

Temperature dependence of CH₃NH₂ molecular defect in CH₃NH₃PbI₃ thin film formed by sequential vacuum evaporation

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Abstract

The sequential vacuum evaporation method (SVE) to fabricate organic-inorganic hybrid perovskite thin film such as CH₃NH₃PbI₃ is a unique candidate for controlling molecular defect. Without a post-annealing process, however, material instability is arising seriously because of the remained MAI and PbI₂ in the thin film. In this study, we performed SVE with variable annealing conditions and confirmed the temperature dependence of CH₃NH₂ molecular defect. Finally, we suggest an optimized state with the control of defect concentration and the improvement of thin film stability.

1. Introduction

Recently, organic-inorganic hybrid perovskite (OHP), ABX₃ (A = Organic cation: CH₃NH₃⁺/NH₂CH=NH₂⁺, B = Metal cation: Pb/Sn, and X = Halide anion: Cl/Br/I) is a promising material for solar-cell, field-effect transistor, and light-emitting diode applications.[1] Currently, the number of published works on OHPs are growing exponentially. Even, nanoscience research using OHP material is just begun, and its single crystal formation with nano-scale size and physical properties such as bandgap engineering were reported. New applications employing these OHP materials are expected to further expand due to the several unique physical properties still unexplored in these materials.

In our previous research, we found several significant THz-wave absorption properties (At 1.5~1.7 THz with 20~50 % absorptance) in MAPbI₃, FAPbI₃, and FAPb(Br_{1-x}, I_x)₃ originated from a kind of defect structures.[2-4] Especially, we found that the absorptance of origin in MAPbI₃ was the CH₃NH₂ molecular defect incorporated perovskite structure (significant Pb-I vibration mode). In this finding, the problem is arising the material stability because there is no post-annealing process to keep this molecular defect structure. Basically, the post-annealing process can induce making more stable OHP with large grains and clear stoichiometry. However, the molecular defect is disappeared during the post-

annealing. (Fig. 1)

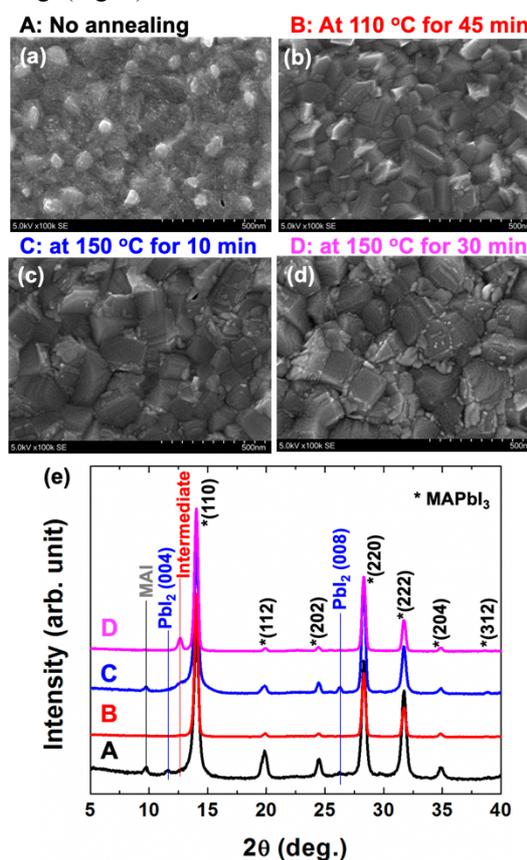


Fig. 1 The surface morphologies and XRD results with variable post-annealing conditions. In the typical annealing condition (B: for solar-cell) for MAPbI₃, there is no MAI, PbI₂ and intermediate phases.

In this study, we have performed variable post-annealing processes on MAPbI₃ thin film fabricated by SVE method. And then we have investigated their atomic structures, defects and chemical states to find an optimized state with the control of defect concentration and the improvement of stability.

2. Experimental details and results

OHP thin films were fabricated by the SVE method in the customized vacuum chamber. A silicon substrate (*n*-type doped Si(100)) was cleaned by sonication in acetone for 10 min, rinsed in heated acetone for 1 min, and then UV-Ozone treatment for 30 min before loading into a vacuum chamber. The base pressure of the chamber installed with the thickness monitor sensor was 8.0×10^{-3} Pa. A Lead(II) iodide (PbI_2 , 99% purity, Sigma-Aldrich) was evaporated with the deposition rate of 10 \AA/s onto the substrates at room temperature to form the film with 100 nm-thick.[2] Continuously, a methylammonium iodide ($\text{CH}_3\text{NH}_3\text{I}$, 98% purity, Sigma-Aldrich) was evaporated with the deposition rate of 2 \AA/s and the 280 nm-thick onto the formed PbI_2 thin film.[2] Finally, we obtained the MAPbI_3 thin films with a thickness of 300 nm.[2] To see the temperature dependence of MAPbI_3 , we performed the annealing processes at the temperature of 110-150 °C for 10-45 min. Over the temperature of 150 °C, the depletion/degradation process of MAPbI_3 is so fast and very difficult to maintain a thin film structure.

To characterize all of the formed and treated thin films, we performed scanning electron microscopy (SEM), x-ray diffraction (XRD), and high-resolution x-ray photoelectron spectroscopy. The used SEM system is HITACHI SU9000 model with the acceleration voltage of 5.0 kV and the emission current of 10 μA . The XRD is RINT-TTRIII/NM with $\text{CuK}\alpha$ source made by Rigaku. We used the Versa ProbeII with a monochromated $\text{AlK}\alpha$ (ULVAC-PHI) for all XPS measurements and obtained the C 1s, N 1s, Pb 4f, and I 4d core-level spectra. In all samples, there was observed with no trace of O 1s core-level spectra.[2] The binding energies were calibrated with reference to the Au 4f_{7/2} level (84.0 eV).

In the no-annealing sample (A), we observe a tiny grain structure. (Fig. 1a) However, it is not clear. After annealing at 110 °C for 45 min (B) which is a typical annealing condition for a solution-processed thin film,[4] the grains appear clearly with the grain size of 70-120 nm. (Fig. 1b) As increasing the annealed temperature at 150 °C for 10 min, the grain size is increased with over 200 nm. (Fig. 1c) By increasing the annealing time for 30 min, however, many small structures occurred at the grain boundary, and it looks a degradation. (Fig. 1d) From these SEM results, we can agree that 1) the annealing process with the high temperature can increase the grain size and 2) the increased annealing time can make a degradation at the grain boundary.

To understand the structural formation, we performed the XRD experiment for all treated samples. (Fig. 1e) In all samples, the typical atomic structures of MAPbI_3 are observed such as (110), (112), (202), (220), (222), (204), and (312) in the range of 5 – 40 degrees. In the A sample, we can observe the trace of MAI, PbI_2 and intermediate phases.[2] In the B sample, however, these structures are completely disappeared. This result is similar to several reports and we confirmed that the typical annealing conditions can remove MAI and PbI_2 phases formed by the SVE method.[2,4] When we increased the annealing temperature from 100 to 150 °C (the sample C), the MAI, PbI_2 and intermediate phases are still alive. In expanding the annealing time from 10 to 30 min (the D sample),

only the intermediate phase has remained mainly with the hybrid perovskite phase, and the MAI and PbI_2 phases are wholly disappeared.

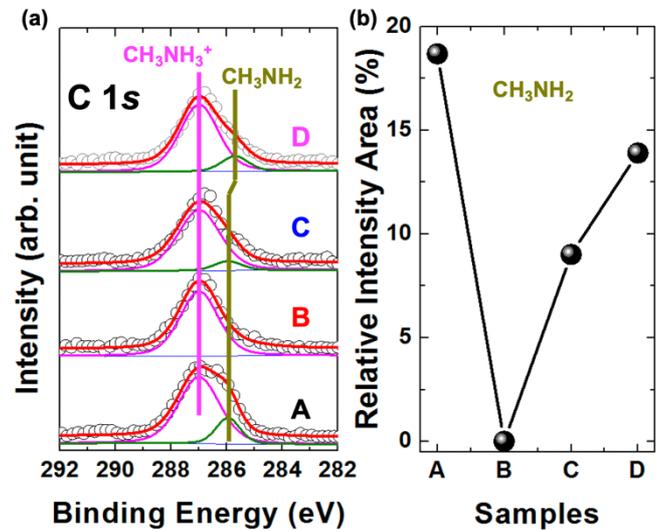


Fig. 2 (a) Curve-fittings for C 1s core-levels of A, B, C, and D. (b) The relative intensity area for the chemical state of CH_3NH_2 molecular defect.

To see the detailed behavior of CH_3NH_2 molecular defect processed under the different annealing temperatures, we performed the curve-fittings of C 1s core-level spectra in sample A, B, C, and D using Doniach–Sünjić curves convoluted with Gaussian distribution with 0.5 eV full width at half maximum. (Fig. 2a) Interestingly, we could not observe any defect intensity in the B sample. However, the C and D samples are still shown with the CH_3NH_2 molecular defect. From the curve-fitting data, we calculated the relative intensity area for each sample. (Fig. 2b) In the A sample, we confirmed over 18 % of the concentration of CH_3NH_2 molecular defect. However, the molecular defect is disappeared after annealing at 110 °C for 45 min which is a typical annealing condition for solar-cell application. Interestingly, the CH_3NH_2 molecular defect is still remaining in the sample C and D annealed at 150 °C for 10 min and 30 min, respectively.

3. Conclusions

From these results, we expect to find an optimized state with the control of defect concentration and the improvement of thin film stability.

Acknowledgements

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