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Pulsed laser annealing of P3HT/PCBM organic solar cells

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1. Introduction

Organic photovoltaics have the potential of playing an important role as alternative energy sources because of their low cost, mechanical flexibility and easy solution processability. Recently, several research papers describe the state of the art fabrication and processing of polymer solar cells [1–5]. Krebs [1] has provided a review on fabrication and processing of polymer solar cells. Different coating methods such as casting, spin coating, doctor blading, screen printing, inkjet printing, pad printing and roll-to-roll techniques are described. For most organic solar cells, post-processing of organic thin films is required. Various post-processing techniques such as chemical processing, light processing (Ir, visible, UV or microwave) have been mentioned [1]. Ameri et al. [2] provided a review on organic tandem solar cells. Jorgensen et al. [3] provided a review on stability/degradation of polymer solar cells during illumination and dark. The paper also discusses various encapsulation techniques for the improvement of stability. Helgesen et al. [4] provided a review on advanced materials and processes for polymer solar cell devices and discussed the link between performance and processing.

To improve the efficiency of organic solar cells, specifically regio-regular poly(3-hexylthiophene) (P3HT) and 1-(3-methox-ycarbonyl)-propyl-phenyl- $(6,6)C_{61}$ (PCBM) polymer material system, many pre- and post-fabrication thermal treatments are necessary. These include solvent-vapor removal [6] and

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ABSTRACT

A pulsed laser heating method has been investigated as a thermal annealing process for the improvement of P3HT/PCBM organic solar cell performance. We have shown that pulsed laser annealing can be used as an alternative to hot-plate annealing and produces comparable photovoltaic properties in P3HT/PCBM organic solar cells. Performance improvements can be achieved by irradiating either the ITO or aluminum electrodes. The increases in efficiency with laser annealing are due to increases in short circuit current density. Also, we have shown that morphology changes induced by rapid laser heating and cooling are similar to slower hot-plate annealing.

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thermal annealing to achieve greater ordered structure for enhanced charge transport [7,8]. It is clear from many research groups that the pre- and post-fabrication thermal treatments are critical in obtaining high power conversion efficiencies in organic solar cells.

Traditionally, thermal annealing has been achieved via methods such as hot plates and furnaces [5,7], where most of the energy does not contribute to the annealing process. Recently microwave energy absorption has been explored for thermal treatment of organic thin films [9]. Laser processing continues to play an important role in silicon solar cell manufacturing processes [10]. Lasers provide a non-contact method of energy transfer in a controlled way and can be localized. In addition, the use of pulsed lasers allows for rapid heating and cooling. Gordon et al. [11] presented results on the use of near infrared laser (λ =830 nm) for direct thermal patterning of π -conjugated polymer. However, no work has been reported on the viability of laser treatments for organic solar cells.

In this paper, we describe the use of laser annealing as a means of improving the performance of P3HT/PCBM solar cells. The ability of laser techniques to isolate temperature sensitive substrate materials, anneal arbitrary geometrical shapes, potentially shorten annealing times and provide a non-contact means of annealing makes this method specially attractive to the industrial production of organic photovoltaic devices. Novel methods of post-annealing becomes even more important as a significant progress has been demonstrated in the fabrication of flexible rollto-roll processed devices [12–15]. Krebs et al. [12] discuss the concept of inverted model devices for roll-to-roll polymer solar cells made by solution processing. Krebs et al. [13] have made a first public demonstration on production of flexible large area

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polymer solar cells. In this paper, we present results of pulsed laser annealing of P3HT/PCBM organic solar cells and show that comparable results to those of furnace annealing can be achieved at relatively fast speed.

2. Experimental procedure

Devices used for this work were fabricated as follows: P3HT from Sigma Aldrich and PCBM from Nano-C Inc. in a weight ratio of 1:1 were dissolved in chlorobenzene for a concentration of 3wt% P3HT:PCBM solution and spin coated at 2500 rpm to obtain a film thickness of 100 nm. Poly(3,4-ethylenedioxythiophene):-poly(styrenesulfonate) (PEDOT:PSS) of solid content of 1.75% by weight was spun cast on ITO-coated glass obtained from Delta Inc. MN. The solution was spin coated at 4000 rpm to obtain a thickness of 40 nm. After annealing the PEDOT:PSS film for 15 min at 110 °C, the P3HT/PCBM solution was spun cast on the ITO glass. Aluminum thickness of 80 nm was deposited as a cathode using electron beam deposition. The active area of the device was $3 \times 5 \text{ mm}^2$ and the Al electrode was slightly larger.

Current density-voltage curves were measured using a Hewlett Packard 6113A DC power supply and a Fluke 8842A multimeter. Illumination was provided by a Thorlabs OSL1 fiber illuminator that was calibrated to produce 100 mW cm⁻² light intensity using a Coherent Model #201 power meter.

For the AFM images, a commercially available thermomicroscope explorer AFM from Veeco, Inc. was used. The AFM images were collected in tapping mode using silicon nitride tip probes with a spring constant of 2.8 N/m and a resonant frequency of 71.7 kHz. The tip radius of the probe was 25 nm.

For laser annealing, a 1064 nm pulsed laser from IPG Photonics Inc. was used. The pulse duration was 50 ns with a 30 kHz repetition rate. The laser spot at the device was 2.6 mm. The active area of the device $(3 \times 5 \text{ mm}^2)$ was laser treated by scanning the sample using a x-y stage operating at the velocity of 1.25 mm/s. For the laser heating of ITO, 18×10^6 pulses were provided to a device area of $3 \times 5 \text{ mm}^2$, while 7.2×10^6 pulses were supplied to a same sized area for the laser heating of aluminum. We estimated the maximum rise in temperature as 250 °C assuming no heat loss during laser heating time.

3. Results and discussion

The solar cell device structure and directions of laser treatment used in this study are shown in Fig. 1. The active layer was annealed by utilizing the absorption of 1064 nm laser wavelength by ITO [16] and aluminum [17]. The laser heating of



Fig. 1. Schematic of organic solar cell device showing laser annealing of ITO and aluminum.



Fig. 2. Dependence of (a) efficiency, (b) short circuit current density (J_{SC}), (c) open circuit voltage (V_{OC}) and (d) fill factor (FF) on laser energy density. A laser of wavelength 1064 nm was incident from the glass side (absorption by ITO).

ITO (solid arrow) and of aluminum (short dash arrow) is shown in Fig. 1.

When laser light of wavelength 1064 nm is incident from the glass side, ITO absorbs the light and generates a rise in temperature. Fig. 2(a) shows the dependence of cell efficiency (η) on laser energy density incident from the glass side.

Below a threshold laser energy density of 3.8×10^4 mJ m⁻², no improvements in efficiency is observed. Above this threshold,

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