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The Effects of Processing Conditions on Polymer Photovoltaic Device Performance

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ABSTRACT

We will discuss recent results for the NREL polymer photovoltaics group. The work reported here explores the impact of polymer morphology on the physics and performance of polymer-based photovoltaic devices. By varying both the annealing temperatures and the solvent used for polym er deposition, we can alter the polymer chain morphology, thus shifting the absorption onset and shape and improving the charge transport properties of the resulting devices. The higher degree of order in the films results in increased photovoltaic performance.

1. Introduction

During the last decade, semiconducting polymers have been rapidly developing as a novel class of optoelectronic materials with applications including both light-emitting diodes (OLEDs) and photovoltaics. This is motivated in large part by their promise of low cost, low-toxicity manufacturing methods, tunable optical properties, and the possibility of lightweight, flexible large area panels. Although the two devices are fundamentally opposite (electricity in and light out for OLEDs and light in and electricity out for photovoltaics) many of the material and scientific issues for these devices are the same and as such, knowledge gained in one field is synergistic with the other.

2. Polymer - Small Molecule Organic Composite Devices

One of our primary focuses has been the use of polymer - small molecule organic heterojuntion devices to probe key aspects of photovoltaic performance. The polymer - small molecule heterojunction interface exhibits high exciton dissociation efficiency, leading to power conversion efficiencies that are greater than cells constructed from either component alone. [1] Typically, electron conducting perylene benzimidazole (PBI) (Figure 1b) films are thermally evaporated to a thickness of 20 nm. The hole conducting polymer, regioregular poly(3-hexylthiophene) (P3HT) (Figure 1a), is then spin cast from an 8 g/l solution in either chloroform or chlorobenzene to create films of 35 nm thickness. P3HT has been chosen both for its increased absorption spectrum (absorption is extended up to 650 nm, whereas the commonly used PPV-based polymer absorption cuts off at 600 nm) as well as its tendency to form more ordered polymer chain film morphologies, with corresponding improvements in charge transport properties. These photoactive layers are sandwiched between patterned indium tin oxide (ITO) and gold electrodes. Here we report on the effects of processing conditions such as solvent choice and annealing temperature on the polymer film morphology. Power conversion efficiencies of 0.47% have been achieved for these planar devices, with open-circuit voltage of V_{oc} = -0.33 V, short-circuit current density of J_{sc} = 4 mA/cm^2 and a fill factor of ff = 35% at one-sun incident light. In comparison to similar devices using the polymer M3EH-PPV [1] in place of P3HT, the polythiophene devices exhibit higher short-circuit current, though the fill factor and especially the open-circuit voltage are reduced. Experiments to determine and hopefully circumvent the reduction in photovoltage are currently underway.

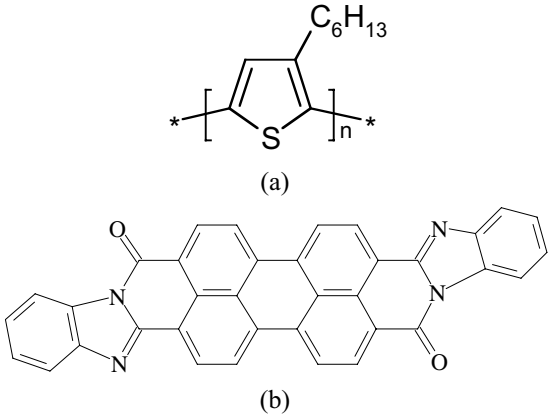

Fig 1. Chemical structures of (a) regioregular P3HT and (b) PBI.

3. Effects of Polymer Annealing Temperature

The degree of order in polymer films can have a drastic effect on both absorption properties and charge transport. Regiorandom P3HT, for example, differs from the regioregular material only by the random variation of the C_6H_{13} side groups from position 3 to position 4 on the thiophene ring, whereas the position is fixed at 3 for the regioregular material. This has a drastic effect on the absorption: the absorption peak for the regioregular material is shifted to lower energies and shows more vibronic structure, all indicative of a higher degree of polymer chain ordering. It has also been demonstrated that the regiorandom material excitations consist primarily of intra-chain excitons, whereas the regioregular material has a larger inter-chain component. [2]

We have demonstrated that the polymer chain morphology can be further influenced through both the film annealing temperature and the choice of solvent for the polymer depositon. Figure 2 compares the absorption spectra of various regioregular P3HT films as a function of annealing temperature. As the annealing temperature is increased

from no annealing (ambient room temperature) to 155°C and finally to 240°C, the strength of the peaks at both 550 nm and 600 nm increases. This indicates an increasing degree of ordering of the polymer chains in the film. [3]

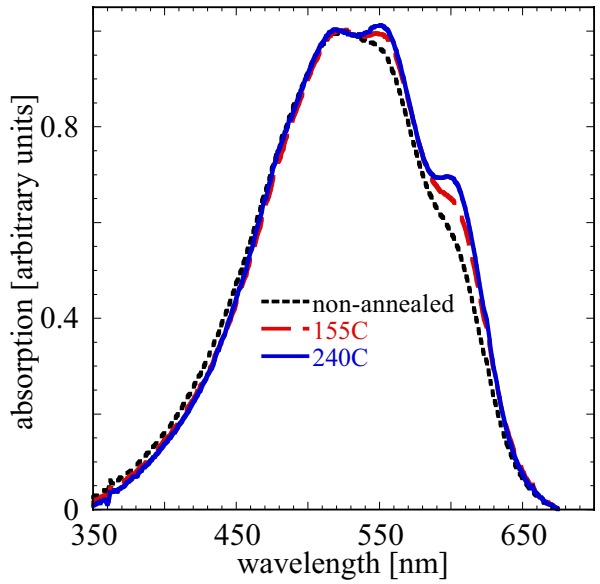

Fig 2. Absorption spectra for non-annealed (dotted black), 155°C annealed (dashed red) and 240°C annealed (solid blue) P3HT films. Absorption is normalized at the 522 nm peak for comparison purposes.

Figure 3 shows device performance for non-annealed and 240°C annealed photovoltaic devices of the type ITO/PBI/P3HT/Au. Short-circuit current density, open-circuit voltage, and fill factor are all increased for the higher temperature annealed device, leading to an improvement of power conversion efficiency going from $\eta = 0.19\%$ for the non-annealed device to $\eta = 0.47\%$ for the 240°C annealed sample. Annealing takes place prior to Au deposition.

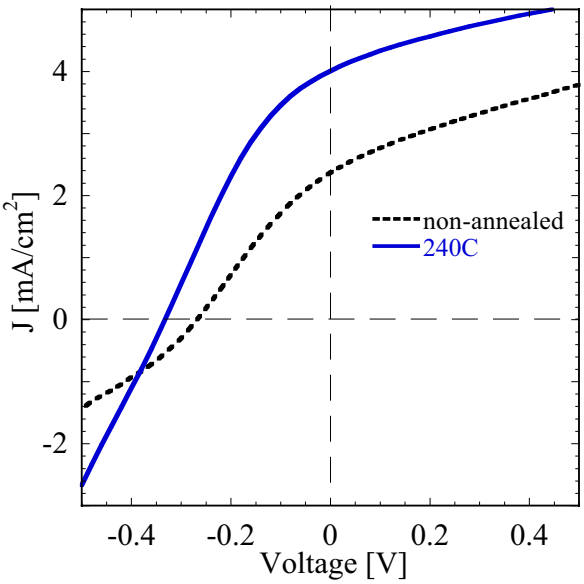

Fig 3. Current density - voltage characteristics for non-annealed (dotted black) and 240°C annealed (solid blue) devices.

4. Effects of Polymer Solvent

The film morphology is also noticeably affected by the choice of organic solvent used for the polymer deposition. Figure 4 shows absorption spectra for films spin-cast from chloroform and chlorobenzene solvents; both solutions are 8 g/l concentration. The strength of the lowest wavelength peak is decreased with a corresponding increase in the strength of the two higher wavelength absorption peaks. These spectral changes are similar to those observed in the annealing experiments, indicating the same type of increased order is occurring. In addition, the two lower wavelength peaks are shifted about 10 nm higher going from the chloroform to the chlorobenzene sample. We conclude that chlorobenzene promotes a higher degree of ordering in P3HT films than chloroform. Experiments comparing the photovoltaic performance of chlorobenzene to chloroform devices are currently underway.

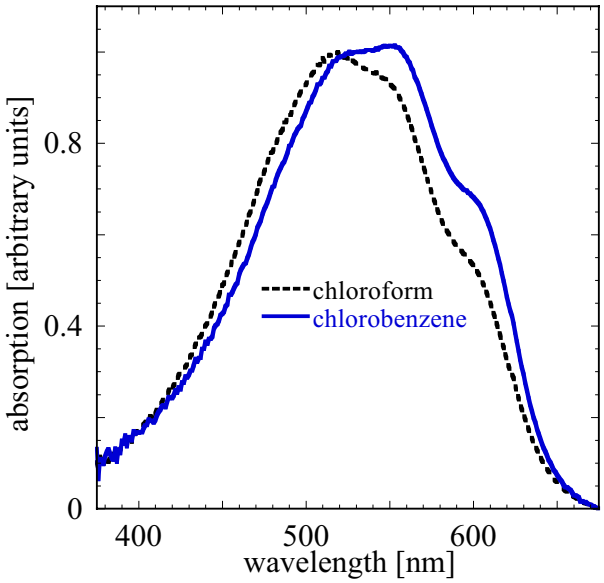

Fig 4. Absorption spectra for P3HT films spin-cast from chloroform (dotted black) and chlorobenzene (solid blue) solvents and annealed at 120°C. Spectra are normalized at the peaks of 519 nm and 529 nm, respectively.

5. Conclusion

We have shown that processing conditions strongly effect the morphology of polymer films, controlling the degree of polymer chain ordering and giving improved photovoltaic performance in organic-based solar cells.

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