Source materials grain size effect on electrode microstructure and its effect on conventional bulk hetero-junction photovoltaics

Arul Varman Kesavan, Praveen C. Ramamurthy*

Department of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

ARTICLE INFO

ABSTRACT

In this work, the effect of silver cathode on the polymer diode and organic photovoltaic device (OPV) performance was investigated. The electron collecting contacts in diode and OPV device have been deposited from both silver pellet and nanoparticles form. Diode was fabricated by sandwiching poly(3-hexylthiophane-2,5-diyl) between ITO and Ag electrodes. It is observed that diode fabricated using Ag nanoparticles showed significant current density improvement. The enhancement in diode performance was studied by *C-V* measurements. Further, OPV cells fabricated using Ag nanoparticles showed improvement in current density which results in improved power conversion efficiency (PCE). The observed performance enhancements in diode and OPV device have been correlated with electrode microstructure and its interface properties. The performance enhancement in diode and OPV cells is evaluated by various electrical parameters such carrier concentration (N), density of trap states, trap distribution width (ω) and current density. These data indicate that the electrode grain size matching with the semiconductor morphology across metal/semiconductor interface is more critical for better charge transfer. Matching the roughness of the interface across the junction by use of appropriate starting material particle/grain size can help in extracting the maximum performance of an organic device.

1. Introduction

Area of flexible electronics finds extensive research interest due to its various advantages over conventional electronic devices. Properties of the conducting organic molecules, molecular weight, absorption, energy band gap can be tuned. All of these properties can be obtained by molecular structure design and chemical synthesis. In an organic electronic device (OED),

fabrication of active layer mainly carried out in a low-temperature processing techniques such spin coating, drop casting, dip coating, etc. Polymer materials are light weight, relatively low fabrication cost, and can be fabricated over the flexible substrates [1]. In recent years, organic semiconductors are widely used in many of the electronic devices, such as organic photovoltaic (OPV), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), organic photo-detector (OPD), etc. The most important and critical part of an organic device architecture is at electrode/active layer interfaces. Formation of less defect interface is a crucial part in the fabrication of the devices. The following parameter plays a major role in deciding the interface properties. Firstly, energetic nature of the metal and semiconductor such as metal work function (ϕm), semiconductor work function (ϕs), electron affinity (χ), ionization potential (IP), energy band gap (E_g),

position of the highest occupied molecular orbit (HOMO) and lowest unoccupied molecular orbital (LUMO). The work function of the metal depends on the crystallographic orientation of the grains or Fermi surfaces. Fermi surfaces are anisotropic in most crystals. Anisotropic Fermi surface is the cause of a different type of atomic packing in the given unit cell. This anisotropic nature of Fermi surface leads to various degrees of binding energy on different crystallographic phase. Consequently, work function will be different from one crystallographic grain orientation to the other [2–4]. The second set of a factor, which decides the device properties are semiconductor processing parameters and electrode deposition condition. Semiconductor deposition condition dictates the uniformity of the film, the thickness of the active layer, surface roughness [5,6]. In the metal electrode deposition step, chamber vacuum, purity of the source material, evaporation rate influences the quality of the film and interface [7,8]. Electrode evaporation rate dictates the surface roughness, as the rate of evaporation increases higher than the mobility of adatom on the active layer surface; consequently, electrode roughness will increase. It is also reported that high melting temperature is associated with active layer annealing [9]. Apart from the energetics of the material parameters, interface behaviour of devices is mainly decided by the process parameter of the metal and semiconductor. The total thickness of the various layers

involved in the organic electronic device (OED) comprises of less than half a micron. Therefore, forming a defect less interface and investigation of such kind of interfaces are critical for efficient device fabrication. Polymeric materials are soft in nature therefore for a small change in the optimized experimental conditions; the device characteristic can change significantly [10,11].

The interface barrier exhibits Ohmic or Schottky type contact depending on the energetics of the metal and semiconductor. The interface behaviour decides the following property of the final device characteristics and therefore it is important to investigate the interface. The restricted charge carrier transport into/out of the semiconducting layer leads to accumulation of charges at the interface. Charge carrier accumulation at the interface will deform the typical device behaviour and leads to the S-shaped current-voltage curve which is also called S-shape kink in the case of photovoltaic devices [12]. The interface charge accumulation is a critical factor because accumulation will lead to the change in the interfacial potential. This change in potential across the semiconductor/metal electrode junction considerably affects open circuit voltage (V_{OC}) and short circuit current (J_{SC}) in the case of the organic solar cells. An improvement in the charge carrier transport can be obtained by defect less interface which will reduce charge carrier traps at the interface [11]. An effective way to attain the defect less interface is to control the active layer and electrode interface morphology. The semiconductor surface morphology can be modified by various means such as annealing the active layer for an optimum period and temperature, surface treating by solvent vapours etc. Therefore, fabrication of homogeneous and smooth surface morphology of polymer semiconductor with a suitable electrode is one of the most significant challenges in organic electronic device fabrication. In this work, Ag cathode was deposited from Ag pellet [Ag-B] and Ag nanoparticle [Ag-N] form. Electrode obtained from Ag-B and Ag-N source was named as Ag-L and Ag-S electrode respectively representing large and small grain size observed in the process. The effect of starting materials on diode and photovoltaic device performance were studied. The electrical characteristics of the device were correlated with the cathode microstructure, cathode/semiconductor interface morphology, and improved interface charge transfer at interface. Enhancement in current density (CD) and fill factor (FF) of photovoltaic was correlated with reduced interface trap states density and improved charge transfer across the interface.

2. Experimental

2.1. Materials

Electrode starting material of 2–3 mm Ag metal pellet were obtained from Alfa Aesar (purity 99.999%) and Ag nanoparticle (purity 99.99%), and average surface area of the nanoparticle is 3.09 $m^2 g^{-1}$ obtained from Sigma Aldrich. Molybdenum boat was used for evaporating Ag pellet and Ag nanoparticle. The regio-regular poly(3-hexylthiophane-2,5-diyl) (rr-P3HT) was obtained from Rieke metals, solvent 1,2-dichlorobenzene was purchased from SD Fine-chem. Limited and indium tin oxide coated glass substrate (ITO) (sheet resistance 70–120 Ω sq^{-1}) was from Delta Technologies Limited, USA.

2.2. Device fabrication and characterization

The Ag electrodes were deposited by thermal evaporation under the vacuum of 1×10^{-5} mbar to obtain the final thickness of $\sim$ 100 nm at the evaporation rate of 2 Å s^{-1}. Ag top electrodes were deposited on cleaned glass slide to study structural, electrical and morphology properties. Device with diode structure ITO/P3HT/Ag were fabricated as follows. ITO substrates were cleaned in an ultrasonic bath by soap water, acetone, and isopropanol and then finally dried with nitrogen gas. P3HT solution was prepared by dissolving 10 mg of P3HT in 1 ml of 1, 2 dichlorobenzene, and the resulting solution was filtered by using

0.45 μm pore size filter to remove the un-dissolved material in the solution. Filtered P3HT solution was spin coated at 1000 rpm for 20 s on ITO substrates. After the spin coating, samples were subsequently annealed for 10 min at 110 °C to remove residual solvent molecules in the active layer and to improve the surface morphology. Finally, Ag electrodes were deposited by thermal evaporation technique to complete the diode structure. The final metal electrode contact area of 4 mm^2 was obtained by using the shadow mask. This experiment was repeated for three times different batches and the tested devices show the similar trend. Three batch of devices and 15 devices were tested.

OPV device structure is fabricated as follows. ITO substrate was cleaned using the previously mentioned procedure. PEDOT:PSS (Heraeus CLEVIOS Al 4083) was filtered using nylone filtered (pore size 0.45 μm) and spin coated over the UV-Ozone treated ITO. The photoactive layer was prepared by dissolving P3HT and PC$_{60}$BM in 1:0.9 ratio in O-dicholorobenzene. The mixture was kept under stirring overnight and filtered with 0.2 μm nylon filter prior to spin coat over the HTL layer. The spin coated photoactive layer was annealed at 140 °C for 10 min to remove the remaining residual trapped solvent and to homogenize the active layer morphology. All the device fabrication was carried out inside Jacomex Glove box and Angstrom thermal evaporator was used to deposit the electrodes. The devices are named as follows for easy identification Diode-L: ITO/P3HT/Ag-L, Diode-S: ITO/P3HT/Ag-S, SolarCell-L: ITO/PEDOT:PSS/P3HT:PC$_{60}$BM/Ag-L and SolarCell-S: ITO/PEDOT:PSS/P3HT:PC$_{60}$BM/Ag-S.

Electrode and P3HT layer thicknesses were measured by Vecco Dektak surface profilometer. The step height of the film was measured to calculate the thickness. Thermal analysis of Ag pellet and nanoparticle was carried out using NETZSCH STA 409 PC-Luxx system under nitrogen atmosphere condition. The X-ray diffraction (XRD) pattern of Ag electrode was recorded on a PANalytical diffractometer. Cu Kα (1.5406 Å) X-ray source was used for the diffraction study. Electrode and P3HT surface roughness were studied by Bruker-DIMENSION icon with ScanAsyst AFM. Scanning electron microscope (SEM) was used to explore the electrode surface morphology. Current-voltage and capacitance-voltage characteristics of the devices were investigated using Keithley 4200SCS. For the AM1.5 G (100 mW/cm^2) light generation Newport Oriel solar simulator Class AAA was used. The external quantum efficiency measurement was carried out using Enli-Tech QE measurement system, Taiwan. Devices were fabricated inside the nitrogen filled glove box cluster (Vec Solution India Pvt. Ltd, Jacomax, Innovative Technology and Angstrom Engineering).

3. Results and discussion

3.1. Diode properties

3.1.1. XRD structure analysis

Fig. 1(a) shows XRD diffraction pattern of Ag-L and Ag-S electrode on a glass substrate and inset illustrates (111) peak. The recorded diffraction pattern corresponding planes were indexed as peak at 38.101° (111), 44.60° (200), 64.678° (220) and 77.549° (311) respectively. The recorded XRD pattern indicate that (111) peak intensity is predominant in both Ag-L and Ag-S which is due to the lowest surface energy of the (111) plane in FCC structure. It is also observed that the peaks in both the spectra are predominant in (111) plane [13,14]. Calculated change in the FWHM among Ag-L (0.13) and Ag-S (0.29) samples is 0.16 which indicates a reduction in crystallite size. As crystallite size decreases, the possibility of incomplete destructive interference is high which leads to the diffraction condition in the wider 2θ range. Crystallite size of the as-deposited Ag thin film samples was extracted from line broadening of X-ray pattern using Scherrer's formula [15]. Calculated crystallite size is 29 ± 3 nm and 16 ± 3 nm for Ag-L and Ag-S respectively. Fig. 1(b) illustrates the modified Williamson-Hall (MWH) method for calculating the crystallite size of the sample after eliminating the micro-strain contribution for FWHM [16]. Furthermore, the crystallite size of the