Exclusion of metal oxide by an RF sputtered Ti layer in flexible perovskite solar cells: energetic interface between a Ti layer and an organic charge transporting layer

Sadia Ameen,†a M. Shaheer Akhtar,†b Hyung-Kee Seo,a Mohammad Khaja Nazeeruddin*c and Hyung-Shik Shin*a

In this work, the effects of a titanium (Ti) layer on the charge transport and recombination rates of flexible perovskite solar cells were studied. Ti as an efficient barrier layer was deposited directly on PET-ITO flexible substrates through RF magnetic sputtering using a Ti-source and a pressure of ~5 mTorr. A Ti coated PET-ITO was used for the fabrication of a flexible perovskite solar cell without using any metal oxide layer. The fabricated flexible perovskite solar cell was composed of a PET-ITO/Ti/perovskite (CH3NH3PbI3)/organic hole transport layer of 2,2’,7,7’-tetrakis [N,N’-di-p-methoxyphenylamine]-9,9’-spirobifluorene (spiro-OMeTAD)-Li-TFSI/Ag. A high conversion efficiency of ~8.39% along with a high short circuit current (Jsc) of ~15.24 mA cm−2, an open circuit voltage (Voc) of ~0.830 V and a high fill factor (FF) of ~0.66 was accomplished by the fabricated flexible perovskite solar cell under a light illumination of ~100 mW cm−2 (1.5 AM). Intensity-modulated photocurrent (IMPS)/photovoltage spectroscopy (IMVS) studies demonstrated that the fabricated flexible perovskite solar cell considerably reduced the recombination rate.

Light weight photovoltaic devices like flexible solar cells have received a great deal of attention due to their low cost production, variable shapes and large-scale roll-to-roll processing which are required for the industrial production of OPV materials.14,15 Several flexible substrates such as poly(ethylene) terephthalate (PET)/indium tin oxide (ITO) and metal sheets are commonly used for the fabrication of flexible solar cells.16,17 Moreover, titanium (Ti) foils and Ti meshes have already been utilized to manufacture large-area flexible solar cells because of their high flexibility, relatively low sheet resistance and superior corrosion resistance.18,19 Recently, Ti thin film has received much attention for excellent applications in microelectronics, machinery, aerospace, and medical industry owing to its remarkable photoelectric performances.20 In general, a Ti thin film has been extensively grown on various substrates using the deposition techniques of atomic layer deposition (ALD), chemical vapor deposition (CVD) and electrochemical techniques like chemical bath deposition.21 The deposition of a Ti thin film through the sputtering method is highly dense and shows good homogeneity with great reproducibility in a large area because of the high-energy bombarding particles20 therefore, the sputtering method is a promising low temperature deposition technique for depositing a Ti layer on various substrates. In particular, a Ti thin film as a barrier layer offers the fabrication of light weight high-performance...
perovskite solar cells using different hole transport materials (HTMs). Conducting polymers such as polypyrrole, \(^{22,23}\) polyaniline \(^{24,25}\) and poly(3,4-ethylenedioxythiophene) (PEDOT) \(^{26,27}\) are substantially used as HTMs in perovskite solar cells owing to their low cost, good stability, and simple preparation of designable structures. Nevertheless, the efficiencies of perovskite solar cells using the above HTMs are significantly lower when compared to the efficiency achieved with spiro-OMeTAD as the HTM. In the present work, we report the fabrication of a metal oxide free flexible perovskite solar cell using RF sputtered Ti as the barrier layer, CH\(_3\)NH\(_3\)PbI\(_3\) perovskite as the light absorber and sipro-OMeTAD as the HTM. The metal oxide free flexible perovskite solar cell of the structure PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD/Ag presents a reasonably high solar-to-electric conversion efficiency of \(\sim\)3.83\% with high photocurrent density and open-circuit potential. An incident-photon-to-current efficiency (IPCE) of \(\sim\)66\% in the wave-length range of \(\sim\)450–700 nm is achieved. The charge transport and reduced recombination processes of the fabricated flexible perovskite solar cells have been studied by intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS).

2. Experimental section

2.1. Deposition of a Ti thin layer on a PET-ITO substrate

Indium tin oxide poly(ethylene terephthalate) (ITO-PET) flexible substrates were thoroughly cleaned by ethanol and de-ionized (DI) water and dried in an oven. RF magnetic sputtering loaded with a Ti target (99.95\%, ITASCO, Korea) was used as the source to deposit a Ti thin layer on the cleaned PET-ITO flexible substrates with different thicknesses in the range of \(\sim\)50–100 nm at room temperature. For achieving the desired thickness, the deposition was carried out by evacuating the chamber to a base pressure of \(\sim\)3 \(\times\) 10\(^{-6}\) Torr using a turbo molecular pump followed by a working pressure of \(\sim\)5 mTorr with an RF power of \(\sim\)150 W under argon gas at a flow of 50 sccm. Herein, Ti layers of different thicknesses were obtained by varying the deposition time, as summarized in Table 1.

2.2. Fabrication of a perovskite solar cell (PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD/Ag)

For the preparation of CH\(_3\)NH\(_3\)I, a reaction mixture of methylamine (27.86 ml, CH\(_3\)NH\(_2\), 40\% in methanol, TCI chemicals) and hydroiodic acid (30 ml of 57 wt\% in water, HI, Aldrich, 99\%) was added in a beaker and placed in a chiller at 0 \(^\circ\)C for 4 h. Thereafter, the obtained precipitates were recovered by rotator evaporation at 50 \(^\circ\)C for 1 h and the yellow product of CH\(_3\)NH\(_2\)I was repeatedly washed with diethyl ether ((C\(_2\)H\(_5\))\(_2\)O, Aldrich, 96\%) as additives was further spin-coated on the metal oxide film at 60 \(^\circ\)C. Afterward, PbI\(_2\) (Aldrich, 99\%) was added in a beaker and placed in a chiller at 0 \(^\circ\)C for 4 h. For CH\(_3\)NH\(_3\)PbI\(_3\) perovskite, equimolar CH\(_3\)NH\(_3\)I and lead iodide (PbI\(_2\), Aldrich, 99\%) were dissolved in \(\gamma\)-butyro-lactone (C\(_4\)H\(_6\)O\(_2\), TCI, 99\%) under stirring and kept at 60 \(^\circ\)C for 12 h. The CH\(_3\)NH\(_3\)PbI\(_3\) perovskite solution was deposited on PET-ITO/Ti flexible substrate using a 0.45 \(\mu\)m pore PVDF membrane syringe filter (Jet Biofil) at ambient temperature. The films were spun coated at a speed of \(\sim\)2000 rpm for 40 s and the perovskite deposited thin films were annealed at 100 \(^\circ\)C for \(\sim\)30 min to achieve PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\) thin films. A separate spiro-OMeTAD solution in chlorobenzene (15 mg ml\(^{-1}\)) with 13.6 \(\mu\)l Li-bis(trifluoromethanesulfonylimide) (CF\(_3\)SO\(_2\)NLi, Li-TFSI, 28.3 mg ml\(^{-1}\), TCI, \(\sim\)98\%) and 6.8 \(\mu\)l TBP (C\(_6\)H\(_4\)N\(_2\), Aldrich, 96\%) as additives was further spin-coated on PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\) thin films at \(\sim\)3000 rpm for 30 s and annealed at 100 \(^\circ\)C for 15 min to get PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD thin films. Lastly, silver (Ag) contacts (thickness \(\sim\)100 nm) were made by thermal evaporation to achieve the final flexible device structure of PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD/Ag, as illustrated in Fig. 1(a).

2.3. Characterizations

Atomic force microscopy (AFM, Nanoscope IV, Digital Instruments, Santa Barbara, USA) was used to investigate the morphology of PET-ITO/Ti and PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD thin film substrates. The transmittances of PET-ITO, PET-ITO/Ti and PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\) thin film substrates were performed by UV-vis (UV-2550, Shimadzu, Japan). Structural modifications were studied by X-ray Photoelectron Spectroscopy (XPS) obtained by AXIS-NOVA CJ109, Kratos Inc., range 0–800 eV. Current density (\(J\))–voltage (\(V\)) measurements were performed for elucidating the performance of the flexible perovskite solar cell using a computerized digital multimeter (model 2000, Keithley) with a variable load under one sun (1.5 AM at 100 mW cm\(^{-2}\)). Current–voltage curves were measured at a sweep rate of 80 mV s\(^{-1}\) starting from short circuit to forward bias, and back from forward bias to short circuit under a light illumination of 100 mW cm\(^{-2}\) (1.5 AM). The incident photon-to-current conversion efficiency (IPCE) was measured by a specially designed IPCE system for solar cells by PV measurements, Inc., USA. Before performing the IPCE measurements, the system was calibrated with a silicon photodiode, which was calibrated using the NIST-calibrated photodiode G425 as the standard. The IPCE results of the flexible perovskite solar cell were collected as a function of wavelength from \(\sim\)400 to 800 nm using a 75 W Xe lamp as the light source for generating a monochromatic beam at a low chopping frequency. The charge collection efficiency and photodark current density were revealed by intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photocurrent/photovoltage spectroscopy (IMPS/IMVS).

Table 1: Summary of the Ti deposition time and photovoltaic parameters of the fabricated PET-ITO/Ti/CH\(_3\)NH\(_3\)PbI\(_3\)/spiro-OMeTAD/Ag flexible perovskite solar cell

<table>
<thead>
<tr>
<th>Ti thickness (nm)</th>
<th>Deposition time (min)</th>
<th>Photovoltatic performance</th>
<th>Photovoltaic performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 nm</td>
<td>15</td>
<td>9.63</td>
<td>0.81</td>
</tr>
<tr>
<td>75 nm</td>
<td>21</td>
<td>11.18</td>
<td>0.813</td>
</tr>
<tr>
<td>100 nm</td>
<td>30</td>
<td>15.24</td>
<td>0.830</td>
</tr>
</tbody>
</table>
photovoltage spectroscopy (IMVS) using IVIUM technologies (CompactStat.e20250, USA).

3. Results and discussion

The surface properties of the deposited Ti thin films on PET-ITO substrates have been examined by analyzing the field emission scanning electron microscopy (FESEM) images, as shown in Fig. 1(b–d). From FESEM observations, a uniform and porous morphology is observed for all Ti deposited thin film substrates. It is noticed that the grain size of Ti slightly increases with the increase in deposition time. In particular, the deposition of a Ti thin film for 30 min over an ITO-PET substrate, as shown in Fig. 1(d) displays a highly uniform, porous and well organized grain morphology.

The topographic and three dimensional (3D) atomic force microscopy (AFM) images of PET-ITO/Ti and PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD with Ti thickness of ∼100 nm are analyzed to understand the morphological features of a thin film, as shown in Fig. 2. The topographic AFM image (Fig. 2(a)) of a PET-ITO/Ti thin film shows highly dense and uniform small particles over PET-ITO, indicating that Ti atoms are well adhered to the flexible PET-ITO substrate. The highly rough surface of PET-ITO/Ti is seen in a 3D AFM image (Fig. 2(b)). From Fig. 2(c), the interconnected homogeneously mixed thin film of nanosized CH$_3$NH$_3$PbI$_3$ grains/spiro-OMeTAD and Ti grains over a flexible PET-ITO substrate is visibly seen, which suggests that the CH$_3$NH$_3$PbI$_3$ grains/spiro-OMeTAD are well mixed with Ti grains in the deposited Ti layer, as depicted in the 3D AFM image (Fig. 2(d)). From a roughness analysis, a PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD thin film presents a lower root mean roughness ($R_{rms}$) of ∼8.9 nm than that of the $R_{rms}$ (∼23.4 nm) of a PET-ITO/Ti thin film. It could be seen that the lower roughness might arise due to the good covering of CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD over the barrier layer.

Transmittance studies are conducted to investigate the transparency of a deposited Ti layer and a Ti/CH$_3$NH$_3$PbI$_3$ layer on the PET-ITO substrates. Fig. 3 depicts the transmittance spectra of bare PET-ITO, PET-ITO/Ti and PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$ thin films. The bare PET-ITO substrate displays ∼82% transmittance in the absorbance range of the visible region, which is consistent with the reported transparency of the PET-ITO substrate. The transmittance decreases to half as compared to bare PET-ITO and shows a slight edge shift after the deposition of a Ti layer by RF magnetic sputtering which suggests quite a transparent nature of the PET-ITO/Ti thin film. Furthermore, the deposition of CH$_3$NH$_3$PbI$_3$ on PET-ITO/Ti records a significant fall in transmittance to ∼11% in the visible region, indicating the interaction of perovskite with the Ti layer on the PET-ITO substrate.

The X-ray photoelectron spectrum (XPS) has been analyzed to explain the existence of chemical species in the PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD thin film, as shown in Fig. 4. Fig. 4(a) shows the doublet Ti 2p XPS spectrum of the PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD thin film. The doublet binding energies at ∼458.2 eV and ∼463.8 eV are ascribed to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ respectively, confirming the existence of Ti species over the surface of the thin film. The resolved C 1s XPS (Fig. 4(b)) is composed of four resolved binding energies with a center binding energy. The resolved binding energies at ∼284.9 eV and ∼285.9 eV are assigned to the C–C/C–H and C–N'/C═N' bonds bonding in spiro-OMeTAD and perovskite respectively. The higher binding energy at ∼287.2 eV might represent the spiro carbon or the oxidized form of spiro-
OMeTAD in the presence of TFSI. Moreover, the carbon to metal bonding is seen due to the appearance of binding energy at ∼288.7 eV, confirming the interaction of carbon species with Pb species. N 1s XPS explains the nature of N element in the PET-ITO/Ti/CH₃NH₃PbI₃/spiro-OMeTAD thin film, as shown in Fig. 4(c). The binding energy at ∼400.1 eV originates from pure spiro-OMeTAD which is similar to the measurements of multilayers of another triphenylamine-based hole conducting molecule. The occurrence of binding energy at ∼398.4 eV is due to N–H/amino bonding in the perovskite layer of the thin film. The higher binding energy at ∼404.1 eV might express the existence of a bond formation between NH₃ and Pb salt. Fig. 4(d) shows Pb 4f XPS of the PET-ITO/Ti/CH₃NH₃PbI₃/spiro-OMeTAD thin film and records two binding energies at ∼138.1 eV and ∼143.1 eV, representing Pb 4f₇/₂ and Pb 4f₅/₂ levels respectively. A spin–orbit split between Pb 4f₇/₂ and Pb 4f₅/₂ is recorded at ∼5.00 eV, which is similar to the perovskite as reported in the literature. The metallic (Pb²⁺) binding energy peak has been confirmed in the perovskite from Pb 4f spectrum, indicating the non-existence of Pb⁶⁺ linked to iodide(i). Furthermore, iodine nature in the thin film has been analyzed by I 3d XPS, as shown in Fig. 4(e). Doublet binding energies at ∼619.2 eV and ∼630.5 eV are obtained, corresponding to I 3d₅/₂ and I 3d₃/₂ core levels respectively. A spin–orbit split of ∼11.3 eV is estimated from I 3d XPS, similar to the reported literature. The spin–orbit split binding energies of Pb 4f and I 3d core levels are almost similar to the previously reported literature on perovskite materials, confirming the Pb²⁺ chemical state along with I⁻ in the prepared thin film.

The photovoltaic properties of the fabricated flexible perovskite solar cells (PET-ITO/Ti/CH₃NH₃PbI₃/spiro-OMeTAD/Ag) are analyzed by taking the current density (J)–voltage (V) characteristics under a light intensity of ∼100 mW cm⁻² (1.5 AM). From Fig. 5(A), the fabricated flexible PET-ITO/Ti/CH₃NH₃PbI₃/spiro-OMeTAD/Ag attains a reasonably high solar-to-electric conversion efficiency of ∼8.39% with a high short circuit current density (Jₘₚ) of ∼15.24 mA cm⁻², a high open circuit voltage...
The photovoltaic parameters of the flexible perovskite solar cells fabricated with different thicknesses of the Ti layer on the ITO-PET substrate are shown in Table 1. Low conversion efficiencies are observed when solar cells are fabricated with ~50 and ~75 nm thicknesses of the Ti layer. As seen in the AFM images, the low roughness of the PET-ITO/Ti/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD thin film and good penetration of CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD to the Ti layer results in the high performance of the flexible perovskite solar cell. Moreover, the direct contact of PET-ITO substrate with the perovskite/HTM might be suppressed due to the introduction of Ti layer on ITO-PET, which might increase the charge recombination rate and enhance the charge collection efficiency. It is believed that high charge carriers might be generated and collected over the CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3} layer through the interface of the compact blocking Ti layer, and may result in high photocurrent density. The incident photon to current conversion efficiency (IPCE) of a PET-ITO/Ti/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD/Ag flexible perovskite solar cell has been examined to deduce the high $J_{SC}$ and light harvesting efficiency. Fig. 5(B) shows a high IPCE of ~66% in a broad adsorption wavelength in the range of ~450–700 nm obtained by the fabricated PET-ITO/Ti/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD/Ag flexible perovskite solar cell. The high IPCE is attributed to the high $J_{SC}$ of the solar cell, as presented in Fig. 5(A). In this case, the introduction of a Ti layer might significantly improve the interfacial contact between CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD PET-ITO substrates, which significantly magnifies the light scattering capacities, photon absorption, and produces large photocurrent.

Fig. 6(a) shows the Nyquist plot measurements of the fabricated flexible PET-ITO/Ti/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD/Ag with a Ti thickness of ~100 nm elucidating the characteristics of charge transfer and the recombination rate. Impedance measurements were carried out at different applied voltages with a frequency range from 100 kHz to 1 Hz under dark conditions. The fabricated flexible PET-ITO/Ti/CH\textsubscript{3}NH\textsubscript{3}PbI\textsubscript{3}/spiro-OMeTAD/Ag shows a single semicircular arc at a lower fre-
frequency, corresponding to the combination of the recombination resistance ($R_{rec}$) and the chemical capacitance of the film ($C_μ$). The appearance of a single semicircular arc is due to the low electron transport through ITO-PET and the Ti layer, which results in the absence of a small semicircular arc at a higher frequency.34 The inset of Fig. 6(a) describes the corresponding equivalent circuit, which is composed of resistance related to the diffusion of holes through HTM ($R_1$), in parallel with HTM capacitance ($C_1$), and a recombination resistance ($R_{rec}$) at a lower frequency with a chemical capacitance, ($C_μ$) related to the electron Fermi level in spiro-OMeTAD.35 From Fig. 6(a), a single semicircle originates due to the dominance of the recombination resistance ($R_{rec}$) at the interface of HTM and the perovskite layer with the chemical capacitance of the film ($C_μ$).36 $R_{rec}$ is usually reciprocal to the recombination rate.34

The high $R_{rec}$ could be explained in two possible ways: (i) bad charge extraction enhances the charge carrier density at the bulk material and (ii) recombination sites are generated at the interfacial contacts. It has been reported that low $R_{rec}$ at high applied voltages is explicitly associated with the low $V_{OC}$ of solar cells.37 In our case, the deposition of a Ti layer on a flexible perovskite solar cell exhibits high $R_{rec}$ which might arise from the charge recombination of the injected electron and an electron acceptor at the interface of the top contact and the CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD layer, resulting in an enhanced $V_{OC}$ of the device. Moreover, Fig. 6(b) depicts the corresponding Nyquist plot in the phase mode of imaginary parts versus frequency. The appearance of a broad phase towards the higher frequencies represents a reduction in the recombination sites at the interface of the Ti/perovskite and the HTM layer, indicating a significant improvement in the photovoltage.

The measurements of impedance with respect to bias voltage have been performed to explain the recombination rates in a PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag flexible perovskite solar cell with a Ti thickness of ~100 nm. Fig. 7(a) shows the plot of change in $R_{rec}$ with respect to bias voltage. It is seen that the values of $R_{rec}$ are decreasing with increasing voltage, similar to previous literature.38,39 Noticeably, in a PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag solar cell, the high $R_{rec}$ at a lower voltage clearly supports the high $V_{OC}$, as seen in Table 1. The conductivity of spiro-OMeTAD (HTM) has been evaluated from the following expression:

$$
\sigma_{HTM} = \frac{L}{R_{HTM}}
$$

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**Fig. 5** (A) $J$–$V$ curves of (a) 50 nm, (b) 75 nm and (c) 100 nm Ti thickness based flexible perovskite solar cells. (B) IPCE curve of the fabricated PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag flexible perovskite solar cell with a Ti thickness of ~100 nm.

**Fig. 6** (a) Nyquist plots, (b) corresponding bode phase plots and inset shows the equivalent circuit diagram of the fabricated PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag flexible perovskite solar cell with a Ti thickness of ~100 nm.
where $L$ is the half of the sum of HTM thickness and Ti thickness.\textsuperscript{40} The conductivity of HTM increases with the increase in bias voltage (Fig. 7(b)), indicating the good conductive nature of HTM in the fabricated device. At a low voltage, the loss of conductivity might due to the presence of few recombination sites during the hole transport process. Herein, the high efficiency of the PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag perovskite solar cell might be credited to high $J_{SC}$ and $V_{OC}$ which are attributed to high transport and low recombination rates.

Intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photovoltage spectroscopy (IMVS) have been studied to further explore the electron transport and recombination properties of the fabricated flexible perovskite solar cell at different voltages of light and different photon fluxes. Fig. 8 shows the IMVS and IMPS of the fabricated flexible perovskite solar cell at different voltages of light. The IMPS and IMVS of the device decreases with an increase in the voltage of light from 0.5 V to 2.0 V. At the maximum voltage of light (2.0 V), the charge-transport time ($\tau_{CT}$) and electron recombination time ($\tau_{R}$) have been estimated by selecting the minimum frequencies from the IMPS and IMVS plots of the fabricated flexible perovskite solar cell. The $\tau_{CT}$ and $\tau_{R}$ values are calculated by the following equations:

$$
\tau_{CT} = \frac{1}{2\pi f_{min}\text{(IMPS)}}
$$

$$
\tau_{R} = \frac{1}{2\pi f_{min}\text{(IMVS)}}
$$

where $f_{min}$ is the characteristic minimum frequency of the IMPS and IMVS plots.\textsuperscript{41} The fabricated flexible perovskite solar cell presents a better $\tau_{CT}$ of $\sim$15.9 ms and $\tau_{R}$ of $\sim$204 ms, suggesting that the flexible perovskite solar cell presents an enhanced charge transport rate and lower the recombination rate during the operation. Furthermore, the order of $\tau_{CT}$ and $\tau_{R}$ values with respect to photon fluxes is presented in Fig. 9. The increase in photon flux results in the decrease in the $\tau_{CT}$ and $\tau_{R}$ values, as shown in Fig. 9(a and b). The low $\tau_{CT}$ and $\tau_{R}$ values originate from the uniform deposition of CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD on PET-ITO/Ti and good interfacial contact between Ti and CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD layers which might increase the electron transport by making it difficult for electrons to recombine with holes and hence, decrease the recombination. On the other hand, the electron diffusion length in the flexible perovskite solar cell could be determined by using the expression:

$$
D_{L} = (D_{n} \cdot \tau_{R})^{1/2}
$$

where $D_{n}$ is the diffusion coefficient of holes.\textsuperscript{40}
where $D_n$ is the diffusion coefficient which is obtained by the IMPS plot.\textsuperscript{42} A $D_n$ value of $\sim 6.7 \times 10^{-8}$ cm$^2$ s$^{-1}$ has been estimated for the fabricated flexible perovskite solar cells. It is known that $D_L$ represents the average distance an electron travels before it recombines with either the absorber (perovskite) or the hole conductor (spiro-OMeTAD).\textsuperscript{43} In general, longer $D_L$ could lead to higher charge collection and light-harvesting efficiencies for achieving a high conversion efficiency. In our case, a good $D_L$ value of $\sim 1.169$ µm is ascribed to the high recombination resistance or lower recombination rate, as evidenced by Fig. 7(a). The obtained $D_L$ value clearly depicts a great chance for a large number of electrons to enter from the PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$ thin film layers to the top Ag layer by improving the charge collection at a lower light intensity. The charge collection efficiency of the fabricated flexible perovskite solar cell is determined by the following relation:\textsuperscript{42}

$$\eta_{CC} = 1 - (\tau_{CT}/\tau_R)$$

Fig. 9(c) shows that the fabricated PET-ITO/Ti/CH$_3$NH$_3$PbI$_3$/spiro-OMeTAD/Ag flexible perovskite solar cell with a Ti thickness of $\sim 100$ nm shows a high conversion efficiency of $\sim 8.39\%$ along with a high short circuit current ($J_{SC}$) of $\sim 15.24$ mA cm$^{-2}$, an open circuit voltage ($V_{OC}$) of $\sim 0.830$ V and a high fill factor (FF) of $\sim 0.66$ under a light illumination of $\sim 100$ mW cm$^{-2}$ (1.5 AM). However, low conversion efficiencies are observed for the fabricated flexible solar cells with $\sim 50$ nm and $\sim 75$ nm Ti thicknesses. The enhanced $V_{OC}$ and FF might be attributed to the improvement in the interfacial contact between the Ti layer and the spiro-OMeTAD-Li-TFSI layer. IMPS and IMVS studies reveal a better charge transport rate, efficient diffusion coefficient, diffusion length and a high charge collection efficiency.

4. Conclusions

The effect of a titanium (Ti) layer on the charge transport and recombination rates in flexible perovskite solar cells has been studied, in which the Ti layer as an efficient barrier layer is deposited on PET-ITO flexible substrates through RF magnetic sputtering using a Ti-source and a pressure of $\sim 5$ mTorr. The deposited Ti coated PET-ITO is directly used for the fabrication of a flexible perovskite solar cell without using any metal oxide layer. The fabricated perovskite solar cell with a Ti thickness of $\sim 100$ nm shows a high conversion efficiency of $\sim 8.39\%$ along with a high short circuit current ($J_{SC}$) of $\sim 15.24$ mA cm$^{-2}$, an open circuit voltage ($V_{OC}$) of $\sim 0.830$ V and a high fill factor (FF) of $\sim 0.66$ under a light illumination of $\sim 100$ mW cm$^{-2}$ (1.5 AM). However, low conversion efficiencies are observed for the fabricated flexible solar cells with $\sim 50$ nm and $\sim 75$ nm Ti thicknesses. The enhanced $V_{OC}$ and FF might be attributed to the improvement in the interfacial contact between the Ti layer and the spiro-OMeTAD-Li-TFSI layer. IMPS and IMVS studies reveal a better charge transport rate, efficient diffusion coefficient, diffusion length and a high charge collection efficiency.

![Fig. 9](image_url)
of the fabricated flexible perovskite solar cell, resulting from the improvement in the interfacial contact between the Ti conduction layer and the hole transporting layer. Thus, thickness of the Ti layer is crucial to achieve high performance of the flexible PET-ITO/Ti(CH₃NH₃)₂PbI₃/spiro-OMeTAD/Ag perovskite solar cell along with an improved electron transport rate, high charge collection, and quite a high $D_e$ value.

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