

Application of PEDOT:PSS Thin Film Fabricated via Hot-casting as Hole Transport Layer of Perovskite Solar Cell

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Abstract: Conductive polymers have received vast attention to be adopted as transparent electrodes, based on their flexibility and ease of fabrication in thin-films via a solution-based process. Thanks to its thermal and chemical stability, PEDOT:PSS has been widely used as a part of solar cells and LEDs, especially as the hole transport layer. However, the high sheet resistance of PEDOT:PSS thin film induces efficiency drag. Therefore, other works have been dedicated to enhancing this property, mainly via secondary doping. This work reports adapting hot-casting to the fabrication of DMSO-doped PEDOT:PSS thin film which yields a significant decrease in the sheet resistance. From atomic force microscopy imaging and sheet resistance measurements, it can be concluded that hot-casting yields a decrease in resistance and surface smoothing, and both of them seem to be due to interconnection among the grain cores. The further application to the hole transport layer of the CH₃NH₃PbI₃ perovskite solar cell was examined and resulted in increased power conversion efficiency. Notably, the hot-casting temperature at which the sheet resistance was minimized did not exactly match the temperature at which the power conversion efficiency maximized. This seems to be due to the morphology smoothing effect of the film.

1 Introduction

Conductive polymers have received vast attention due to their flexibility, in contrast to indium tin oxide (ITO) which is the most widely used material for transparent electrodes in photoelectronic devices. In particular, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is commonly used as a hole transport layer due to its chemical and thermal stability. Despite its promising stability and optical properties, it has not been used as a transparent electrode due to low conductivity. Therefore, there has been a lot of research dedicated to enhancing the conductivity by using solvents as secondary dopants in order to align the PEDOT and PSS chains and increase crystallinity.^[1-11] The secondary dopant is far different from the primary dopant. The secondary dopant is a chemically inert substance (in this case a solvent) that is applied to a primary-doped material in small amounts. The enhanced characteristics of PEDOT:PSS film remain even when the solvent completely evaporated. Fundamentally, this is caused by a change in microstructure, in size of PEDOT:PSS grain, of the film. For instance, Nardes, *et al.* reported high conductivity over 2000 S/cm with sorbitol, and Kim, *et al.* informed enhanced the conductivity of 1418 S/cm by doping it with ethylene glycol.^[12, 13] However, the film is vulnerable to be exfoliated from its substrate during solvent treatment, especially in the solvent-dipping process. Another limitation is that is hard to produce a large area of the film while maintaining consistent properties.

Meanwhile, it has been reported that PEDOT:PSS forms a grain structure in both the dispersed and film state.^[14] The grains have a core and shell rich in PEDOT and PSS, respectively. Conductive PEDOT forms a linearly aligned structure of nanocrystals in the grain core, whereas the PSS-rich shell is highly insulative.^[15] Therefore, the pristine PEDOT:PSS thin film has a low conductivity of only a few S/cm. Here, application of the hot-casting technique to PEDOT:PSS film fabrication is used to reduce the sheet resistance of PEDOT:PSS thin film. In addition, the hot-casted PEDOT:PSS thin films are used as a hole transport layer in perovskite solar cells.

2 Materials and Methods

PEDOT:PSS thin film fabrication. The PEDOT:PSS dispersed solution was doped with DMSO in the ratio of 5 wt%. The doped dispersion was strained with 0.45 μm filter to remove any agglomerate and debris.^[13,15] PEDOT:PSS film was prepared by spin-casting 2.4 mL of aqueous solution on 1 mm-thick glass sheet with an area of $2 \times 2 \text{ cm}^2$. Before spin-casting, each glass substrate was ultrasonically cleaned with acetone, DI water, and ethanol for 7 min, respectively. The glass substrates were baked for at least 10 min at 120°C in N_2 atmosphere condition. to remove any solvent on it. Both spin-casted and the hot-casted film were fabricated in the condition of 4000 rpm for 30 sec in an N_2 atmosphere glove box. The glass substrate was thermally stabilized at least 10 min prior to hot-casting.

Perovskite solar cell fabrication. Firstly, for etching the ITO substrate, the substrate was masked using polyimide tape and the ITO layer was partially removed using zinc powder and 4M hydrochloric acid. The removed ITO substrate was sufficiently washed with distilled water. To remove all foreign substances on the ITO substrate, the substrate was ultrasonically washed with acetone, 2-propanol, and distilled water for 10 minutes each then dried with high-pressure nitrogen gas and subsequently dried three times for 1 minute in a chamber of 0.9 atm.

The PEDOT:PSS film used as the hole transport layer was prepared by mixing PEDOT:PSS dispersion doped with 5 wt% DMSO and ultrasonicated for 1 hour or more. The prepared mixed solution was spin-coated at 3000 rpm for 60 seconds. The PEDOT:PSS films were prepared by both ordinary spin-casting and hot-casting, respectively. Hot-casting was performed at 20°C intervals in the range of 120°C to 180°C. To prepare a perovskite photoactive layer, CH₃NH₃I and PbI₂ were mixed in equimolar ratios and DMF:DMSO(4:1 Volume ratio) solvent and stirred at 60°C for 12 hours. The perovskite layer used as the photoactive layer was prepared using an anti-solvent method. The perovskite solution was dropped on a glass substrate in an amount of 1 mL and rotated at 2500 rpm in an N₂ atmosphere, and then chlorobenzene as an anti-solvent was further dropped thereafter for 10 seconds after reaching 2500 rpm to crystallize the perovskite layer. Then, the spin speed was maintained at 2500 rpm and increased to 3500 rpm for 45 seconds each total of 90 seconds. This induces a perovskite intermediate phase to form a crystal layer with fewer defects.^[16] Perovskite film subsequently annealed at 100°C for 10 minutes to induce crystallization.

The electron transport layer, PCBM was dissolved in toluene at a concentration of 20 mg/mL and stirred for 10 minutes. It was spin-coated at 1000 rpm for 20 seconds and 6000 rpm for 20 seconds in an N₂ atmosphere. As a metal electrode, gold was deposited on the glass substrate by a thermal evaporation method using a mask. Thermal evaporation was performed with a thickness of 80 nm.^[17] Fig. 1 shows the ITO electrode process chart and the manufacturing process chart of the solar cell.

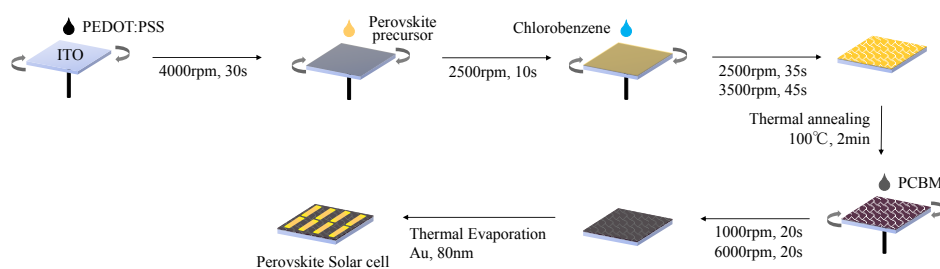


Figure 1. Fabrication process of perovskite solar cell.

3 Results

The sheet resistance is an important value, directly related to the mobility of electrons and holes. To be useful as a transparent electrode of the solar cell, the sheet resistance should be comparable with that of ITO. The resistance of as-formed PEDOT:PSS film was $66.7 \pm 3.6 \Omega/\text{sq}$. The sheet resistance of the post-annealed film was slightly decreased while that of the hot-casted film was highly decreased to $39.9 \pm 4.2 \Omega/\text{sq}$, especially at higher temperatures as shown in Fig. 2.

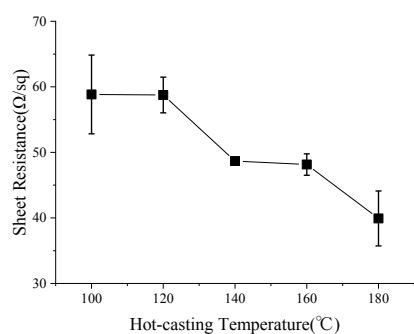


Figure 2. Sheet resistance of hot-casted PEDOT:PSS thin film.

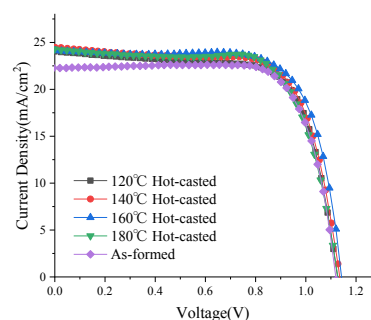


Figure 3. J-V curves of perovskite solar cells.

The power conversion efficiency (PCE) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ based perovskite solar cells was examined. The PCE of the perovskite solar cell with as-formed PEDOT:PSS film was at least 18.74% and increased with higher hot-casting temperature. J-V curves and measured data are plotted in fig. 3 and table 1. Notably, the open-circuit voltage (V_{oc}) increased up to 1.14 V at a hot-casting temperature of 160°C (see Table 1). Also, PCE was highest in the 160°C hot-casted sample, which does not seem to be consistent with sheet resistance decrement.

The morphology of the films was studied using atomic force microscopy (AFM). Different morphologies were quantitatively compared using the root-mean-square (RMS) roughness. RMS depth of as-formed, 180°C post-annealed, 180°C hot-casted PEDOT:PSS film was 1.121 nm, 1.132 nm, 0.822 nm, respectively. AFM images are displayed in fig. 4. It is notable that the morphology of as-formed and post-annealed film shows similar roughness whereas the hot-casted film is considerably smoother.

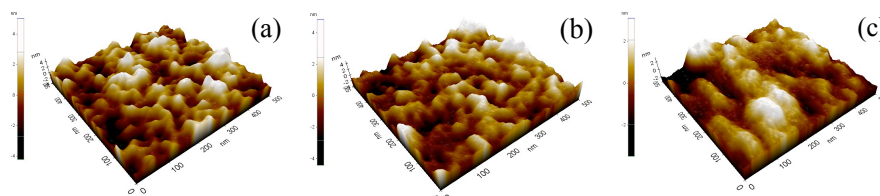


Figure 4. AFM images of PEDOT:PSS thin film, (a) as-formed, (b) 180°C post-annealed, (c) 180°C hot-casted.

Hole transport layer (PEDOT:PSS)	V _{oc} (V)	J _{sc} (mA/cm ²)	Fill Factor	PCE
As-formed	1.119	22.28	75.16	18.74
120°C Hot-casted	1.126	24.04	70.49	19.09
140°C Hot-casted	1.134	24.48	70.16	19.49
160°C Hot-casted	1.142	24.14	72.32	19.95
180°C Hot-casted	1.127	24.29	70.12	19.20

Table 1. Electrical properties of perovskite solar cell which applied various PEDOT:PSS thin film as a hole transport layer.

4 Discussion

From sheet resistance measurements and AFM imaging, the current study suggests a model for hot-casting on PEDOT:PSS thin film fabrication. The pristine PEDOT:PSS film shows low conductivity due to the core-shell structure, in which the insulative shell blocks current flow between cores of adjacent grains. Electrical enhancement by hot-casting seems to be due to aggregation and formation of the complex structure of PEDOT:PSS grains. The hot-casting appears to induce inter-core penetration of the shell, forming a conductive PEDOT-rich core network. AFM imaging provided convincing evidence of the interconnection between grain cores (see Fig. 4c). Notwithstanding the network development effect by DMSO doping, hot-casting appears to be of further assistance. Based on these observations, it is proposed that post-annealed film does not form any aggregation, which suggests that the incipient procedure of PEDOT:PSS has great significance for the film microstructure.

Despite achieving the lowest sheet resistance at 180°C hot-casting, PCE of perovskite solar cell in which the PEDOT:PSS film was hot-casted at 160°C hot-casting showed the best performance. The reason for this is that PCE is influenced by both conductivity of the carrier transport layer and morphology simultaneously. Even though the sheet resistance of the hole transport layer was highly reduced at higher hot-casting temperatures, the morphology was also smoothed, which has an effect on the exciton segregation efficiency. An exciton is a pair of electron and hole bound through Coulombic force, generated if the perovskite layer absorbs light. This is followed by diffusion of the exciton takes place. If it encounters the interface between the perovskite layer and the charge transport layer due to energy level difference, it segregates into an electron and a hole. The more excitons are dissociated, the higher the PCE can be achieved. Due to the morphology smoothing, the exciton segregation efficiency seems to have dwindled, contrary to an increment of conductivity. The balance between these two incompatible properties was achieved at 160°C, thus yielding the highest PCE of the perovskite solar cell.

5 Conclusions

The electrical performance of the PEDOT:PSS thin film was highly enhanced by applying hot-casting as a novel fabrication technique. Both low sheet resistance and RMS roughness were achieved with hot-casting at high temperatures. Based on observations via AFM imaging, these seem to be due to the interconnection among the PEDOT-rich core of grains. As the hot-casted PEDOT:PSS thin film was applied in the perovskite solar cell as a hole transport layer, both electrical conductivity and morphology affect exciton dissociation, and two incompatible variables balanced at 160°C hot casting to show the highest PCE. Since the hot-casting is affordable with a small amount of additional cost and easy to produce large-area transparent electrodes in real-time continuously, it is expected that it can be easily applied to commercial flexible transparent electrodes.

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