용액공정을 용용한 구리 나노입자 첨가형 P3HT: PCBM 기반 태양전지 제조

Manoj Ovhal*, 임수만**, 강재욱***

본 연구는 용액공정 측, 스크림 코팅, 바 코팅 및 스크립 프린팅 공정을 이용하여 구리나노입자 첨가형 P3HT : PCBM 태양 전지 제조하였고 생산된 효율을 비교하였다. 여기서, 은 (Ag) 상부 전극은 금속 증착에 의해 증착되고 미리 증착된 폴리머 박막 상에 스크립 인쇄로 인쇄하여 비교실험하였다. 실리 절화 전극(Rsh)은 각각 0.7 Ω □⁻¹ 및 2 Ω □⁻¹ 이었고, 두께는 100 nm 및 80 nm이었다. 그 결과, OPV에서 스크립 코팅 및 바 코팅을 하고 금속 증착된 표면은 각각 4.39 및 0.63 %의 효율을 나타냈다. 스크립 인쇄된 Ag 전극 OPV는 단락문제를 야기시켰다. 이것은 스크립 인쇄기가 일작기 OPV에 가한 인쇄력으로 인해 환상층 구조가 데미지를 입었기 때문으로 사료된다. 한편, 스크립 코팅 공정은 주변 조건에서 수행된 바 코팅 공정에 비해 신뢰성이 높았으나, 바 코팅으로 처리된 활성층은 OPV 구조에서 대변적 제조용으로 사용할 가능성을 볼 수 있었다. 그러나 스크립 프린팅의 경우, OPV 제조 공정에서 스크립 프린팅 공정을 채택하기 위해서는 스크립으로 인한 상층 손상을 제거하기 위한 더 많은 연구가 필요하다.

요 약

The present work is mainly focused on fabrication of copper nanoparticles incorporated P3HT: PCBM solar cell top electrode with spin coating, bar coating and screen-printing process and the efficiency produced by each method was compared. Herein, Silver (Ag) top electrode deposited by metal evaporation and screen printing on pre-deposited polymeric thin film. The sheet resistance (Rsh) of Ag electrodes were 0.7 Ω □⁻¹ and 2 Ω □⁻¹ with the thickness of 100 nm and 80 nm respectively. As a result, the metal evaporated Ag electrode based OPV covered by spin coating and bar coating in active layer shows 4.39 and 0.63 % efficiency, respectively. Whereas, the screen-printed Ag electrode OPVs were shorts. This short problem was raised due to the impression force applied by screen printer squeezer on the OPVs. Although spin coating process was more reliable compared with bar coating process performed in ambient condition, bar coated active layer has shown possibility to be used in OPV structure. For screen printing, however, more research to remove upper layer damage caused by squeezing was required to adapt screen-printing process in the OPV fabrication process.

Keywords: Bar coating, OPVs, Spin coating, Thermal Evaporator and Screen printing.

ABSTRACT

The present work is mainly focused on fabrication of copper nanoparticles incorporated P3HT: PCBM solar cell top electrode with spin coating, bar coating and screen-printing process and the efficiency produced by each method was compared. Herein, Silver (Ag) top electrode deposited by metal evaporation and screen printing on pre-deposited polymeric thin film. The sheet resistance (Rsh) of Ag electrodes were 0.7 Ω □⁻¹ and 2 Ω □⁻¹ with the thickness of 100 nm and 80 nm respectively. As a result, the metal evaporated Ag electrode based OPV coated by spin coating and bar coating in active layer shows 4.39 and 0.63 % efficiency, respectively. Whereas, the screen-printed Ag electrode OPVs were shorts. This short problem was raised due to the impression force applied by screen printer squeezer on the OPVs. Although spin coating process was more reliable compared with bar coating process performed in ambient condition, bar coated active layer has shown possibility to be used in OPV structure. For screen printing, however, more research to remove upper layer damage caused by squeezing was required to adapt screen-printing process in the OPV fabrication process.

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I. Introduction

The Organic photovoltaic (OPVs) have earned the more attention in past several decades. The intensive studies have been done to improve OPVs efficiency by means of materials, device structure with low cost, light weight, flexible, large area, and mass production [1]. Heliatek R&D team reached a highest record of 13.2 % efficiency by OPVs multi-junction cell [1, 2]. In order to increase the efficiency of OPVs, the surface plasmon effect of metal nanoparticles plays an important role. The surface plasmon effect due to metal NPs embedded in active layer of OPVs significantly improves the efficiency. The metal NPs under the electromagnetic light shows resonance. This leads to increase in optical path of metal NPs. This optical path creates and polarized electrons and holes over the metal NPs. At high power this electrons or holes gets ejected. Further, the ejected electron and holes reasonably improves the efficiency of OPVs [2, 3]. The spin coating is the most favorable fabrication process for OPVs. This method is convenient, but has several disadvantages, such as stress caused by spinning motion, poor uniformity of edges on large areas devices, a large amount of wastage, even at high scale production of OPVs in industries. The spin coating process is time consuming and cause to improve in cost [4]. So, there is a need of an alternative method for depositing solution by coating processes, such as bar coating, screen printing, doctor blade, slot die, and electro-spray process etc. The alternative methods generally have high ability to be used in large area product with high cost effect [5, 6].

In this study, the Cu NPs incorporated P3HT: PCBM active layer were fabricated by spin coating and bar coating. The top electrode was deposited using metal evaporator and screen printing process in OPVs. The metal evaporated top electrode OPVs with spin and bar coating shows the PCE of 4.3 and 0.63%, respectively. Whereas, the screen printed top electrode does not show any response. The reason for these results have been studied and envisaged.

II. Experiments

2.1 Chemicals

Zinc acetate dihydrate (Zn(CH3COO)2·2H2O, Aldrich, 99.9%), Ethanolamine (NH2CH2CH2OH, Aldrich, 99.5%), 2-methoxyethanol (CH3OCH2CH2OH, Aldrich, 99.8%), PEDOT:PSS (Clevios PVP AI 4083), Copper nitrate (Cu(NO3)2·2.5H2O, Alfa Aesar, 98.0-102.0%), Polyvinylpyrrolidone (PVP, Alfa Aesar, M.W. 40000), Acetone, Isopropyl alcohol (IPA), Ethanol, Ethyl alcohol, DI water, Thermal evaporator silver pellets (Omega Hwayon) and Screen printer Silver paste (FTL). Comparison of Ag pellets and paste properties is shown in table 1.

Table 1: Comparision between Silver pellets and Silver paste.

<table>
<thead>
<tr>
<th></th>
<th>Silver Pellets</th>
<th>Silver Paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Pellets metallic</td>
<td>Flakes</td>
</tr>
<tr>
<td>Size</td>
<td>0.3 to 3 µm</td>
<td></td>
</tr>
<tr>
<td>Binder</td>
<td>-</td>
<td>Polyester</td>
</tr>
<tr>
<td>Solvent</td>
<td>-</td>
<td>ECA</td>
</tr>
<tr>
<td>Viscosity</td>
<td>-</td>
<td>72751 cPs (23 °C )</td>
</tr>
<tr>
<td>Drying and melting temperature</td>
<td>962 °C</td>
<td>150 °C</td>
</tr>
<tr>
<td>Resistance at 5 mm</td>
<td>0.6 Ω</td>
<td>2 Ω</td>
</tr>
</tbody>
</table>

2.2 Synthesis of Copper NPs

The easy, low cost and low temperature chemical solution process method was used to synthesis of Cu NPs. The 100 ml of DI water and 50 ml of ethyl alcohol were placed in a 250 ml flask and heated to 75 °C. After the temperature reached 10 ml of 0.05 M copper nitrate (Cu(NO3)2· 2.5H2O, Alfa Aesar, 98%), 0.0025 M Polyvinylpyrrolidone (PVP, Alfa Aesar, M.W. 40000) was added and mixed for 20 minutes. Thereafter, 5 ml of 0.1 M NaOH was mixed and maintained at 75 °C for 5 minutes with stirring, followed by cooling at room temperature. The synthesized Cu nanoparticles were separated by centrifugation at 13,000 rpm for 40 minutes. To remove unreached PVP, the precipitate was collected and acetone was added. After washing for 5 minutes with ultrasonic, it was re-dispersed in ethanol for 30 minutes [7].
2.3 Fabrication of OPVs

Indium tin oxide (ITO)/glass substrates with a sheet resistance of 10 Ω cm−1 were ultrasonically cleaned in acetone, followed by boiled in iso-propanol, and subjected to UV-ozone treatment for 15 min. For the ZnO precursor, Zinc acetate (1.64 g) and ethanolamine (0.5 g) in 2-methoxyethanol (10 g) were added and stirred vigorously for 30 min. The ZnO precursor was then filtered with a 0.25 μm polypropylene (PP) filter and spin-coated onto ITO substrates at speed of 5000 rpm for 40 s, further heated at 150 °C. The active layer was form by Cu NPs (0.1 g) incorporated in P3HT (50 mg) and PCBM (50 mg) in chlorobenzene (2.5 ml) stirred for 15 hr at 60 °C. This active layer was spin coated on ZnO layer at 700 rpm for 1 min and annealed at 150 °C. Similarly, on another device the active layer was coated using 20 µm wire bar coating process. The PEDOT:PSS were diluted in IPA by 1:10 ratio. This diluted PEDOT:PSS was deposited onto the active layer at 4000 rpm for 1 min and heated at 150 °C. The devices were subsequently transferred to a vacuum chamber. Finally, Ag as a top electrode was deposited through a shadow mask at a rate of 0.2 nm s−1 using thermal evaporation under vacuum with a pressure of 10−8 Torr [8]. Whereas, in screen printing process 10 µm width of electrode and 2 mm2 mesh were used. The screen printed top Ag electrodes immediately were heated at 150 °C for 10 min. The final OPVs device structure was inverted as Glass / ITO / ZnO / P3HT:PCBM / PEDOT:PSS / Ag as shown in Figure 1 [9, 10].

2.4 Characterizations

The surface morphology of Cu NPs was carried out using scanning electron microscope system (NOVA NanoSEM 450, FEI company). The micrograph was captured at 120 000 X magnification. The films thicknesses were measured by surface profiler (KLA Tencor, P-10 model). The active layer fabricated by bar coater (Opams). The Optical microscope images of spin and bar coated active layer were taken at 20 μm scale. The IOSC performance was measured under simulated AM 1.5 illuminations with irradiance of 100 mW cm−2 (Oriel Sol 1A, Newport); the irradiance was calibrated using a standard Si photodiode detector fitted with a KG5 filter. Current density–voltage (J–V) curves were measured and analysed using Keithley 2400 Source Meter. In order to accurately define the active area, a shadow mask with an exposed area of 0.09 cm² was employed for the J–V measurements.

III. Results

In current study, the Cu NPs were synthesized by chemical solution process. The particle size of Cu NPs was confirmed by SEM micrographs. The Cu NPs were irregular spherical in structure and its size were found to be approximately 29 nm showed in Figure 2.

Figure 1: Inverted OPVs device structure

Figure 2: SEM image of Cu NPs. The yellow line indicates average particles size.

The 0.1 wt% of Cu NPs were incorporated in P3HT:PCBM solution. Further, in OPVs fabrication, the thickness of ZnO layer on ITO/glass was measured by surface profiler. It was found to be approximately 20 nm. Whereas, the thickness of active layer fabricated by spin coating and 20 µm bar coating were 210 ± 8 nm and 198 ± 25 respectively. The optical images of the spin and bar coated devices were shown in Figure 3.
Figure 3: Optical images of Cu NPs incorporated P3HT:PCBM with a) Spin coating b) Ag electrode by screen printing on (a), c) Bar coating and d) Ag electrode by screen printing on (c).

Figure 4: Digital images of Spin + Screen and Bar + Screen

It confirms the active layer spin coated device shows uniform film. Whereas, the bar coated devices were showing grooves and trenches. The PEDOT:PSS of approximately 30 nm were spin coated on top of active layer. The thickness of Ag electrode by thermal evaporator was 100 nm and by screen printing it was 80 nm. The final device structure is shown in Figure 4. The light current density-voltage ($J-V$) characteristics of thermal evaporated and screen printed top electrode of OPV devices were measured and analysed using Keithley 2400 Source Meter.

Figure 5: $J-V$ characteristics curve of spin coated active layer with top Ag electrode using thermal evaporation. Bar coated active layer with top Ag electrode using thermal evaporation process.

Figure 6: $J-V$ characteristic curve of spin coated active layer with top Ag electrode using screen printing. And bar coated active layer with top Ag electrode using screen printing process.

The Figure 5 shows the ($J-V$) characteristics of top Ag electrode thermal evaporated and spin coated active layer of OPVs shows a short-circuit current density ($J_{SC}$) of 16.634 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.541 V, and a fill factor ($FF$) of 48.84%. This corresponds to a efficiency of PCE ($\eta$) of 4.39%. Further, the OPVs devices fabricated active layer by 20 µm bar shows $J_{SC}$ of 3.09 mA cm$^{-2}$, a $V_{OC}$ of 0.424 V, and a $FF$ of 49.63% with PCE 0.63%. This decrement in PCE was due to grooves formed by bar coating. Further, the same devices with top Ag electrode by screen printing method, spin coated active layer OPVs shows a
short-circuit current density ($J_{SC}$) of 26.50 mA cm$^{-2}$, an open-circuit voltage ($V_{OC}$) of 0.01 V, while the bar coated OPVs shows short-circuit current density ($J_{SC}$) of 34.23 mA cm$^{-2}$ and, an open-circuit voltage ($V_{OC}$) of 0.00 V, that means the devices were short [5]. The light current density-voltage ($J-V$) characteristics value shown in table 2 the values extracted from Figure 5 and 6.

<table>
<thead>
<tr>
<th>Conditions</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
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<tbody>
<tr>
<td>Spin + Thermal</td>
<td>0.54</td>
<td>16.63</td>
<td>48.84</td>
<td>4.39</td>
</tr>
<tr>
<td>Bar + Thermal</td>
<td>0.424</td>
<td>3.09</td>
<td>49.63</td>
<td>0.63</td>
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<tr>
<td>Spin + Screen</td>
<td>0.01</td>
<td>26.50</td>
<td>NaN</td>
<td>NaN</td>
</tr>
<tr>
<td>Bar + Screen</td>
<td>0.00</td>
<td>34.23</td>
<td>NaN</td>
<td>NaN</td>
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</tbody>
</table>

IV. Discussion

The Cu NPs incorporated P3HT: PCBM with thermal evaporated top Ag electrode shows PCE 4.13%, whereas the screen printed OPVs were shorts. The 20 µm grooves size of bar in bar coating process with thermal evaporated top Ag electrode OPVs shows very low efficiency of 0.63% [11, 12], whereas the screen printed OPVs were shorts. After the results, it is found that, in the screen printing process the OPVs polymer layers were merge into each other’s due to high impression force by screen printer squeezer [5]. During screen printer optimization on glass surface the pressure was fixed for better printing, but the force on glass was high for OPVs polymer layers. The screen printed top electrode in OPVs surely reduce the cost and fabrication time [5, 13]. For this, screen printing squeezer pressure and viscosity of Ag ink need to be optimize precisely.

V. Conclusion

The OPVs inverted structure as Glass/ITO/ZnO/P3HT :PCBM/PEDOT:PSS/Ag were fabricated by spin and bar coating. The Ag top electrodes were deposited by metal evaporation and screen-printing process. First, bar coated active layer has shown a possibility to be used in OPV structure although the efficiency was lower than that of spin coating. Secondly, the top electrodes deposited by metal evaporation OPVs were shows response in light with high efficiency of 4.39 % efficiency. Whereas, the top electrodes deposited by screen printing OPVs were short. This problem arises due to unoptimized screen printer squeezer pressure and viscosity of Cu NPs doped P3HT: PCBM ink.

References

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