Nanoimprinted large area heterojunction pentacene-C₆₀ photovoltaic device

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(Received 20 February 2007; accepted 24 May 2007; published online 18 June 2007)

A pentacene-C₆₀ bilayer heterojunction organic photovoltaic device with interpenetrating donor-acceptor interface was fabricated by nanoimprinting the pentacene layer prior to C₆₀ deposition. An amorphous silicon substrate nanostructured using an excimer laser was imprinted onto the pentacene layer at high temperature and pressure, using a nanoimprinting lithography system to form a textured pentacene surface. A fivefold improvement in power conversion efficiency was observed due to increased exciton dissociation at the large area heterojunction. Using the proposed technique, highly efficient bilayer large area heterojunction photovoltaics based on small molecule organic materials can be envisaged. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2749863]

Low power conversion efficiency (PCE) from solar irradiation to electricity is a fundamental drawback in the commercialization of organic photovoltaic devices (OPVs).¹ Recent reports indicate a progressive improvement of PCE in OPV devices in both bilayer and bulk heterojunction forms.^{2,3} However, these PCE values are inadequate for commercialization.⁴ Increase of PCE is inherently coupled with enhanced photon absorption for increased exciton generation and subsequent exciton dissociation efficiency gains to form free charge carriers. As described by Forrest, the absorption efficiency (η_A) and exciton dissociation efficiency (η_{ED}) are related to the absorption coefficient (α) and exciton diffusion length (L_D) of the photoactive material, respectively.⁵ These are expressed mathematically in Eqs. (1) and (2).

$$\eta_A = (1 - e^{-\alpha d}), \quad (1)$$

$$\eta_{ED} = e^{-d/L_D}. \quad (2)$$

Efforts of optimizing η_A by increasing device thickness (d) lead to a reduction of η_{ED} due to small L_D of organic materials. Typical L_D values are limited to less than 10 nm in polymers and up to 80 nm in small molecule organic materials.⁶ However, favorable aspects including high α ($\sim 10^5 \text{ cm}^{-1}$) and flexibility in solution based processing promote polymer based photovoltaics, by enabling the use of bulk heterojunction OPV structures minimizing limitations of lower L_D .⁷ A bulk heterojunction OPV consists of an interpenetrating donor-acceptor blend, localizing charge separating interfaces, and exciton generation sites in close proximity ($< L_D$). Small molecule organic material such as pentacene, which has shown greater charge mobilities than polymers,⁸ are not used in bulk heterojunction structured OPV due to material insolubility. OPVs with very high PCE can be envisaged using these small molecule organic materials if fabrication of hybrid bilayer-bulk heterojunction-type devices with donor-acceptor junction interpenetration is possible. This letter reports on a pentacene-C₆₀ OPV device fabricated with a nanostructured pentacene layer, forming an

interpenetrating fingerlike junction to improve exciton dissociation. Improvement in PCE of this device is compared with a pentacene-C₆₀ bilayer heterojunction cell fabricated under identical conditions without nanoimprinting.

Twice sublimed pentacene (99.99%) was purchased from H.W. Sands and C₆₀ (99.99%) was purchased from MER Corporation. All organic materials were used as received, without further purification. Devices were fabricated on indium tin oxide (ITO) coated (100 nm) glass substrates, cleaned using a three stage ultrasonic bath treatment in toluene, an aqueous surfactant solution, and acetone. Immediately prior to use, the ITO substrates were suspended in the vapor of refluxing acetone, followed by microwave oxygen plasma treatment. Discrete heterojunction OPVs were fabricated in a stratified method, commenced by sublimation of pentacene under vacuum (1×10^{-5} Torr) at a deposition rate of $\sim 0.1 \text{ nm s}^{-1}$ onto precleaned ITO substrates. Afterwards, the deposited pentacene layer was nanoimprinted using a nanoimprinting lithography (NIL) system (Obducat AB, Sweden).

The NIL system can be used to imprint features in the order of 10 nm on organic polymer or small molecule films. Two techniques exist for the creation of such small-scale patterns. One method uses heating of polymer coated substrates to reach the glass transition temperature of the polymer followed by stamping of a pattern using a hydraulically pressurized piston (maximum pressure of 70 bars) and subsequent cooling. An alternative method is to use a monomer which polymerizes on exposure to UV light, therefore allowing the imprinting to be carried out at ambient temperature.

The geometry of the surface modification attained through imprinting primarily depends on the properties of the stamp used for imprinting. Since L_D of pentacene is $65 \pm 16 \text{ nm}$,⁹ it is necessary to nanostructure the surface with features of the same order, and hence the features of the stamp. Laser nanostructuring of amorphous silicon is reported to result in surfaces with rms roughness in tens of nanometers.¹⁰ For this work, a laser nanostructured silicon film on a 0.7 mm thick glass substrate was used as the stamp.

A KrF Lambda Physik excimer laser (LPX 210i), operating at 248 nm with 25 ns full width at half maximum pulse duration, was used for nanostructuring of the 300 nm thick

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FIG. 1. (a) Film structure before nanoimprinting, (b) heating the pentacene deposited ITO substrates to 155 °C, (c) applying the imprinting pressure of 40 bars for 60 s at 155 °C, and (d) releasing the stamp at 100 °C and ambient pressure.

amorphous silicon film. A $4 \times 10 \text{ mm}^2$ pulse with an asymmetrical peak profile along the length and a constant energy along the width was scanned along the long direction over the sample. The steeper edge of the pulse was used deliberately as the leading edge to increase the surface roughness. The samples were irradiated in air, mounted on a translation stage for large area irradiation. A 0.2 mm overlap was maintained between the two scan lines resulting in a uniformly nanostructured $5 \times 5 \text{ cm}^2$ nanocrystalline silicon stamp. The scanning speed for the experiment was 2.5 mm s^{-1} with a pulse repetition rate of 20 Hz. The energy density used was 150 mJ cm^{-2} , with an error up to 10% due to pulse to pulse variations of the excimer laser.¹¹

As shown by Fig. 1, the nanoimprinting procedure was conducted by heating the pentacene film on ITO coated glass substrates (a) to 155 °C under 5 bar pressure (b), stamping the heated substrate at 40 bar pressure for 60 s (c), and allowing the substrate to cool down to 100 °C at which point the stamp is detached from the imprinted surface (d). The

acceptor material, 50 nm of C_{60} , was deposited on top of the nanoimprinted pentacene layer by vacuum sublimation at a deposition rate of $\sim 0.1 \text{ nm s}^{-1}$. Afterwards, Al backelectrodes to a 50 nm thickness were deposited at $\sim 0.5 \text{ nm s}^{-1}$ using a shadow mask without breaking vacuum to create devices with active areas of 7 mm^2 . Current density–voltage (*JV*) measurements were performed using 100 mW cm^{-2} AM1.5 simulated solar irradiation. Surface characterizations of the laser nanostructured stamp and imprinted organic surface were performed using a Digital Instruments Dimension 3100 atomic force microscope in tapping mode.

As shown by Fig. 2(b), laser nanostructured stamp resulted in an average rms roughness of 9 nm with average feature height of 23 nm. This was a ninefold increase in rms roughness compared to an as deposited pristine amorphous silicon film, which is less than a nanometer [Fig. 2(a)]. The typical full width at half maximum of an average surface protrusion of the stamp was estimated to be $\sim 65 \text{ nm}$ from the microscopic data, which is narrower than industrially available metal stamp features, which is desirable for pentacene- C_{60} device. An optimum temperature of 155 °C, well below the sublimation temperature of pentacene,¹² was selected for imprinting a 70 nm pentacene layer to avoid material degradation. Figure 2(d) shows a cross sectional atomic force micrograph of a postnanoimprinted pentacene layer, which shows an average height and rms roughness of 48 and 16 nm, respectively. The surface features of a 70 nm film of pristine pentacene, shown in Fig. 2(c), have an average height and rms roughness of 27 and 6 nm, respectively. The nanoimprinted pentacene film had significantly increased in rms roughness with approximately two fold increase in average feature height. The reference device was an ITO/pentacene (70 nm)/ C_{60} (70 nm)/Al cell, without the imprinting phase of the fabrication steps.

JV characteristics of both devices are shown by Fig. 3. The short circuit current density (J_{sc}) of the imprinted device ($0.48 \pm 0.02 \text{ mA cm}^{-2}$) showed a twofold increase compared

FIG. 2. Surface roughness profiles of (a) pristine *a*-Si substrate, (b) laser nanostructured *a*-Si substrate, and (c) pristine pentacene layer deposited on ITO and (d) nanoimprinted 70 nm pentacene layer obtained from atomic force microscopy.

FIG. 3. *JV* characteristics of nanoimprinted and reference ITO/pentacene (70 nm)/C₆₀ (70 nm)/Al (50 nm) devices.

to the J_{sc} of the reference device ($0.22 \pm 0.01 \text{ mA cm}^{-2}$). Also the open circuit voltage (V_{oc}) of the imprinted device ($0.3800 \pm 0.0003 \text{ V}$) is observed to be larger than the V_{oc} of the reference device ($0.2700 \pm 0.0003 \text{ V}$). The fill factor improves from $16.0 \pm 0.1\%$ of the reference cell to $27.0 \pm 0.1\%$ for the imprinted cell. PCE of the nanoimprinted device ($0.051 \pm 0.005\%$) showed a fivefold increase from the PCE of the reference device ($0.009 \pm 0.001\%$).

The increase of J_{sc} can be attributed to the increased exciton dissociation at the heterojunction, as a result of the increase in interfacial area through nanoimprinting of the active material. Also, nanoimprinting of the heterojunction can translate toward nanotexturing of the Al backcontact, thus improving the light trapping within the active layer which increases the exciton population contributing to an increased J_{sc} . While the origin of V_{oc} is controversial,^{13–15} it is generally accepted that the theoretical upper limit of V_{oc} is governed by the difference in potential between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor material in OPV devices. The nonalignment of the electrode work functions to the molecular HOMO and LUMO levels can induce a reduction of the V_{oc} values from this theoretical limit. The increase of V_{oc} in the nanoimprinted device, relative to the reference device, can possibly be attributed to the high temperature and pressure induced modification of the HOMO/LUMO energy levels of the imprinted pentacene layer and the ITO-pentacene interface. Even though the PCE of the imprinted device is greatly improved as compared to the reference device, it is lower than PCE of a pristine pentacene-C₆₀ device fabricated without a vacuum break.^{9,16}

Breaking vacuum after sublimation of the active organic material can cause atmospheric contamination of the heterojunction which reduces exciton dissociation, leading to the reduction of the J_{sc} in these devices. Hence, if this technique is further improved such that the nanoimprinting and device synthesis can be performed under a controlled atmosphere environment, it is possible to fabricate very highly efficient ($>7\%$) OPV devices based on pentacene-C₆₀ organic material system, which already have reported PCE of 1.5% measured at AM1.5.⁹

In conclusion, a pentacene-C₆₀ bilayer heterojunction organic photovoltaic device with an interpenetrating donor-acceptor interface was fabricated by nanoimprinting the pentacene layer. A laser nanostructured, silicon film on a glass substrate was used as the imprinting stamp to nanoimprint a 70 nm pentacene layer at high temperature and pressure using a nanoimprinting lithography system. A fivefold improvement in power conversion efficiency was observed, believed to be due to increased exciton dissociation at the nanoimprinted junction. Using the proposed technique, high efficient bilayer-bulk heterojunction hybrid photovoltaics based on small molecule organic materials can be envisaged in the future.

The authors wish to thank the EPSRC for a Portfolio Partnership award which has facilitated the research conducted in this project and the studentship awarded.

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