Ying Liu, Michelle D. Casper, Arif O. Gozen, Sharvil Desai, Ethan Klem, Jay Lewis, Jon-Paul Maria, Michael D. Dickey, and Jan Genzer*

**Buckled Topography to Enhance Light Absorption in Thin Film Organic Photovoltaics Comprising CuPc/C$_{60}$ Bilayer Laminates**

**Abstract:** Organic photovoltaic (OPVs) devices are promising due to their low cost, light weight, and compatibility with high throughput processing on flexible substrates. This paper demonstrates a simple process utilizing thin-film instabilities to enhance light absorption in OPVs in a way that is compatible with planar processing and the customary thermal annealing steps. Placing a thin, transparent polystyrene (PS) film between the glass substrate and the transparent conductive indium tin oxide (ITO) electrode results in the formation of periodic surface buckles in the PS layer due to induced strain caused by thermal expansion mismatch between the ITO and PS films. OPVs comprising bilayer laminates of copper phthalocyanine (CuPc) and fullerene (C$_{60}$) deposited onto buckled the ITO/PS substrate show enhanced light absorption due to the longer path-length and improved power conversion efficiency (20%) relative to a similar planar device. This approach is appealing because it takes advantage of naturally-occurring surface topography (i.e., buckling) without the need for any sophisticated patterning. This work is distinguished from other buckling strategies for OPVs by the use of ITO as a transparent, conductive electrode and the absence of additional processing steps.

*Corresponding author: Jan Genzer, Department of Chemical and Biomolecular Engineering, NC State University, Raleigh, NC 27695-7905, USA, e-mail: jan_genzer@ncsu.edu
Ying Liu, Sharvil Desai, Michael D. Dickey: Department of Chemical and Biomolecular Engineering, NC State University, Raleigh, NC 27695-7905, USA
Michelle D. Casper: Department of Materials Science and Engineering, NC State University, Raleigh, NC 27695-7901, USA
Ethan Klem, Jay Lewis: RTI International Research Triangle Park, NC 27709-2194, USA
Arif O. Gozen, Jon-Paul Maria: Department of Chemical and Biomolecular Engineering, NC State University, Raleigh, NC 27695-7905, USA; and Department of Materials Science and Engineering, NC State University, Raleigh, NC 27695-7901, USA
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1 Introduction

This paper describes the use of buckling instabilities to produce topographical surface patterns that enhance light harvesting in organic photovoltaics (OPVs). OPVs, including polymer-based and small molecule-based OPVs, are subject to an engineering tradeoff between efficient light harvesting (favored by thick films) and efficient charge transport (favored by thin films) [1–6]. We address this limitation by introducing surface topography that increases the optical path length and thereby increases the number of photoelectrons generated per incident photon relative to an OPV of identical thickness on a flat surface. Topography originating from buckling instabilities is appealing because it does not require the use of expensive lithographic processes. In this paper we describe the fabrication of such buckled OPVs and characterize their photovoltaic and optical properties.

OPVs represent a promising class of PVs due to their low manufacturing budget compared to their inorganic counterparts and their compatibility with flexible substrates [7–9]. OPVs may be fabricated using simple deposition techniques, i.e., spray coating, spin casting, screen printing, or roll-to-roll transfer [10]. Moreover, the optical, mechanical, and electrical properties of OPV devices may be tuned on a molecular level via organic synthesis. Planar OPVs have recently surpassed ≈ 10% power conversion efficiency [11–21] and reached ≈ 12% efficiency with tandem cells [22].

An ideal PV device should absorb all the incident photons and efficiently separate holes and electrons to opposing electrodes. While the absorption of photons can be increased by increasing the thickness of the organic layer beyond a certain thickness (≈ 100 nm for typical organic semiconductors) [23], the efficiency decreases primarily due to the low carrier mobility in the organic layer [5]. Thin film OPVs favor efficient charge separation in the active layer because they provide short, unimpeded conductivity paths, minimal space charge accumulation, series resistance, and charge recombination [2, 5, 24]. Consequently, thinner films offer improved operating voltage, better fill factor, and higher power conversion efficiency [6]. Here we seek to increase the number of photons absorbed by these thin films using a topographically-corrugated surface featuring sinusoidal buckles.
Topography can enhance light harvesting via small surface features that induce scattering or via large-scale structures that funnel light. Macro-scale optical funneling has been demonstrated previously by folding planar OPVs into a “v-shape”; however, these geometries occupy a large volume [25–27]. Scattering structures are comparable in size to the active layer thickness (typically 50 ∼ 300 nm) in OPVs thus low-cost fabrication is challenging [28, 29]. Light harvesting/funneling structures have been formed by casting polymers over topographic molds. However, there are practical challenges to fabricating defect-free devices on such undulating surfaces [30]. While other types of optical traps (e.g., microlenses, surface plasmon structures) have also been employed, their implementation requires complex processing, and the efficiency improvements are modest in the context of the fabrication investment to prepare them [28, 29, 31–37]. Tuning OPV topography is possible with lithographic and imprint techniques; however, such approaches present a departure from the low-cost manufacturing motivation [38–40]. Regardless, the use of lithographically defined structures helps to improve light harvesting [41]. Previous experiments showed that OPVs incorporating lateral scattering features with a 2 μm pitch and an aspect ratio (i.e., ratio of amplitude to wavelength of the features) of 0.3 doubled light absorption in a substantial fraction of the visible spectrum and produced ≈ 20% increase in conversion efficiency when compared to a flat reference device. Furthermore, simulated thin layer solar cells with periodic surface textures spanning a range of characteristic lengths and feature heights confirm the that topography can influence dramatically the ability to harvest photons and improve photovoltaic performance [41].

Here we demonstrate that preparing OPV devices on substrates featuring topographical buckles can enhance light harvesting and leads to higher device efficiency. This approach is simple and compatible with low-cost, planar processing techniques. Ultimately, the method converts a conventional nuisance of thin film multilayers (i.e., buckling instability) into an opportunity for engineered light management.

Periodic surface buckles are generated by compressing a thin rigid film (i.e., metals, oxides or oxide-like layers) attached to a thick elastic substrate (i.e., elastomers, hydrogels, or thermoplastics). In the present work, stresses that induce buckling instabilities arise from thermal expansion coefficient mismatch between the rigid (indium tin oxide, ITO) and deformable (polystyrene, PS) layers [42–50]. Figure 1 depicts the basic mechanism. We use PS as the base material because it is inexpensive, transparent, easy to process, and has been studied previously in the formation of buckles [47]. While other groups employed buckles to engineer light harvesting [51, 52], they have done so with the expense of additional steps to the process flow. The present method is compatible with planar processing techniques for OPV fabrication. Below we describe the fabrication and charac-
Figure 1: a) Schematic depiction of thin film instabilities used to fabricate an OPV. Sputtering deposits a thin rigid ITO layer on a PS film supported by a glass slide. An OPV is built upon the buckled ITO/PS/glass substrate by depositing the “active” layer of organic molecules capped by an electrode made of aluminum, Al. b) Close-up diagram of buckled topography to increase light absorption pathways.

terization of buckled organic photovoltaics and measure the optical properties of these substrates.

2 Results and discussion

Planar and buckled OPVs were prepared on commercially available ITO/glass and on ITO/PS/glass substrates, respectively. The ITO and PS layers were deposited by RF magnetron sputtering and spin coating, respectively. The as-deposited ITO on PS/glass substrate is amorphous (cf. Figure 2) and thus possesses low conductivity. Crystalline ITO provides better transparency and conductivity, but it can only be formed by annealing at elevated temperatures (∼ 350 °C) that would thermally degrade the PS [53, 54]. Following optimization of deposition conditions for ITO, we obtained as-deposited ITO films with average optical transmission comparable to commercial ITO between 400 and 650 nm (the absorption range for the active layer). The full transmission spectra of as-deposited ITO films as a function of thicknesses on glass substrates are shown in Figure S1 in Supporting Information. As expected, thicker films are more electrically conductive, but less transparent to light than thinner films. Table 1 compares the optical and electrical properties of the two types of ITO with 280 nm thickness. Measurements by atomic force microscopy indicate that all of the ITO thin films have similar RMS surface roughness, as listed in Table 1.
Buckled Topography to Enhance Light Absorption

Figure 2: X-ray diffraction (XRD) spectra collected from amorphous as-sputtered ITO (red) and crystalline commercial ITO (black). The as-sputtered films are not crystalline, as expected.

Table 1: Transmission, sheet resistance, resistivity and roughness of as-deposited ITO (280 nm thick) and commercial ITO (280 nm thick, purchased from Thin Film Devices Inc.).

<table>
<thead>
<tr>
<th>ITO type</th>
<th>Transmission a (%)</th>
<th>Sheet resistance (Ω cm)</th>
<th>Resistivity (Ω cm)</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>77</td>
<td>30 ∼ 50</td>
<td>8.4 ∼ 14.0 × 10^{-4}</td>
<td>0.3</td>
</tr>
<tr>
<td>Commercial</td>
<td>83</td>
<td>8 ∼ 10</td>
<td>2.2 ∼ 2.8 × 10^{-4}</td>
<td>1.5</td>
</tr>
</tbody>
</table>

a Wavelength range of 400 ∼ 650 nm.

Next we studied the formation of a buckled topography on the ITO/PS/glass substrate to enhance the light absorption in our device. A buckled substrate featuring a PS (1.6 μm)/ITO (200 nm) bilayer provided a sensible compromise where the buckles are large enough for strong interactions with visible light, and yet not so large as to cause cracking in the ITO. Furthermore, the ITO is sufficiently thick to avoid concerns of large series resistance.

Figure 3a shows a profilometry scan of a representative buckled substrate exhibiting buckles that are oriented randomly in-plane. Their ability to interact with visible light is demonstrated in Figure 3b, which shows diffraction of a red laser light transmitted though the buckled surface. This grating effect is of critical importance since it is a known mechanism for concentrating energy in the active layer [35, 39, 55, 56].

Although polymer based OPVs, e.g., the well-established system of poly-3-hexylthiophene (P3HT) and phenyl-C_{61}-butyric acid methyl ester (PCBM), are
widely studied, the molecular weight and purity of the polymers are difficult to control. Moreover, the solution-based film coating can be incompatible with other film materials in the device. Small molecule-based OPVs provide a clean fabrication environment using compatible vacuum deposition processes. [21, 57]

We chose a bilayer laminate of small molecules featuring copper phthalocyanine (CuPc) and fullerene (C$_{60}$) because of their ease of processing and reproducibility [58–60] A bilayer laminate of CuPc and C$_{60}$ was prepared on flat and buckled ITO surfaces; the entire prototype solar cell stack comprised Ag/Al/C$_{60}$/CuPc/ITO(200 nm)/PS(1.6 μm)/glass. Samples were prepared with and without buckles. The buckles were produced by annealing ITO/PS films resting on glass at 120 °C for 30 min. The buckles had a characteristic wavelength of ≈ 14 μm and exhibit an aspect ratio of 0.06.

An integrating sphere was employed to measure the spectral reflectivity in both sample types to determine the impact of buckles on optical properties. Samples were illuminated from the substrate (i.e., glass) side and reflected off of the Al side, thus light traversed the film stack at least twice. This path is similar to that taken by light during normal operation of OPVs. Control samples were measured to ensure that the PS layer has minimal effect on reflectance. Figure 4 shows the spectra for buckled and planar devices, indicating that a buckled topography enhances light absorption. The absorbance peaks characteristic of C$_{60}$ and CuPc are expected in the range of 400 ∼ 540 nm and 550 ∼ 800 nm, respectively [60]. The average light absorption is enhanced ≈ 10% over the entire visible range, while the average light absorption in the range of 500 ∼ 600 nm and 700 ∼ 800 nm is enhanced by 15% and 12%, respectively. The maximum enhancement (i.e., increase of absorption relative to the absorption of planar OPV) reaches ≈ 20% at ≈ 550 nm and ≈ 800 nm. It is possible that the incident light may also be guided in the active layer given that the refractive index of CuPc and C$_{60}$ is larger than that of PS [41, 52]. The increase in absorbance in the visible range is similar to that observed by other
Figure 4: Light absorption relative to Al reference for planar and buckled Ag/Al/CuPc/C₆₀/ITO/PS/glass films. The increased percentage of absorption in buckled films relative to planar films is also shown as “enhancement”.

Figure 5: a) The dark and illuminated $I-V$ curves for both planar and buckled devices. Planar device: $V_{oc} = 0.46$ V; $J_{sc} = 6.08$ mA/cm$^2$; PCE = 1.59%; FF = 0.57, and buckled device: $V_{oc} = 0.45$ V; $J_{sc} = 10.04$ mA/cm$^2$; PCE = 1.92%; FF = 0.42; b) Comparison of average open-circuit voltage, $V_{oc}$ (V), short-circuit current density, $J_{sc}$ (mA/cm$^2$), fill factor, FF and efficiency, PCE (%) based on 7 planar devices and 4 buckled devices. Error bars represent the standard deviation of uncertainty.
groups who created periodic topography using wrinkling and folds [52], grating structures [41, 61], and imprint lithography [39, 40].

Figure 5a shows the current–voltage ($I-V$) curves for our best devices where the only difference is the presence of buckles. There is a 20% increase in PCE for the buckled device relative to the device prepared in flat geometry. While there is a 65% increase in current density with buckles, it is accompanied by a 25% decrease in fill factor (FF). Furthermore, the slope in $I-V$ at $\approx 0$ V is larger for the buckled device implying a lower shunt resistance, which may be attributed to an interface contact issue on the rough surface. Figure 5b presents a statistical comparison between planar and buckled devices. There is an 11% increase in average efficiency, a 36% increase in current density, and a 15% decrease in fill factor for buckled devices. These values are consistent with previous reports [39, 41, 52]. As expected, the open-circuit voltage was roughly the same for all of the devices ($\approx 0.45$ V). We attribute the reduction in shunt resistance to contamination as the buckled samples have two additional processing steps that are not conducted in a clean environment. However, the dramatic increase in short-circuit current suggests that these buckles increase the effective optical path length.

3 Conclusion

In this paper, we report on the fabrication of OPVs prepared on substrates featuring periodic buckling corrugations formed by a simple process that is compatible with planar processing. These substrates possess improved photovoltaic efficiency and optical absorption relative to identical devices featuring flat layer laminates. We show a 20% improvement in efficiency resulting from increased photocurrent in our best device and 11% improvement on average. We also identify ideal sputtering conditions for depositing functional ITO without post-annealing. Large wavelengths ($\approx 14 \mu m$) results from the thick ITO film (200 nm) necessary to satisfy high conductivity and transparency. Although we use buckles with one wavelength and amplitude here, we note that it is possible to tune the dimensions of the buckles by varying the thickness of the PS and the thickness of the ITO (Figure S2 in Supporting Information). Therefore, OPVs with different buckling wavelength can be built to optimize device performance. We chose small molecule-based OPVs comprising on CuPc and C$_{60}$ bilayers due to simple processing. In this work we built OPVs directly on top of buckled substrates. Ultimately, we envision a planar substrate that can be coated using conventional (planar) thin film deposition techniques and then be strain-modulated to induce topography to improve light harvesting. Studying appropriate polymers and casting solvents can provide new research opportunity
for similar work on polymer-based OPVs. Doing so would enable a wider range of materials to be deposited including those that are cast via spin coating. There may be opportunities to increase efficiency further by increasing the aspect ratio of the topography [41, 52, 61].

4 Experimental

Film Preparation. Polystyrene (PS) (Aldrich) used in this study has a number-average molecular weight ($M_n$) of 230 kDa and $T_g$ of 94 °C. PS films were spin-coated on pre-cleaned and UVO-treated 50 mm × 50 mm × 1.1 mm boro-aluminosilicate glass (Delta's technology Limited) from filtered PS/toluene solution, and annealed in air at 110 °C on a hotplate for 3 hours. The bottom ITO electrode was deposited by radio frequency (RF) magnetron sputtering using commercial ITO target (Kurt J. Lesker Company). The power of 30 W was held constantly during sputtering. The distance between the sample and the target was 8.5 cm. The base pressure of sputtering was 1.6 × 10^{-6} Torr and process pressure was 4 mTorr. The sputtering rate was 5 nm/min.

CuPc/C$_{60}$ OPV Fabrication. As-sputtered ITO/glass substrates were cleaned by soaking in acetone and isopropanol (IPA) respectively for 10 min during sonication, followed by UVO treatment (10 min). CuPc (TCI), C$_{60}$ (MER), and bathocuproine (Lumtec) films were deposited by thermal evaporation with a thickness of 20, 40, and 12 nm, respectively. The Al electrode was then deposited by thermal evaporation with a thickness of 50 nm. The Ag electrode (thickness 100 nm) was then deposited by thermal evaporation. The completed device was encapsulated in an N$_2$ glove box without exposure to air using epoxy around the perimeter of a glass cover slip.

Film Characterization. Roughness of the ITO surface was measured by atomic force microscopy (Qscope 250, Ambios Technology Corp.). Map scans were obtained with a profilometer (Veeco Dektak 150 Surface Profiler). Reflectance measurements were conducted using an integrating sphere (6” diameter, OL 770 LED Test and Measurement System, Gooch and Housego).

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References


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