](image)

3. Conclusions

We attempted hetero-epitaxial growth of CH$_3$NH$_3$PbI$_3$ on rubrene single crystals by vapor deposition for the purpose of constructing CH$_3$NH$_3$PbI$_3$ films with high crystallinity. Hetero-epitaxial growth of CH$_3$NH$_3$PbI$_3$ on rubrene single crystals was verified. It was also observed that the CH$_3$NH$_3$PbI$_3$ epitaxial film had high flatness and step of about 6.2 Å which is corresponding to the lattice constant of CH$_3$NH$_3$PbI$_3$. The CH$_3$NH$_3$PbI$_3$ crystal grows layer-by-layer on the rubrene single crystals. Crystal orientation of CH$_3$NH$_3$PbI$_3$ changed and larger grain was obtained under the elevated growth temperature. we can see several types of orientation in CH$_3$NH$_3$PbI$_3$ film deposited alternatively.

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References