The impact of dynamic two-step solution process on film formation of Cs$_{0.15}$(MA$_{0.7}$FA$_{0.3}$)$_{0.85}$PbI$_3$ perovskite and solar cell performance

Jueming Bing, Jincheol Kim, Meng Zhang, Jianghui Zheng, Da Seul Lee, Yongyoon Cho, Xiaofan Deng, Cho Fai Jonathan Lau, Yong Li, Martin A. Green, Shujuan Huang and Anita W. Y. Ho-Baillie

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**Perovskite and Fabrication process**

**Perovskite - ABX3**
- X - anion, e.g. halide (I, Br, Cl…)
- A – larger cation, e.g. MA, FA…
- B – smaller metal cation, e.g. Pb, Sn…

**Sequential deposition:**
- i) solving solvent incompatibility;
- ii) separate optimizations;
- iii) allowing different deposition methods

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(a) Nature photonics, 8(7), 506.
(b) Small, 11(1), 10.
Sequential Solution Process

(a) Some first applications
- Dipping 15.0% MAPbI$_3$ [1]
- Spin-coating 17.0% MAPbI$_3$ [2]

(b) PbI$_2$-complex
- PbI$_2$(DMF) [3]
- PbI$_2$(DMSO) [4]

(c) Motion Dispense
- ($\text{FAPbI}_3$)$_{1-x}$($\text{MAPbBr}_3$)$_x$ [5]
- Cs$_{0.1}$($\text{FA}_{0.4}\text{MA}_{0.6}$)$_{0.9}$PbI$_3$ [6]
- Stoppage between deposition of the two precursors

(d) Dynamic Process
- MAPbI$_3$ [7] ;Lack of understanding on film formation

This Work – Dynamic Process

- Sequential process without stoppage – being complete dynamic
- First application on triple cation perovskite
- First time study of the role of dynamic process in improving film formation

Deepen the understanding of film formation
Methodology

Glass/FTO/c-TiO₂/mp-TiO₂
/Cs₀.₁₅(MA₀.₇FA₀.₃)₀.₈₅PbI₃/Spiro-OMeTAD/Au
Device Performance

Efficiency (%)

- Static 1.2M
- Dynamic 1.0M

- Static 1.2M
- Dynamic 1.0M

Jsc (mA/cm²)

- Static 1.2M
- Dynamic 1.0M

- Static 1.2M
- Dynamic 1.0M

FF (%)

- Static 1.2M
- Dynamic 1.0M

- Static 1.2M
- Dynamic 1.0M

Voc (mV)

- Static 1.2M
- Dynamic 1.0M

- Static 1.2M
- Dynamic 1.0M

Current Density (mA/cm²)

- Static RS
- Dynamic RS
- Static FS
- Dynamic FS

Voltage (V)

18.4%

16.3%
Film Thickness and Morphology

Thickness distribution across the film (2cm*2cm) of (a) static process and (b) dynamic process

Dynamic processed film presents **thicker absorption layer, smaller difference in thickness** across different locations.
Film Thickness and Morphology

Dynamic processed film presents larger grain size with smaller grain boundary difference.
Film Morphology: XRD

- Higher (100)/(210) ratio by dynamic process -> more crystals with preferred orientation
- Lower PbI$_2$/(100) ratio by dynamic process -> better perovskite conversion ability
Dynamic processed film presents **longer lifetime with lower non-radiation recombination, and more uniform better PL response**
Why Dynamic Process is Better?

(1) Prolonged intermediate phase Pbl₂-CsI-MAI-FAI-DMSO

(2) Slower perovskite crystallization, preferred (100) orientation

(3) After annealing, highly ordered (100) perovskite with regular grain size
**Film Formations - FTIR**

- Stronger 1713 cm\(^{-1}\) (C=N stretching), 1469 cm\(^{-1}\) (C-N stretching), and 999 cm\(^{-1}\) (C-H bending) in static
  → Quick formation of perovksite
Film Formations - FTIR

- Wider 3200 cm\(^{-1}\) (N-H stretching) in static
  \(ightarrow\) Film disorder and leftover organic molecules
- Lower non-perovskite hydration phase and $\delta$-FAPbI$_3$ by dynamic process -> avoid rapid reaction with longer intermediate phase
- (100) and (200) grow together by dynamic process -> preferred orientation and more orderly crystallization even at lower temperature
Conclusion

• an effective and reliable sequential deposition method with improved performance and repeatability;

• an in-depth study of film formation process with advantages of dynamic process lie in:
  • i) better precursor insertion and intercalation;
  • ii) “suspending” the reaction while “prolonging the intermediate”; and
  • iii) avoiding rapid intramolecular exchange.

• New insights for future optimisation of sequential fabrication process
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ln \alpha = ln \alpha_0 + \frac{h \nu}{E_U}
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