

# Solvent Vapor Annealing of $\text{CH}_3\text{NH}_3\text{PbI}_3$ Films for Improved Photovoltaic Performance of Perovskite Solar Cells

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**Abstract**— *In this study, we investigated how solvent engineering affected the photovoltaic characteristics of perovskite solar cells (PSCs) fabricated using dehydrated lead acetate as the lead source. The photoactive layer was produced by depositing the perovskite solution using a one-step spin-coating method, followed by either 5 minutes of solvent annealing in DMF or IPA vapour or 5 minutes of thermal annealing on a hotplate at a temperature of 90 °C. An inverted planar design was used for the PSC device's construction. Thermal annealing (TA), annealing in DMF vapour, and annealing in IPA vapour were used to form the perovskite active layers. The efficiency of the solar cells produced by solvent annealing in an IPA is 13%, the open circuit voltage (Voc) is 0.977 V, the short circuit photocurrent density (Jsc) is 20.74 mA/cm<sup>2</sup>, and the fill factor is 61.21%. Our research showed that the PSCs produced using solvent engineering methods are have higher PCE, more stable and reproducible.*

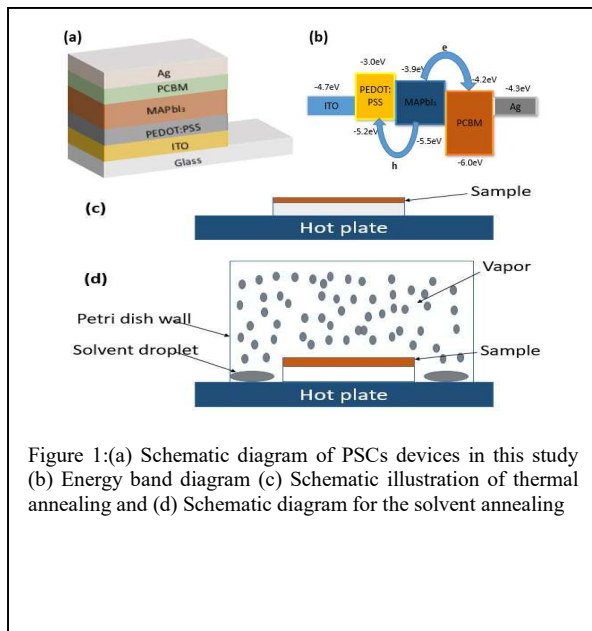
**Keywords**—Solvent annealing, Lead acetate, Perovskite solar cells, Thermal annealing

## I. INTRODUCTION

Over the past decade, important improvements have been achieved in the creation of perovskite solar cells (PSCs). Power conversion efficiency (PCE) moved from 3.8% in 2009 to 25.2% at this time [1]. Due to the perovskite materials' outstanding benefits, including their high absorption coefficient, variable bandgap, long diffusion length, fast solution processing, and low excitation binding energy [2], quick progress has been observed. These distinct benefits of perovskite materials allow for the use of various device architectures, including mesoporous  $\text{TiO}_2$  scaffolds and planer heterojunction designs [3]. The traditional (n-i-p) or (p-i-n) structures can both be used to describe a planar design. In contrast to mesoporous architecture, which has a complex cell structure and a higher processing temperature above 450 °C, planar architecture has a simple structure and a low processing temperature below 100 °C [4]. Because of lack of hysteresis during the J-V measurement and the processing temperature is low, the p-i-n architecture is starting to appeal to PSCs researchers [5]. The p-i-n structure may be processed at low temperatures, making it

compactable for flexible substrates and a variety of functional materials, including organic charge transport layers [6].

Different deposition processes were employed to create the PSCs, including 1-step and 2-step spin coating, dip coating, spray coating, vapour deposition, vapour-aided solution deposition, and blade coating techniques. The methylammonium lead halide PSCs ( $\text{CH}_3\text{NH}_3\text{PbI}_3$ ) were made using a variety of precursor materials. By combining lead iodide ( $\text{PbI}_2$ ) and methylammonium iodide (MAI) in a 1:1 solution, it is possible to create  $\text{CH}_3\text{NH}_3\text{PbI}_3$ . Additionally,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  can be produced by the reaction of MAI with various non-halides lead. With  $\text{Pb}(\text{OAc})_2$  being used as the Pb source, PSCs have made good progress. [5], [7], [8]. Due to the ease with which the N-methylammonium acetate  $\text{CH}_3\text{NH}_3\text{COO}$  was removed, the PSCs formed from  $\text{Pb}(\text{OAc})_2$  have the advantage of speeding up the crystal development of  $\text{CH}_3\text{NH}_3\text{PbI}_3$ , which in turn usually produces smooth perovskite films with fewer pinholes. The perovskite films produced are often smaller in grain size as a result of the quick crystal growth process, which results in more defect sites and grain boundaries. One method for enhancing the light absorbing layer's grain sizes and quality is the solvent annealing method. Solvent engineering techniques have been used in numerous studies to enhance the quality of the active layer [9]. Majority of these works use lead halide-based precursors. But according to J. Qing et al., the PCE of PSCs made from lead acetate can be increased by solvent annealing from 10.11% to 12.7% in DMF vapour [10]. In this research, the perovskite layer is deposited using the single step deposition techniques prior to annealing. To create the photo active layer, we applied thermal annealing (TA) as well as solvent annealing processes. We annealed the perovskite films in the DMF and IPA vapour for 5 minutes as part of the solvent annealing technique. The best PCE of 13% is provided by PSCs created with IPA vapour. In comparison to PSCs manufactured using TA, which only preserve 42% of their original value after seven days of storage in ambient conditions, devices made with solvent annealing methods demonstrated higher stability.



## II. EXPERIMENTAL PROCEDURE

### A. Materials

Ossila provided the methylammonium iodide, “poly (3,4-ethylene dioxythiophene): poly (styrene sulfonate), and phenyl-C61-butyric acid methyl ester (PCBM)”, which were employed without additional purification. Alfa Aesar provided the lead acetate trihydrate ( $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ ), dimethylformamide (DMF), and isopropyl alcohol (IPA). The “dehydrated lead acetate ( $\text{Pb}(\text{Ac})_2$ )” was produced by further processing the lead acetate trihydrate ( $\text{PbAc}_2 \cdot 3\text{H}_2\text{O}$ ) by dehydrating it in a flowing nitrogen gas for an extended period of time at a temperature of 80 °C.

### B. Film formation and device fabrication

Before being dried with flowing nitrogen gas, the glass/ITO substrates were washed for quarter an hour in an ultrasonic bath with soap solution, deionized water, acetone, and IPA, respectively. Finally, the glass and ITO were exposed to an ultraviolet-ozone (UVO) environment for 17 minutes. The substrate measures 2.5 cm by 2.5 cm and features a 0.2 cm<sup>2</sup> active area. The hole transport layer (HTL) was formed by TA at 140 °C for 16 minutes after the PEDOT:PSS was deposited on the glass/ITO substrate at a rate of  $4 \times 10^3$  revolution per minute for one minute. The photoactive solution was created by dissolving 3.0 mmol of MAI and 1.0 mmol of  $\text{Pb}(\text{Ac})_2$  in 1 mL of DMF. The solution was deposited on the HTL a speed of  $4 \times 10^3$  revolution per minute for one minute followed by TA or solvent annealing to produced the perovskite active layer. Three sets of samples were created; the samples from the thermal annealing process are designated as TA, the samples from the DMF and IPA vapour annealing processes are designated as DMF and IPA, respectively. For the DMF vapour annealing, we placed the samples on the hotplate at a temperature of 90 °C. Following the addition of around 10  $\mu\text{l}$  of DMF, the samples were then covered with a petri dish. The samples were annealed in a DMF vapour environment for 5 min. The same process was

repeated for the IPA vapour annealing, about 10  $\mu\text{l}$  of IPA was dropped on the hotplate closed to samples and were covered immediately with glass petri dish. The samples underwent a 5-minute annealing process in an IPA vapour atmosphere. For the TA, the samples were annealed on a hotplate at 90 °C for 5 minutes. Figures 1 (c) and (d) depict the schematic diagram for the creation of a perovskite film using the TA and vapour annealing processes. The PCBM was deposited on the active layer at a speed of 1500 revolution per minute for 30 seconds.

The 90 nm Ag electrode underwent thermal evaporation to complete the device. Inverted planar heterojunction solar cells with the standard “Glass/ITO/PEDOT:PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/Ag” architecture make up the manufactured device (see Fig. 1(a)).

“A xenon-lamp solar simulator (Spectra-Physics, Oriel Instruments, USA) was used to analyse the current density-voltage (J-V) properties of the PSCs under simulated AM 1.5 global sun irradiation (100 mW/cm<sup>2</sup>)”.

## III. RESULTS AND DISCUSSION

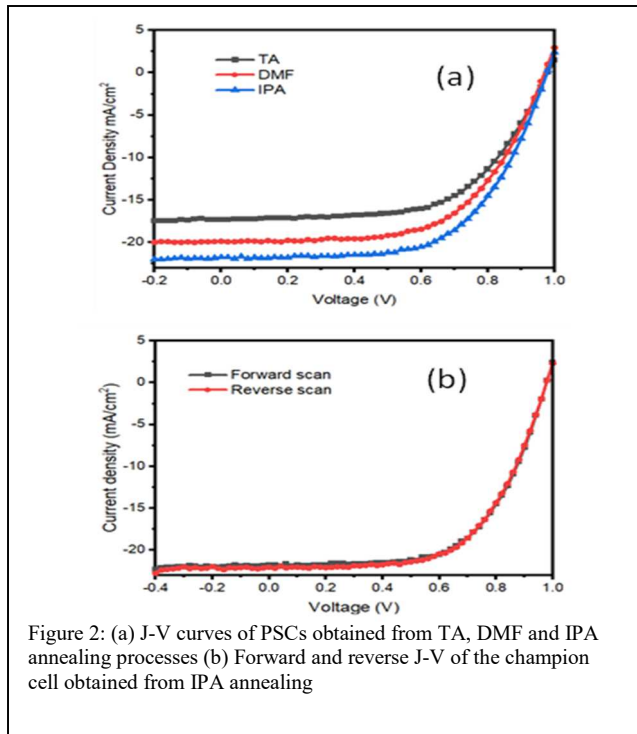
In this work, a single-step spin coating method was adopted to produce the MAPbI<sub>3</sub> solution before either thermal annealing or solvent annealing in a DMF or IPA vapour at 90 °C for 5 min. Figure 1(b) represents the energy band diagram for the PSCs, and figures 1(c) and (d) represent the schematic diagrams for the thermal annealing and solvent annealing processes, respectively.

From Fig. 1(a), the PSCs used in this investigation were organised as “ITO/PEDOT: PSS/CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>/PCBM/Ag”, where PEDOT: PSS and PCBM serve as the layers that transport holes and electrons, respectively. Due to the drawbacks of the traditional method, p-i-n structure is adopted in place of it in this instance. For instance, the bottom electron transport layer in mesoporous device structures is an n-type TiO<sub>2</sub> layer. However, the TiO<sub>2</sub> scaffold typically requires a high temperature (>450 °C) sintering process, which is a major restriction for the flexible substrates and roll-to-roll method and consequently drives up the manufacturing cost. Meanwhile, J-V hysteresis is frequently present in high levels in typical planar devices based on TiO<sub>2</sub>. In contrast, the perovskite/PCBM structure often displays very little hysteresis as illustrated in fig 2b. The p-i-n architecture PSCs used in this research exhibit low J-V hysteresis and promising device performance, according to recent studies [8]. Figure 1b shows the inverted PSCs' related energy band diagram. With a 4.2 eV conduction band energy and a 6.0 eV valance band, PCBM is capable of transporting electrons from CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> and collecting them at the cathode while blocking holes from the same compound. In other words, this PCBM serves as both a hole-blocking layer and an electron extraction layer. likewise, it has been claimed that PCBM can decrease J-V hysteresis and successfully passivate CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> [11]. In addition, the PEDOT:PSS layer serves as an electron-blocking layer and can help holes

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go more easily to the anode. It is anticipated that this structure would perform well.

Table1: Photovoltaic parameter of PSCs fabricated from thermal and solvent annealing



Devices	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
TA	0.975	17.47	59.85	10.14
DMF	0.970	19.86	60.18	11.60
IPA	0.977	21.74	61.21	13.00

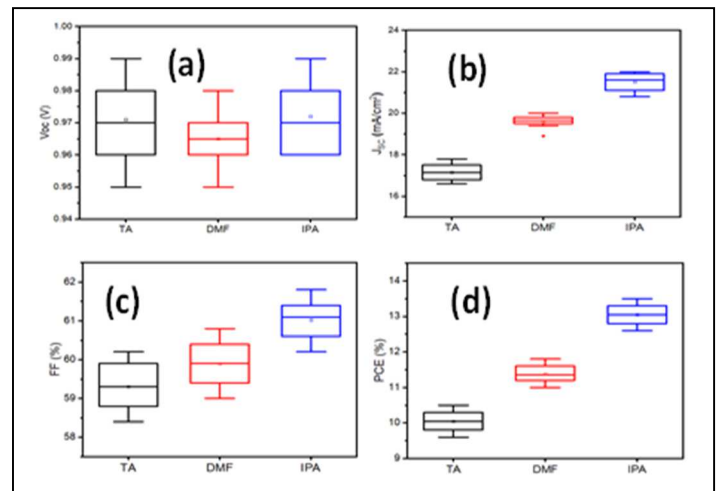


Figure 3: Statistical parameters of PCE Voc, FF, and Jsc for PSCs derived from TA, DMF and IPA

Figure 2a depicts the J-V curves of PSCs produced via thermal annealing and solvent annealing methods. The device properties of PSCs made via TA and solvent annealing are shown in Table 1. The best-performing devices, according to Figure 2a and Table 1, were produced using solvent annealing. The maximum PCE is 13%, with J<sub>sc</sub> values of 21.74 mA/cm<sup>2</sup>, Voc values of 0.977 V, and FF values of 61.21% for PSCs devices made using IPA vapor. Although DMF PSCs somewhat outperform TA PSCs in comparison, they clearly fall short of IPA PSCs. The PbI<sub>2</sub>-MAI-DMF intermediary phases and one-step solvent engineering deposition of the perovskite precursor layer may be the causes. During the annealing process, these intermediate phases will transform and release DMF vapor. Since the creation of perovskites is a reversible reaction, adding more DMF to the annealing process will result in an excessive DMF vapour and hinder the recrystallization of CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub>. The perovskite quality may be enhanced by DMF, however, too much DMF vapor during solvent annealing will cause the reaction to proceed in an opposite way, lowering device performance in comparison to IPA PSCs. It should be noted that while IPA and DMF vapor can enhance the quality of perovskite films, an excessive DMF ratio in the combined vapor or an excess of DMF alone will be detrimental to the films due to a quicker rate of decomposition. The discrepancies in the Voc and J<sub>sc</sub> for all of the devices may be caused by the quality of the perovskite layer as the PSCs are all produced using the same method aside from the annealing processes. A good perovskite layer might be the source of an increased Voc.

Fig. 3 presents the box plots of 20 PSCs devices, the plots clearly show that the devices obtained from IPA and DMF performed better statistically. The devices obtained through the IPA and DMF show better reproducibility, which is an important factor to consider when fabricating PSCs. The enhanced reproducibility is attributed to the quality of the film produced through the solvent engineering techniques.

After 7 days, the PCE of the TA PSC dropped down to 42% of its original value. The IPA and DMF vapor treatments significantly increased the PCSs' stability. PCEs were able to maintain 70% of the original values after 7 days. This demonstrates how the stability of the PSCs is considerably improved by the better perovskite quality.

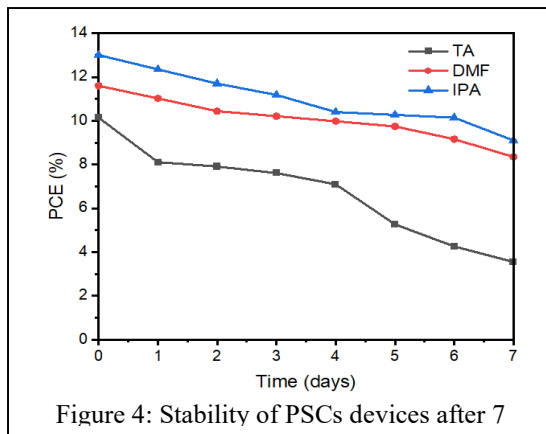


Figure 4: Stability of PSCs devices after 7

#### IV CONCLUSION

In this study, we employed a solvent annealing strategy to enhance the quality of films using the one-step deposition method. The photovoltaic parameters of PSCs was improved from 10.14% to as high as 13% when annealed in IPA vapour and 11.60% when annealed in DMF vapour. The PSCs obtained through the solvent annealing methods show better stability and reproducibility

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