

# Reaction Rate Analysis of Chemical Vapor Deposited Bi-based Perovskite Thin Film

Ziguang Yang, Keito Togami, Maika Tanabe, Shoma Kimura, and Motoaki Kawase\*

*Department of Chemical Engineering, Faculty of Engineering, Kyoto University.*

*Kyotodaigakukatsura, Nishiky-ku, Kyoto, 615-8510 Japan*

*\*Corresponding author: kawase@cheme.kyoto-u.ac.jp*

## Highlights

- Lead-free perovskite thin film was produced by chemical vapor deposition.
- Effect of processing parameters on thin film deposition rate was discussed.
- Reaction model was proposed, and kinetic constants were determined.

## 1. Introduction

Perovskite solar cells using the organic metal halide as the light absorption layer have attracted attention for high conversion efficiency. It has advantages including flexibility, light weight, durable mechanical properties, and low raw material cost. A new alternative, methylammonium bismuth iodide ((CH<sub>3</sub>NH<sub>3</sub>)<sub>3</sub>BiI<sub>9</sub>, MABI) is gaining attention because of its higher moisture resistance and lower toxicity than the most researched methylammonium lead iodide (CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>, MAPI).<sup>[1]</sup> However, there is still much to improve for this novel material on power conversion efficiency. To commercialize perovskite solar cells many studies have been done on material selection, process technique innovation, and defects or interface improvement.<sup>[2]</sup> This work focuses on the kinetic analysis of perovskite thin film formation to fill the knowledge blank and contribute to further thin film quality improvement and economic analysis.

## 2. Methods

Fig. 1 shows the schematic of MABI production apparatus by chemical vapor deposition (CVD). This work is the first proposal of using highly reactive material, bismuth oxide to produce film growth precursor (BiI<sub>3</sub>). HI gas was supplied to the reaction tube (SUS316), diluted with helium gas through inlet 1, and reacted with bismuth oxide to generate BiI<sub>3</sub> as expressed by equation (1).



The remaining HI gas and BiI<sub>3</sub> vapor were diluted further with helium from inlet 2. Following this, it reacted with helium-diluted methylamine (MA) from inlet 3 at the junction to form methylammonium iodide (MAI) and flowed downstream, to the deposition section. The reaction at the mixing junction was expected to be expressed by equations (2) and (3).

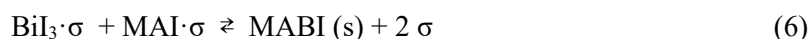


TiO<sub>2</sub> coated fluorine-doped tin oxide (FTO) substrates (8 mm×50 mm×1.1 mm, Astratec) were placed in series and deposited at 1.33×10<sup>3</sup> Pa of total pressure. Product was characterized by the X-ray diffraction (XRD) patterns (Rigaku, UltimaIV), and film morphologies were observed by a scanning electron microscope (JEOL, JCM-7000).

## 3. Results and discussion

All deposited thin films showed XRD patterns consistent with reference MABI XRD pattern. In a non-isothermal setting where upstream is at higher temperature than downstream, MABI deposition started around 180 °C when BiI<sub>3</sub> and MAI had partial pressure of 0.16 Pa and 1.04 Pa, respectively. Increase in the reactant partial pressure shifted the deposition to a higher temperature zone. Above 180 °C MABI growth rate was reduced below that at 160 °C; higher reactant partial pressure promoted the deposition

above 180 °C. This could be interpreted as decomposition of MABI has a higher activation energy than its formation and the increase in reactant partial pressure promoted the formation rate sufficiently as temperature is raised. The effects of reactant partial pressure on deposition rate were investigated in isothermal deposition settings. As Fig. 2 shows, the effects of MAI partial pressure on the film growth rate include a linear increase region and an inversely proportional decrease region. Similar trend was also noticed for the BiI<sub>3</sub> partial pressure. The following Langmuir's adsorption and surface reaction model can well explain the experimental results:



The corresponding overall MABI growth rate equation can be expressed as:

$$r = k \frac{K_{\text{BiI}_3} p_{\text{BiI}_3} K_{\text{MAI}} p_{\text{MAI}}}{(1 + K_{\text{BiI}_3} p_{\text{BiI}_3} + K_{\text{MAI}} p_{\text{MAI}})^2} - k' \left( 1 - \frac{K_{\text{BiI}_3} p_{\text{BiI}_3} + K_{\text{MAI}} p_{\text{MAI}}}{1 + K_{\text{BiI}_3} p_{\text{BiI}_3} + K_{\text{MAI}} p_{\text{MAI}}} \right)$$

Where  $k$  is the MABI formation reaction rate constant and  $k'$  for its decomposition.  $K_{\text{BiI}_3}$  and  $K_{\text{MAI}}$  are the adsorption equilibrium constants of BiI<sub>3</sub> and MAI, respectively, and  $p_{\text{BiI}_3}$  and  $p_{\text{MAI}}$  represent their partial pressures. The determined values are listed in Table 1.

The values in the table suggest that both increase in decomposition rate and reduction in precursor surface coverage (since adsorption equilibrium constant is little) make the film growth more difficult when raising process temperature.

#### 4. Conclusions

MABI thin film has been deposited on the substrates and confirmed by XRD patterns. MABI formed via the surface reactions between adsorbed precursors. Higher reactant partial pressure is necessary to promote the film growth rate as temperature is raised since the decomposition rate increases more remarkably than the formation and the precursor surface coverages are low.

#### References

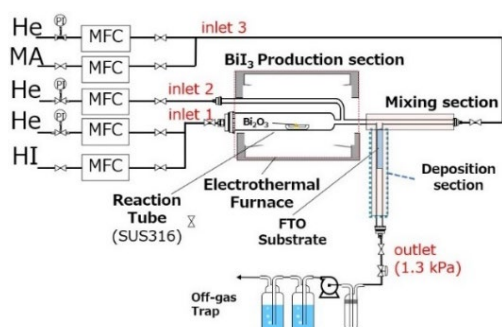
- [1] Kawase, M., Novel chemical vapor deposition process of perovskite methylammonium. 26th International Symposium on Chemical Reaction Engineering (ISCRE 26) (Online, Dec. 5–8, 2021), 06p3-00.
- [2] Nair, S., Patel, S. B., & Gohel, J. V. Recent trends in efficiency-stability improvement in perovskite solar cells. *Materials Today Energy*, 17 (2020) 100449.

#### Keywords

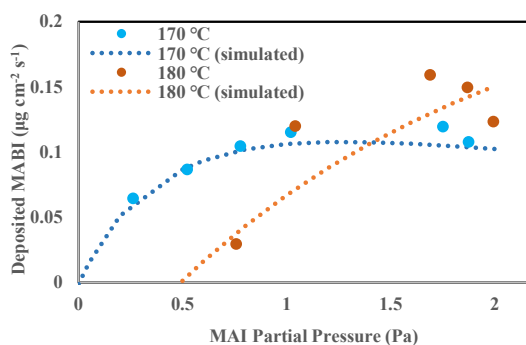
Chemical vapor deposition; perovskite solar cells; surface reaction.

**Table 1.** Kinetic constants of the rate equation.

Temperature / °C	Formation rate constant, $k / \mu\text{g cm}^{-2} \text{s}^{-1}$	BiI <sub>3</sub> adsorption equil. const. / Pa <sup>-1</sup>	MAI adsorption equil. const. / Pa <sup>-1</sup>	Decomposition rate constant, $k' / \mu\text{g cm}^{-2} \text{s}^{-1}$
170	0.606	34.5	2.96	0.004
180	3.30	6.52	0.264	0.135



**Figure 1.** The schematic of reaction instruments.



**Figure 2.** MABI deposition mass vs. MAI partial pressure.