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# Surface relief gratings on poly(3-hexylthiophene) and fullerene blends for efficient organic solar cells

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The use of periodic submicrometer structures as an efficient light-trapping scheme was investigated for high performance organic solar cells (OSCs) based on poly(3-hexylthiophene) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)$C_{61}$. The gratings on an active layer are achieved by a soft lithographic approach using photoinduced surface-relief gratings (SRGs) on azo polymer films and poly(dimethylsiloxane) as a master and stamp, respectively. Incident photon to current conversion efficiency and the power conversion efficiency of OSC with gratings increased primarily due to enhanced short circuit current density, indicating that SRGs induce further photon absorption in active layers by increasing the optical path length and light trapping. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2802561]

Conjugated polymer based organic solar cells (OSCs) as cost efficient and flexible power sources have undergone considerable development.[1–8] Among the available polymer solar cell systems, poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)$C_{61}$ (PCBM) networks produced by spin coating have efficiencies of up to 4–5%; however, further improvement in efficiency is required for practical applications.[7,8]

One limiting factor to the efficiency of P3HT and PCBM based bulk-heterojunction (BHJ) solar cells is weak absorbance of the photoactive layer. To overcome this problem, the thickness of the active layer must be increased to absorb more incident light. However, a thick active layer increases the series resistance of the device due to the limited charge carrier mobility of the conjugated polymers, inevitably leading to a reduced fill factor.[8] An alternative approach to improve light absorption without increasing the thickness of the photoactive layer is to enhance the optical path length by trapping light strongly in the active layer. Periodic structures for light trapping have been used extensively to enhance absorption in silicon solar cells, thereby increasing the power conversion efficiency.[9–11] However, until very recently, only a few approaches for trapping light in OSCs or photodiodes have been reported[12–15] and to date, trapping light in P3HT/PCBM based OSCs has not been implemented.

In this letter, an attempt was made to enhance the light absorption and the power conversion efficiency ($\eta$) of OSCs by forming surface relief gratings (SRGs) on P3HT/PCBM based active layers using a soft lithographic technique, combined soft-embossing,[12] and photoresponsive azo polymers[16,17] as a master. In contrast with photolithographic processes, the approach used in this study is a damage-free process for patterning polymers. Furthermore, the use of azo polymers as a master has several advantages such as a one-step process, feasible duplication, controllability of the grating profiles, capability of superimposing multiple patterns, and ease of fabrication.[16–20]

The fabrication of elastomeric molds with SRGs using azo polymer films is presented schematically in Fig. 1(a). To prepare a master, SRGs on poly (disperse orange 3) (PDO3) (Ref. 21) were formed by exposure to an interference pattern of $Ar^+$ laser beams (488 nm, 100 $mW/cm^2$). Then the polysiloxane prepolymer, prepared by mixing an elastomer base and curing agent (Sylgard 184, Dow Corning) in a ratio of 10:1 (wt/wt), was poured onto the azo masters with SRGs followed by curing at 60 °C. Finally the PDMS mold was separated from the master and was used as a stamp for soft contact printing. Preparation of the PDMS mold with SRGs,

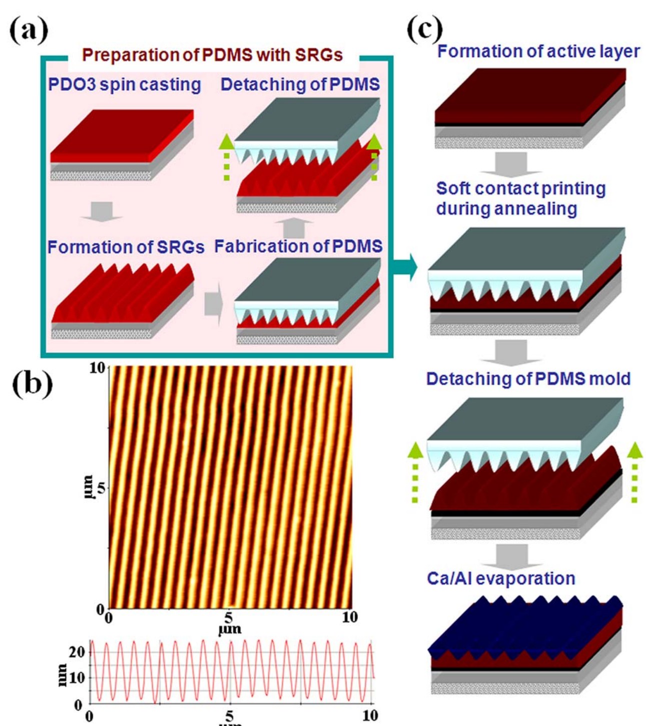


FIG. 1. (Color online) (a) Schematic process flow of the fabrication of azo polymer films and elastomeric molds with SRGs. (b) AFM image of the PDMS mold with SRGs. (c) Schematic process flow for the fabrication sequence for bulk heterojunction solar cells with SRGs.

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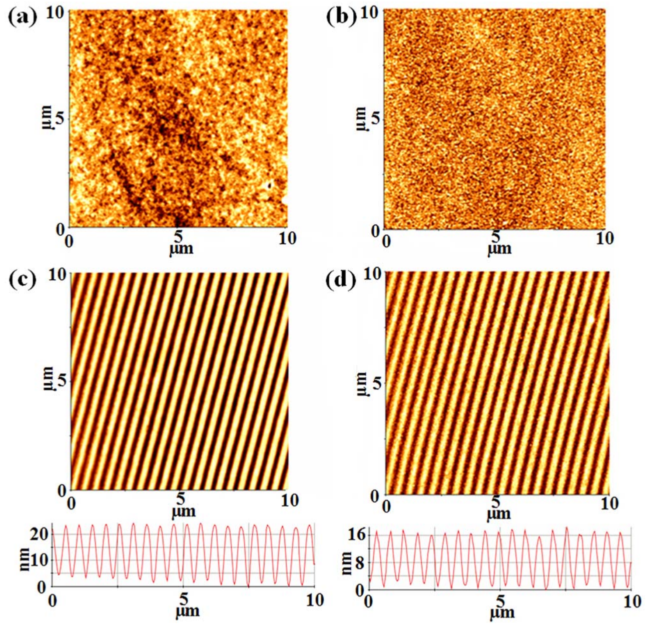


FIG. 2. (Color online) AFM images: (a) the flat active layer of the reference cell, (b) the reflective cathodes of the reference cell, (c) the active layer patterned via soft contact printing, and (d) the reflective cathodes evaporated onto the patterned active layer.

with a period of 500 nm and height of 20 nm, was confirmed by atomic force microscopy (AFM), as shown in Fig. 1(b). The sequence for fabricating BHJ solar cells with SRGs is illustrated in Fig. 1(c). Glass substrates coated with indium tin oxide (ITO) (Samsung Corning Co, Ltd.) having a sheet resistance of $\sim 10\Omega/\text{sq}$ were cleaned and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) (Baytron P VPAI 4083) was spin coated onto the ITO, with a thickness of ~20 nm. A solution of 30 mg of P3HT (Rieke Metals) and 24 mg of PCBM (Nano-C) in 2 ml of chlorobenzene was then spin coated on top of the PEDOT:PSS layer, forming the active layer with a thickness of ~80 nm. To pattern the active layer, the PDMS mold with replicated SRGs was put in conformal contact with the active layer and kept for 20 min in nitrogen during annealing process performed at 110 °C to enhance the degree of P3HT ordering.[3] After peeling off PDMS mold, calcium (20 nm) and aluminum (100 nm) were thermally evaporated in a vacuum at $10^{-6}$ torr.

As shown in Figs. 2(a) and 2(b), the active layer and metal cathode of conventional OSCs show typical surfaces with rms roughnesses of ~0.78 and ~1.7 nm, respectively. Formation of SRGs on the P3HT/PCBM active layer with the same grating period and height of 500 and 20 nm as the PDMS mold was confirmed by the AFM image shown in Fig. 2(c). In addition, the period, height, and shape of the reflective cathode that was evaporated onto the patterned active layer were nearly identical to those of the patterned active layer, as shown in Fig. 2(d).

Due to the periodic grating on the active layer and cathode, incident light reaching at the backside grating can be diffracted backward according to the following equation:

$$m\lambda = n_{\text{active}} p(\sin\theta_i + \sin\theta_d), \tag{1}$$

where $m$ is the diffraction order, $\lambda$ is the wavelength of incident light, $n_{\text{active}}$ is the refractive index of the active film, $p$ is the period of grating, and $\theta_i$ and $\theta_d$ are the incidence and diffraction angles, respectively. A constant $n_{\text{active}}$ was considered as 2 in the spectral wavelength range between 300 and 700 nm for simplification.[22,23] Then, in the case of normal incidence, for $300\text{ nm} \leq \lambda \leq 500\text{ nm}$ and for $500\text{ nm} < \lambda \leq 700\text{ nm}$, $m$ can take values of 0, ±1, and ±2 and values of 0 and ±1, respectively, because $\sin\theta_d \leq 1$ and $p = 500$ nm in our study. Because the zeroth order reflection is reduced by grating structures, the diffraction occurs and the diffracted light at high orders can be bent by 90°; therefore, the optical path length is increased considerably.

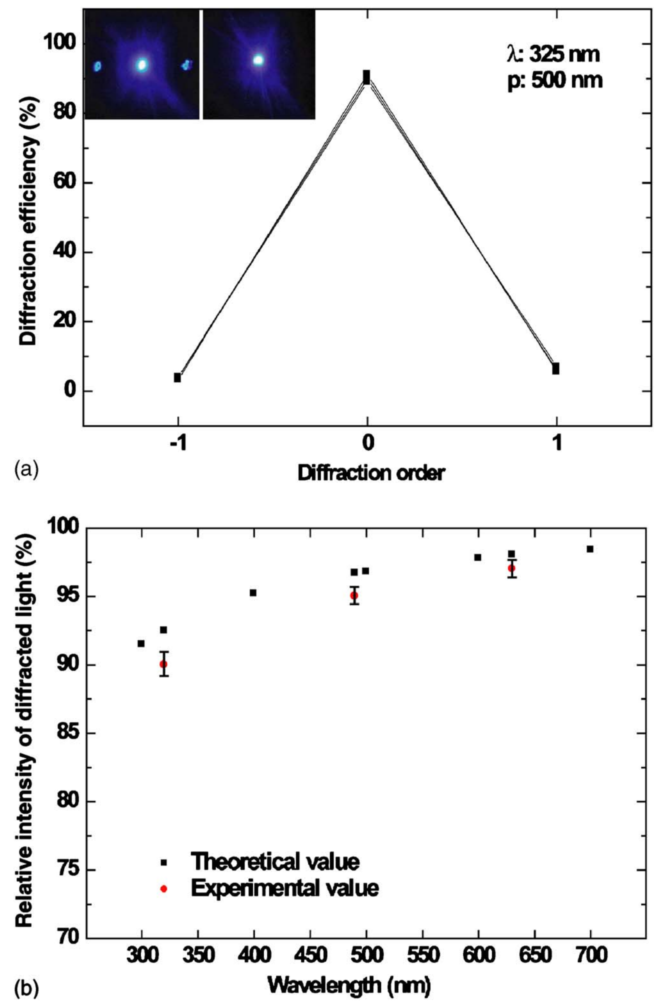


FIG. 3. (Color online) (a) diffraction efficiency at 500 nm grating under $\lambda = 325$ nm illumination; the sum of all diffraction orders is set to 100%. Insets: photographic images of diffracted light in cells with and without SRGs. (b) Diffraction efficiency as a function of wavelength. Intensity of diffracted light is normalized to the cell without grating.

To quantitatively demonstrate the light-bending resulting from SRGs shown in Fig. 2, the diffraction efficiency at each diffraction order (at $\lambda = 325$ nm) and the diffraction efficiency as a function of wavelength (at $\lambda = 325$, 488, and 632 nm) were measured, as shown in Figs. 3(a) and 3(b), respectively. HeCd, $Ar^+$, and HeNe lasers with $\lambda = 325$, 488, and 632 nm, respectively, were used to illuminate the OSC with SRGs, and the light intensities of each diffraction order were measured using a Si photodiode. Figure 3(a) shows that only the 0th and ±1st diffraction orders occur when $\lambda = 325$ nm and $p = 500$ nm and the insets of Fig. 3(a) present images of the diffracted light in two cells with and without SRGs. Figure 3(b) shows that the experimentally measured diffraction efficiency in the $\lambda$ region between 300 and

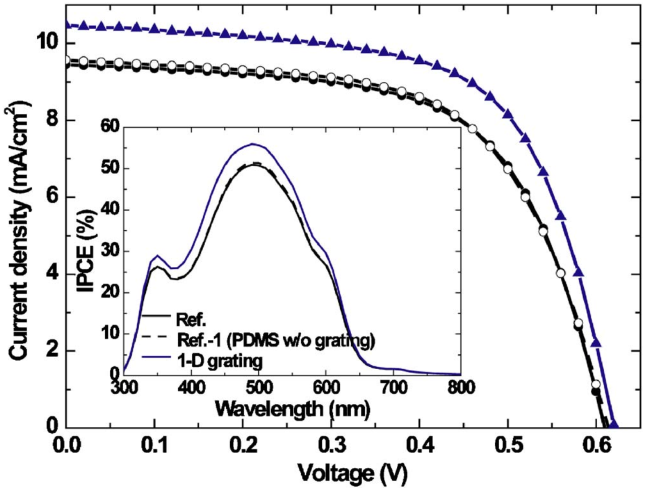


FIG. 4. (Color online) $J$-$V$ characteristics for three kinds of solar cells: a reference cell (closed circles), a second reference cell treated with the PDMS mold and without SRGs (open circles), and a patterned cell by the PDMS mold with SRGs (closed triangles). Inset: IPCE spectra for the three cells.

700 nm corresponds well with theoretical values.[24] Based on these results, it is clear that an increase in the optical path by diffraction of light could be achieved in a broad range, especially important wavelength region for the P3HT/PCBM based OSCs.

To investigate the effect of grating on the performance of OSCs, photocurrent density-voltage ($J$-$V$) curves and incident photon to current conversion efficiency (IPCE) were measured and are shown in Fig. 4. Here, three kinds of solar cells were fabricated as follows: a reference cell without any pattern treatment, a second reference cell treated with a plain PDMS mold without SRGs, and a patterned cell formed using the PDMS mold with SRGs. As demonstrated in Fig. 4, the performance characteristics of the two reference cells were similar under 1 sun with air mass 1.5 Global illumination as follows: an open circuit voltage ($V_{oc}$) of 0.61 V, short circuit current densities ($J_{sc}$) of 9.45 and 9.57 mA/cm$^2$, fill-factors (FF) of 62% and 61%, and $\eta$ of 3.56% and 3.58%. These results indicate that the used soft lithographic method does not damage on the active polymer layer. In contrast, the cell with SRGs exhibited $V_{oc}$ of 0.62 V, $J_{sc}$ of 10.5 mA/cm$^2$, FF of 63%, and $\eta$ of 4.11%. Here, most of the increase in the cell efficiency was from the increased $J_{sc}$ through the application of periodic structures rather than $V_{oc}$ or FF. This observation is in agreement with the IPCE measurement. It means that SRGs induce more photogenerated charge carriers by stronger absorption of an active layer, resulting from the increase of optical pass length and light trapping.

In conclusion, SRGs as a efficient light-trapping scheme were investigated for high performance OSCs based on P3HT/PCBM. The effects of grating on the optical path length were investigated by optical and electrical characterizations of the cells. Periodic structures were applied via a damage-free soft lithographic approach using photoresponsive azo polymers and PDMS as masters and as stamps, respectively. The device with SRGs demonstrated improved performance, resulting from the enhancement of $J_{sc}$, indicating that periodic structures such as SRGs enable further photon absorption in the active layer.

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