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Comparison of Spin-Coated and Spray pyrolysis Coated Active Layer in Perovskite Solar Cells

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Abstract—In this research, the TiO_2 blocking layer of perovskite solar cells was made by two different methods, spin-coating and spray pyrolysis. Optical properties of active layers were studied using diffused transmittance spectroscopy (DTS), and the photovoltaic properties of the solar cells such as J_{sc}, V_{oc}, FF and the efficiency were measured. Due to the importance of transmission, the light from the blocking layer and the mesoporous TiO_2 layer, the diffuse spectrum of these layers and also the importance of light absorption in the perovskite of the absorption spectra of this layer were investigated. Diffuse transmittance spectroscopy (DTS) was used to study the active layer from the view point of optics. Optical properties of the spin coating layer were not significantly different in the two methods, but after the deposited perovskite layer, it was observed that the optical properties of the perovskite layer in the range of visible light were different in both the spin coating and spray pyrolysis methods.

Index Terms—Perovskite Solar Cell; Blocking Layer TiO_2; Spin-coating; Spray pyrolysis

I. INTRODUCTION

The organic-inorganic perovskites used for photovoltaics (PV) have an ABX_3 formula that is comprised of a monovalent cation, A = [methylammonium (MA) $CH_3NH_3^+$; formamidinium (FA) $CH_3(NH_2)_2^+$; ethylammonium (EA) $CH_3CH_2NH_3^+$]; a divalent metal B= (Pb^{2+}; Sn^{2+}); and an anion X = (Cl^-, Br^-; I^-) [1].

Low-cost perovskite solar cells (PSCs) have achieved certified power conversion efficiencies (PCEs) of 22.1%. This highest efficiency are Pb-based with mixed MA/FA cations and Br/I halides. In this paper, the structure of $MAPbI_2$ has been used. PSCs consist of n-type electron transport layer (ETL), perovskite layer, and p-type hole transport layer (HTL) similar to a p–i–n structures [2].

ETL involves blocking layer (BL) and mesoporous TiO_2 (mp-TiO_2) layer. In highly efficient PSCs, those exceeding a power conversion efficiency of 20%, TiO_2 is used as ETL, although the use of other oxide materials, such as SnO_2, ZnO, and Zn_2SnO_4, has been reported. The compact TiO_2 layer can be produced either by electrochemical deposition, thermal oxidation, dip-coating, atomic layer deposition, spin-coating, and spray pyrolysis [3].

$MAPbI_3$ has a combination of desirable properties, including large absorption coefficient in the visible spectrum, favourable direct band gap, high carrier mobilities, and long carrier-diffusion lengths for both electrons and holes. Typically, deposition of $MAPbI_3$ perovskite thin films is done using the one-step or the two-step solution-processing methods.

HTLs are mainly based on organic semiconductors such as 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD); poly(3,4 ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS); poly-triarylamine (PTAA) and NiO.

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Usually, the last layer is a metallic layer of high-conductivity made of gold (Au) or silver (Ag); with the thickness of more than 50 nm [3]. This layer was deposited using thermal evaporator or sputtering and a shadow mask. This layer can also be replaced with carbon.

In this work, the blocking layers were made using spin-coating and spray pyrolysis methods. The optical properties of these two different active layers were studied. Then, PSCs were fabricated using these active layers to investigate the effect of spin-coating and spray pyrolysis method on the performance of cells.

II. MATERIALS AND METHOD

The commercial materials used are listed as follow: titanium di-isopropoxide (TTIP); Hydrochloric acid (HCl); TiO_2 past (18NR-T,Dyesol); PbI_2; Methyl Ammonium (MA); 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD); FTO substrate.

In this research, transparent conductive oxide, Fluorine-doped Tin Oxide (FTO) used as substrates. FTO glass substrates were selectively etched with Zn powder and 0.1 M HCl in deionized water, followed by mechanical attrition with a toothbrush. After that, the FTO substrates were cleaned in an ultrasonic bath with Soapy water, 0.1M HCl in isopropanol, Acetone, and ethanol for 10 minutes at 60°C, respectively, and were annealed at 500°C for 30 minutes.

A solution consisting of TTIP and HCl in Ethanol was utilized to deposit BL on the substrates using the spin-coating technique. They were annealed at 500°C for 30 minutes.

In spray pyrolysis method, a solution consisting of 0.1M of titanium di-isopropoxide bis (acetylacetonate, 75% vol. 2-propanol) in absolute ethanol (1:39, v/v ratio) was sprayed at 380°C to made BL. Then, the layers were annealed at 500°C for 30 minutes.

Subsequently, a TiO_2 solution (18NR-T, Dyesol) in ethanol was spin-coated on TiO_2 BL at 4000 rpm for 30s to fabricate the mp-TiO_2 layers. They were annealed at 500°C for 30 minutes. PbI_2 solution in N, N'-dimethylformamide (DMF) was spin-coated on mp-TiO_2 layer

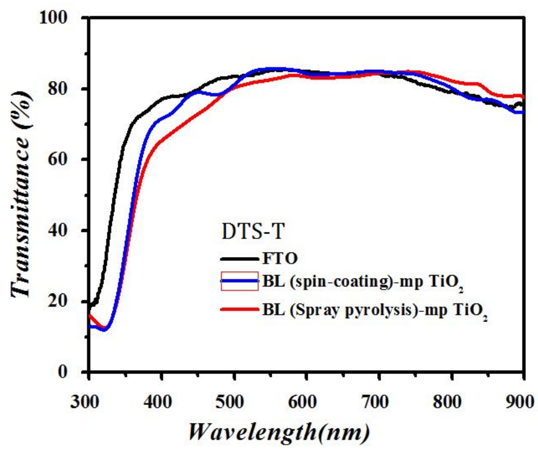

Fig. 1. The transmittance spectra of FTO, blocking layer that these layers prepared by spin-coating and spray pyrolysis methods on mp-TiO_2.

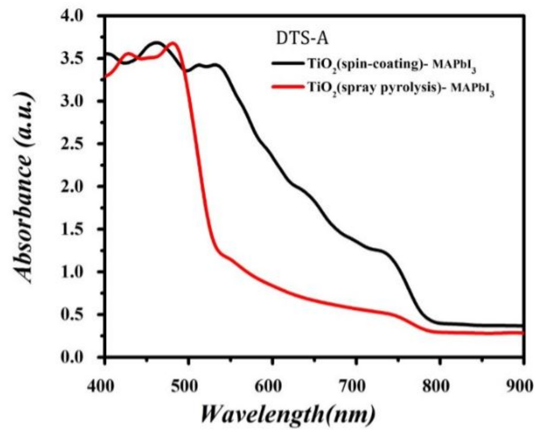

Fig. 2. The absorption spectra of the BL/mp-TiO_2/Perovskite that BL is prepared by spin-coating and spray pyrolysis methods.

TABLE 1. Best values for V_{oc}, J_{sc}, FF, and PCE, for Perovskite solar cell, that blocking layer is prepared with spin-coating and spray pyrolysis methods.

Cell	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	PCE (%)
BL(spin-coating)	14.81	0.72	0.35	3.76
BL(spray pyrolysis)	5.1	0.82	0.38	1.61

at 6500 rpm for 5s. As-prepared PbI_2 layer was immediately dip-coated in fresh 10 mM MAI solution in anhydrous isopropanol. Then, they were annealed at 70°C for 30 minutes to obtain a dark-colored perovskite layer. This was followed by spin-coating a solution of Spiro-MeOTAD as a HTM. Finally, 80 nm Au layer was deposited using thermal evaporation technique.

III. RESULTS AND DISCUSSION

The diffuse transmittance spectra of FTO, BL (spin-coating) and mp-TiO_2 on FTO, as well as BL (spray pyrolysis) and mp-TiO_2 on FTO are observed in Figure 1. They have transmittance of about 80% in a wide range of visible wavelengths from 500 to 750 nm. This means that the addition of the BL and the mp-TiO_2 layer do not reduce the amount of light, which is absorbed by the perovskite. Since the TiO_2 band gap is around 3.2 eV [2], there are no absorbance at the wavelengths higher than 400 nm due to electron transitions. In this range of wavelengths, since their transmittances are similar, it could be found that light do not lost in the TiO_2 layers when they are deposited on FTO. Therefore, no considerable scattering centres inside TiO_2 layer are observed. Reduction in transmitted light occurs at lower wavelengths, where transmitted light strongly comes down. FTO glasses with BL and mp- TiO_2 have similar trend, which occur at higher wavelength rather than FTO glass. This confirms that the TiO_2 band gap is less than the FTO band gap. In the range of 300 to 500 nm, the light transmission rate with the BL and the mp-TiO_2 layer on the FTO decreases about 6% to 59% ratio to the FTO. At wavelengths of 750 nm, there is not an Impressive difference in the transmission of light from the FTO and The layers on the FTO which deposited with BLs not seen. However, an increase in the passage of about 5% is observed for a sample which BL is prepared by the spray pyrolysis method, which indicates that in this range of layers have acted as anti-reflection layers and increased the light transmission rate.

The absorbance spectra of BL (spin-coating), mp-TiO_2 and $MAPbI_3$ on FTO; as well as BL (spray pyrolysis), mp-TiO_2 and $MAPbI_3$ on FTO are shown in Figure 2. Hybrid perovskites exhibit strong optical absorbance, allowing for a much-reduced thickness necessary to efficiently facilitate the collection of charge carriers. Absorption across the entire visible spectrum is achievable with an only 500 nm thick perovskite film, far less than the 2μm limitations typically required by solar cell active layers. The absorption peak for both samples are sharp, indicating a direct band gap. In the absorption spectra of two selles, an absorption onset at about 790 nm is found, corresponding to an optical bandgap of about 1.57 eV, in good agreement with the trend reported by Byung-wook Park et al [4]. In comparison to the $MAPbI_3$ film that BL prepared by spin-coating, the $MAPbI_3$ film that BL prepared by spray pyrolysis an increasing absorption can be seen at wavelengths below 720 nm and further below 540 nm, which can be attributed to absorption in the PbI_2 and $MAPbI_3$ fractions in this material, respectively. The other word, it could be said that the PbI_2 cannot be converted completely to $CH_3NH_3PbI_3$ unless the layer is quite dense and thick.

Both of cells are built, achieve absorption up to the tail end of the red region of the spectrum, approximately 800 nm. This means that the conduction band and the valence band in the Perovskite structure have not been shifted. In other words, the better performance of solar cells which BL were prepared by spin-coating, attributed to the absorbing properties. It is clear that the light absorption properties of in the two samples are completely different, which confirms that perovskite is sensitive to construction.

Figure 3 shows the J–V characteristics of the cells with the structure: FTO/TiO_2 BL/mp-TiO_2/$CH_3NH_3PbI_3$ /Spiro-OMeTAD/Au. Table 1 shows the summary of the photovoltaic parameters of the cells. The best photovoltaic performance with J_{sc} of 14.81 mA.cm^{-2}, V_{oc} of 0.72 V, FF of 0.35, and an overall power conversion efficiency of 3.76% was obtained for the cell consisting of BL, which made using spin-coating. Since the amount of absorbed light in the visible range is higher, the higher current density was obtained for this cell.

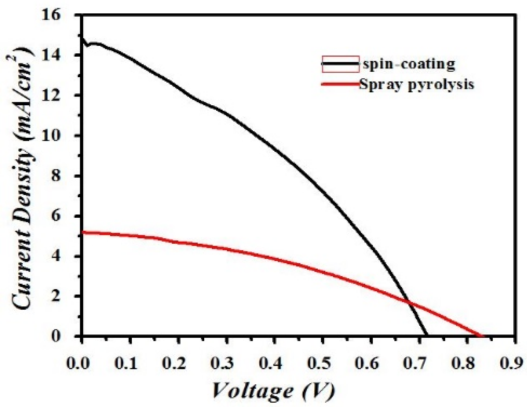

Fig. 3. J-V curves of the PSCs is, which blocking layer was prepared by spin-coating and spray pyrolysis methods.

IV. CONCLUSIONS

In this study, the optical properties of the active layer and the photovoltaic properties of PSCs which BLs were made using the spin-coating and spray pyrolysis methods were investigated and compared. Finally, it can be concluded that the titanium BL in both spin-coating and spray pyrolysis methods don't prevent sunlight from reaching the perovskite absorbent material and The perovskite absorption rate, which The BL was built in a spin-coating manner, is higher than that of the cell which BL was built with spray pyrolysis, which is why the amount of J_{sc} in the first state is higher, which results in higher efficiency than the second mode has been.

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