Contents lists available at ScienceDirect





Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Screen printed silver top electrode for efficient inverted organic solar cells



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ARTICLE INFO

Article history: Received 5 August 2013 Received in revised form 22 April 2015 Accepted 24 April 2015 Available online 27 April 2015

Keywords: A. Metal C. X-ray diffraction C. Atomic force microscopy A. Multilayers

D. Electrical properties

ABSTRACT

The present work is mainly focused on replacement of the vacuum process for top electrode fabrication in organic solar cells. Silver top electrode deposited through solution based screen printing on pre-deposited polymeric thin film. The solution based printing technology provides uniform top electrode without damaging the underlying organic layers. The surface crystallinity and surface morphology of silver top electrode are examined through X-ray diffraction, field-emission scanning electron microscope and atomic force microscope. The purity of silver is examined through X-ray energy dispersive spectroscopy. The top electrode exhibits face centered cubic structure with homogeneous morphology. The sheet resistance of top electrode is found to be $0.06 \,\Omega/\text{sq}$ and an average pattern thickness of ~15 μ m. The power conversion efficiency is 2.58%. Our work demonstrates that the solution based screen printing is a significant role in the replacement of vacuum process for the fabrication of top electrode in organic solar cells.

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1. Introduction

Photovoltaic technologies are of great interest in the development of clean and renewable energy. In this aspect, organic solar cells carry several advantages such as light weight, low cost, solution processability and large scale production at low temperature [1–3]. The development of solution processed organic solar cells using bulk heterojunctions of blended polymer/fullerene are of great interest in the fabrication of organic active layers [4,5]. There are different types of solution based non-printing/printing techniques existed for the fabrication of organic devices, including spin coating, dip coating, inkjet, screen printing, doctor blade, roll to plate, slot die and electrospray process [4-8]. The above mentioned techniques have an attractive interest in the fabrication of small/large scale production of organic solar cells except the final step of top electrode deposition, which is performed through vacuum based techniques [9,10]. In order to avoid the underlying layer damage, alternative technologies need to be developed for top electrode fabrication.

http://dx.doi.org/10.1016/j.materresbull.2015.04.052 0025-5408/© 2015 Elsevier Ltd. All rights reserved.

In this aspect, development of solution based screen printing is more suitable for top electrode fabrication on pre-deposited organic layers. This technique offers low cost, high speed, good adaptability and process at room temperature. Screen printer mainly consists of screen, stencil, squeegee, and ink to achieve uniform patterns [8]. Herein, squeegee is used to force the ink onto the substrate through the open mesh to attain a desired pattern with respect to stencil design. The achieved pattern thickness is mainly depends upon the squeegee moving speed, applying force to push the ink through the screen onto the substrate, distance between the screen and the substrate and also ink properties (concentrations and viscosity). In screen printing, ink viscosity is \sim 10–100 times higher than that of ink used in dip/spin coating process [11]. Currently, screen printing is used in the flexible electronic industries. The large area polymeric printed pattern of P3HT, MEH-PPV and PEDOT:PSS are observed using screen printing in organic solar cells and light emitting diodes [8,12]. This technique is not only used for the fabrication of active layers and buffer latters but also used in the fabrication of metal top electrode using solution based metal inks with high viscosity.

This paper mainly focuses on the printing of silver top electrode through solution based screen printing. The crystallinity and surface morphology of silver are examined through X-ray diffraction, FE-SEM and AFM analysis. The pattern thickness and sheet resistance of silver are determined through ellipsometry and

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four point probe measurements. Finally, the patterned silver is used as top electrode for inverted organic solar cells, which is examined through current density–voltage (J-V) analysis.

2. Material and methods

2.1. Materials

Silver ink is received from Toyochem, Japan. Zinc oxide nanoparticles, poly(3-hexylthiophene-2,5-diyl), poly (6,6-phenyl C61-butyric acid methyl ester) and *n*-methylethanolamine are purchased from Sigma–Aldrich, Republic of Korea. Ethanol is received from Dang chemicals, Republic of Korea and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) is purchased from Agfa Materials, Japan. All the chemicals are used without further purifications.

2.2. Fabrication of inverted organic photovoltaic cell

Fabrication of inverted organic device (ZnO/P3HT:PCBM/ PEDOT:PSS/Ag) on ITO coated glass (15 Ω /sq) consists of four steps viz., (i) fabrication of ZnO on ITO coated glass, (ii) deposition of active layer (P3HT:PCBM), (iii) deposition of PEDOT:PSS and (iv) fabrication of silver top electrode.

Zinc oxide nanoparticles (1 g) are uniformly dispersed in ethanol medium using *n*-methylethanolamine as a stabilizer. The solution mixture is stirred at a range of 800–1000 rpm for 2 h at 50 °C. Finally, the homogeneous dispersion of ZnO NPs ink is obtained and used for thin film deposition on ITO coated glass substrate. Before the fabrication of ZnO film, substrate is cleaned with acetone, isopropanol, di-water and followed by UV treatment for 20 min. Thin film deposition is achieved via spin coating with rotational speed of 1000 rpm for 30 min. Finally, the deposited ZnO thin film is sintered at 150 °C for 2 h.

The second step is the fabrication of active layer. Here, the preparation of P3HT:PCBM (1:1) ink using *o*-dichlorobenzene as a solvent medium. The composite ink is achieved under vigorous stirring (1500 rpm) at $60 \,^{\circ}$ C for 24 h [13]. The freshly prepared composite ink is uniformly deposited on ZnO layer coated ITO substrate via spin coting. The non-agglomerated homogeneous deposition of composited thin film is achieved in the range of 800–1000 rpm (rotational speed) for 30 s and the deposited thin film is sintered at 120 $^{\circ}$ C under N₂ atm.

(a) Squeegee ink Screen Substrate (b) Ag PEDOT:PSS PAHT:PCuBM ZNO Glass substrate

Fig. 1. Schematic picture of screen printing process, (b) schematic diagram of inverted organic solar cells.

The third step is the fabrication of buffer layer (PEDOT:PSS) on pre-deposited active layer via spin coating. The PEDOT:PSS ink is uniformly deposited on active layer at rotational speed of 300 rpm for 30 s and the film is sintered at $140 \degree$ C for 10 min.

The final step is the deposition of top electrode (silver) using solution based screen printing technique. The schematic picture of screen printer as shown in Fig. 1a. In screen printing, stencil screen is used for silver pattern on pre-deposited buffer layer (PEDOT: PSS). Screen printing requires squeegee to drive the ink linearly across the screen, which is dripped through the stencil screen onto pre-deposited PEDOT:PSS layer to achieve an uniform silver pattern. The pattern thickness is significantly controlled by squeegee moving speed, applied force and ink viscosity. This printing technique requires relatively high viscosity (>10–100 times) than that of ink used for spin coating. Finally, the printed top electrode (silver) is dried at 150 °C for 10 min in hot air over and pattern thickness is nearly ~15 μ m. The fabricated inverted organic solar cell is kept in glove box under N₂ atm. The schematic diagram of fabricated organic device is shown in Fig. 1b.

3. Results and discussion

The crystalline structure of silver top electrode is investigated by X-ray diffraction analysis (Rigaku D/MAX 2200H, Bede Model 200). Fig. 2 shows the diffraction pattern of silver pattern deposited through screen printing. The observed diffraction peaks at 2θ = 38.1°, 44.2°, 64.7° and 77.5° corresponds to (111), (200), (220) and (311) plans of face centered cubic (fcc) structure of silver [14], which is clearly indexed well with standard JCPDS card No. 04-0783. No other characteristic peaks are observed, which is confirmed the purity of silver pattern.

The surface morphology and grain size of the silver pattern are examined by field emission scanning electron microscope (JEOL. Ltd., SEM 1200EX II). Fig. 3a shows the surface morphology of silver top electrode, which is revealed the homogeneous deposition of silver pattern via screen printing. The FE-SEM analysis confirmed that the silver particles are strongly interconnected with each other with void free surface morphology, which is due to microstructured silver pattern [15]. The uniform surface morphology of silver tend to reduce the sheet resistance (~0.06 Ω /sq), which lead to enhance the charge conduction in organic device. The surface roughness of silver pattern is examined using atomic force microscope (AFM). Fig. 3b represents the micrograph of silver



Fig. 2. X-ray diffraction analysis of silver pattern.

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