Residual solvent additive enables the nanostructuring of PTB7-Th:PC$_{71}$BM solar cells via soft lithography

Chao Wang, Eliot Gann, Anthony S. R. Chesman, and Christopher R. McNeill

AFFILIATIONS
1 Department of Materials Science and Engineering, Monash University, Wellington Road, Clayton, Victoria 3800, Australia
2 Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, Australia
3 CSIRO Manufacturing, Ian Wark Laboratories, Clayton, Victoria 3168, Australia

ABSTRACT
The nanoimprinting of polymer solar cells via soft lithography is an attractive approach for enhancing light absorption in the active layer. Many efficient polymer solar cells utilize a high boiling point solvent additive such as 1,8-diiodooctane (DIO) during active layer deposition to optimize morphology. By studying active layer films based on the PTB7-Th:PC$_{71}$BM system prepared with different amounts of the solvent additive DIO, it is shown that the soft imprinting of such blends critically relies upon the presence of residual solvent additive that plasticizes the film. In particular, a minimum of ~2 volume % of DIO in the casting solution is found to be necessary to enable effective imprinting. The microstructure of imprinted layers is also comprehensively characterized using atomic force microscopy, grazing incidence wide-angle X-ray scattering and resonant soft X-ray scattering, demonstrating that soft lithography can be used to effectively impart structure on the nanophotonic length scale without changing the nanoscale morphology and microstructure.

I. INTRODUCTION
The direct conversion of solar energy to electricity is becoming an increasingly important means of generating clean, renewable energy. Among the many existing photovoltaic technologies, organic photovoltaic (OPV) technology possesses many attractive features including solution-processability, low cost of production, flexible substrates, semi-transparency and ease of fabrication. The invention of the bulk heterojunction (BHJ) architecture is regarded as a milestone in the development of OPV technology, whereby an interpenetrating network of donor and acceptor phases is spontaneously formed during the solution deposition of a blend film. Through the development of OPV technology, several effective methods have been developed to optimise nanoscale phase separation including solvent annealing, thermal annealing and solution additives. In recent years, the power conversion efficiency (PCE) of organic solar cells based on polymer/fullerene blends has exceeded 10%, with the development of high-performance non-fullerene acceptors pushing the efficiency of polymer solar cells beyond 13%. Despite these promising improvements, the low efficiency of organic solar cells compared to other photovoltaic technologies is still an aspect that is hindering their commercialization.

The performance of organic solar cells is limited by two critical factors: the short diffusion length (~10 nm) of excitons that are the primary product of photoexcitation, and the low mobility of charge carriers. The BHJ concept has largely overcome the limitations imposed by the low exciton diffusion length, with the large donor-acceptor interfacial area enabling efficient exciton dissociation. However a mismatch in the typical length scales of optical absorption and charge transport exists because the thickness of the active layer is limited by the low carrier mobility. Hence, the...
optimum active layer thickness of an OPV device is typically around 100 nm,\textsuperscript{27,28} despite the fact that optical absorption can be improved by using larger active layer thickness.\textsuperscript{24–26} Thus strategies to improve light absorption in organic solar cells while maintaining good carrier collection yields have attracted significant attention.

Many different approaches have been developed to increase light trapping in the thin active layer of an organic solar cell. In particular the use of nanostructures to increase the path length of light in the active layer by scattering the normally-incident light has been widely explored. Nanostructures can be introduced in the form of scattering nanoparticles,\textsuperscript{28,29} nanostructured electrodes\textsuperscript{30} or nanostructuring of the active layer itself.\textsuperscript{31} Many different approaches have also been employed to generate nanostructures including the use of nanowires,\textsuperscript{32} nanoparticles,\textsuperscript{33} block copolymers,\textsuperscript{34} layer-by-layer deposition,\textsuperscript{35} and nanoimprinted lithography (NIL).\textsuperscript{36–38} Among these techniques, NIL is a particularly attractive technology for the nanostructuring of electrodes and/or the active organic semiconductor layer. The NIL technique relies upon the use of a reusable nanostructured mold, which is used to imprint the desired nanostructure directly onto the material to be patterned or a precursor material.\textsuperscript{39–41} NIL molds with specified periodic nanostructures can be produced (for example) by the patterning of silicon wafers with electron beam lithography. Silicon-based molds are hard, which can make reproduction of nanostructures over large areas and non-conformal substrates difficult.\textsuperscript{42} Soft nanoimprint lithography overcomes the difficulties associated with hard molds by using a soft nanostructured mold, typically based on cross-linked poly(dimethylsiloxane) (PDMS).\textsuperscript{43–45} PDMS-based molds can easily be prepared from silicon masters by pouring a PDMS pre-solution onto a silicon mold, curing, and then delaminating.\textsuperscript{46} Alternatively, a PDMS mold with quasi-periodic structures can be easily and cheaply produced via the spontaneous buckling of a thin metal film deposited on a PDMS substrate.\textsuperscript{47–49} PDMS-based molds easily conform to non-planar surfaces, are easily released after molding and do not adhere or react with polymers that are being molded.

There have already been numerous studies using soft NIL to pattern layers in organic solar cells using a variety of approaches.\textsuperscript{20,27,29,37,43–46} Cheng et al.\textsuperscript{37} for example used soft lithography to pattern the active layer of solar cells based on a blend of poly(3-hexylthiophene) (P3HT) with [6,6]-phenyl-C\textsubscript{61}benzothiophene-2,5-diyi] (PC\textsubscript{61}BM). In this work, Cheng et al. cited the ‘wetness’ of the spin-coated P3HT:PC\textsubscript{61}BM layer as important for the imprinting process, with annealing also being required for the imprinting of the P3HT:PC\textsubscript{61}BM layer by soft lithography. Alternatively Li et al.\textsuperscript{47} combined both Au nanoparticles (NPs) and nanostructuring of the active layer to improve light absorption in devices based on poly[(4,8-bis-(2-ethyl-hexyl)-thieno-2,5-b’]-dithiophene-2,6-diyl-alt-(2-(2’-ethyl-hexyl)thieno-[3,4-b]thiophene-4,6-diyl)] (PTB7-Th) blended with [6,6]-phenyl-C\textsubscript{71}butyric acid methyl ester (PC\textsubscript{71}BM). The use of nanoparticles of diameter either 20 nm or 50 nm were blended in with the active layer, with PDMS molds with grating periodicities of either 750 nm or 350 nm used to nanostructure the active layer to give a back-reflecting metallic nanograting top electrode. Since thermal annealing is detrimental to PTB7-Th:PC\textsubscript{71}BM solar cells, imprinting was performed without heating, but instead was performed under vacuum, with the additive 1,8-diiodooctane (DIO) used in the spin coating of the active layer. The best performing devices used 50 nm nanoparticles with a 750 nm period grating, improving the PCE to 8.79% compared to 7.59% for the control device.\textsuperscript{27} In the work reported by Jeong et al., soft NIL was employed to structure the active layer of PTB7:PC\textsubscript{71}BM and PTB7-Th:PC\textsubscript{71}BM based polymer solar cells, employing a PDMS mold with a grating structure of period 556 nm. Following spin coating of the active layer, the PDMS mold was immediately placed in contact with the active layer and then dried on a hot plate under a pressure of ~53 Pa.\textsuperscript{27} The PCE of the nanostructured device increased from 7.40% to 8.50% (PTB7:PC\textsubscript{71}BM cells), and 7.17% to 9.13% (PTB7-Th:PC\textsubscript{71}BM cells) with the authors also claiming that the nanoimprinting process improved the crystallization and chain alignment of the polymers. Lee et al. reported a novel approach where they combined block co-polymer lithography (BCL) with soft lithography to create PDMS molds structured on multiple length scales to improve light absorption in PTB7-Th:PC\textsubscript{71}BM solar cells.\textsuperscript{27} BCL was used to template structures on a sub-100 nm length scale with a grating (periodicity of 278 nm) used to structure on a larger length scale. In this way an increase in PCE from 7.75 to 9.63% was achieved. An outstanding issue from these previous works that is rarely commented upon is how soft PDMS molds are able to imprint polymer/fullerene blends with often little or no pressure required and what is the role of solvent additive plays during imprinting process. Indeed, previous reports using soft molds to imprint polymer/fullerene blends have typically used solvent additives,\textsuperscript{48–50} suggesting that residual solvent additive is necessary to enable molding of the active layer with PDMS-based molds at room temperature, however this has not previously been explored or commented on in the literature. In this work, we study the effectiveness of soft imprinting of the PTB7-Th:PC\textsubscript{71}BM system as a function of DIO content, and find that use of the solvent additive DIO is critical for enabling nanoimprinting with soft molds. Furthermore we examine the microstructure of such layers and find that soft NIL can enable structure to be patterned on a photonic length scale without changing the fine nanoscale morphology and microstructure.

II. EXPERIMENTS

A. Materials

The donor polymer poly[4,8-bis-(5-(2-ethylhexyl)thieno-2,5-yl)]benzo[1,2-b:4,5-b‘]dithiophene-2,6-diyl-alt-[2-(2’-ethyl-hexyl)thieno-[3,4-b]thiophene-4,6-diyl]] (PTB7-Th) was purchased from 1-Materials. Inc. The acceptor fullerene derivative phenyl-C\textsubscript{71}butyric acid methyl ester (PC\textsubscript{71}BM) was purchased from Nano-C. Chlorobenzene, 1,8-diiodooctane (98%), polyethyleneimine, 80% ethoxylated solution, zinc acetate dehydrate (99.999% trace metals basis) were all purchased from Sigma-Aldrich. ITO coated glass was purchased from Luminescence Technology Corp. Syngard 184 silicone elastomer base and curing agent used for preparing PDMS were purchased from Dow Corning Co.

B. PDMS preparation

PDMS used for nanoimprinting was prepared by mixing the silicone elastomer base and curing agent with a ratio of 10:1, followed by degassing under vacuum for 15 mins and pouring into a plastic petri dish to form a 1 mm thick layer. Thermal curing was carried
out at 70 °C for 2 hours. After curing, the PDMS layer was cut into 12 mm × 12 mm pieces and Al deposited via vacuum evaporation (∼10⁻⁶ mbar) with an average thickness of 25 nm as determined by a quartz crystal thickness monitor.

C. Active layer preparation

PTB7-Th and PC71:BM (weight ratio of 1:1.5) were dissolved in chlorobenzene (CB) and placed on a hot plate at 70 °C for 12 hours. The concentrations of PTB7-Th and PC71:BM were 14 and 21 mg/mL respectively for active layer thickness dependent samples, while for the rest of samples the concentration of PTB7-Th and PC71:BM were kept at 10 and 15 mg/mL respectively. This parent solution was then separated into 6 vials for preparing solutions with different DIO concentration ranging from 0 – 5 vol.%. These solutions were then kept on the hot plate for another 12 hours. Preparation of solutions was conducted within a nitrogen glove box.

D. Device fabrication

Devices were fabricated with an inverted architecture: ITO/ZnO/PEIE/active layer/MoO3/Ag. ITO-coated glass substrates were cleaned firstly by sonication for 10 minutes in acetone, followed by sonication for another 10 minutes in isopropanol before oxygen plasma cleaning for 10 minutes. A 0.073 M ZnO precursor solution was prepared by dissolving 160 mg of zinc acetate dehydrate in 61 mg of ethanolamine and 10 mL of 2-methoxyethanol with vigorous stirring for 12 hours for the hydrolysis reaction at 60 °C. A 0.073 M ZnO precursor solution was then spin-coated onto cleaned ITO-coated glass at 3000 rpm for 30 s and annealed on a hot plate at 200 °C for 30 minutes to form a thin conducting layer. A PEIE layer was subsequently spin-coated on top of the ZnO layer at 5000 rpm for 30 s and annealed on a hot plate at 110 °C for 15 mins to form a thin hole-blocking layer. The active layers of the solar cells were spin-coated from blend solutions at 1000 rpm for 60 s. For imprinted devices, the PDMS mold was put in conformal contact with the active layer directly after spin-coating. After the PDMS mold had been placed on the active layer, the sample was kept in the glove box at room temperature for 2 hours. Control the PDMS mold had been placed on the active layer directly after spin-coating. After 15 mins to form a thin hole-blocking layer. The active layers of the device (CCD) detector. Two scattering patterns were collected at 30 and 150 mm sample to detector distances, respectively, and combined in software. Two-dimensional scattering patterns were reduced to one-dimensional profiles by using a customized version of Nika.

III. RESULTS AND DISCUSSION

A. Stamp preparation and characterization

The PDMS molds used in this work, see Figure 1, were fabricated by the vacuum evaporation of aluminum onto PDMS substrates. The spontaneous formation of quasi-ordered structures by the thermal evaporation of metals onto PDMS has been previously described by Bowden et al. and Koo et al. and interpreted in terms of the buckling of the metal films due to thermal contraction of the PDMS substrate upon cooling (11,42) (the PDMS substrate expands during vacuum evaporation due to heating from the deposition source). PDMS substrates were prepared with ~ 1 mm thickness using a commercial preparation kit (see experimental section for full details) and placed into a vacuum evaporator for deposition of Al. Figure 1 shows the optical and atomic force microscopy (AFM) images of an unpatterned PDMS substrate and a PDMS substrate deposited with an average aluminum thickness of 25 nm as specified by the thickness deposition monitor. Visually, the Al-coated PDMS substrate does not show a mirror-like finish but rather appears matte, with the AFM image showing a pseudo-ordered structure with sub-micron features consistent with the observations of Koo et al. (41) Considering the surface roughness, the uncoated PDMS substrate has a root-mean-square roughness (Rq) of 0.86 nm, while the
Al-coated PDMS substrate has a surface roughness of $R_q = 41.6$ nm. From the AFM image of the Al-coated PDMS substrate a maximum peak-to-trough distance of 253 nm is found with an average peak to peak distance of 689 nm. There is a large variation in the average peak-to-peak distance giving a range of length scales, which could be beneficial for broadband light scattering. It was found that depositing different amounts of Al (varying the average Al thickness) produced variation in feature size, see Figure S1 in the supplementary material. An average aluminum thickness of 25 nm found to optimize device performance, with Figure S2 and Table S1 in the supplementary material providing device data for different aluminum thickness.

B. Active layer imprinting—Importance of DIO

Schematic diagrams of the device geometry used and the chemical structures of the active layer materials employed are shown in Figure 2. A so-called ‘inverted’ device architecture was used, with the indium tin oxide (ITO) layer coated with ZnO and PEIE (polyethylenimine ethoxylated) in order to facilitate electron collection from the ITO electrode. A blend of the low band-gap polymer PTB7-Th with PC$_{71}$BM was used as the active layer (weight ratio of 1:1.5 PTB7-Th:PC$_{71}$BM), with an unpatterned thickness of 120 nm. Imprinting was achieved simply by placing the mold on top of the active layer immediately after spin-coating and leaving in contact with the active layer for 2 hours. Only a small pressure was applied at the edge to initiate point contact in order to adhere the PDMS stamp to the active layer. No external pressure was otherwise applied to the PDMS stamp. (The active layer films were prepared under the same conditions as for devices.) After removal of the PDMS stamp, a thin layer of MoO$_x$ was deposited followed by 100 nm of silver to complete the device (full details can be found in the experimental section). The efficiency of the PTB7-Th:PC$_{71}$BM system requires the use of a high boiling point additive such as DIO in order to optimize the active layer morphology. DIO has been shown to suppress the formation of large PC$_{71}$BM domains which is critical for harvesting PC$_{71}$BM excitons and facilitating charge separation. DIO is also known to remain in spin-coated PTB7-Th:PC$_{71}$BM films for several hours after spin-coating, raising the possibility that residual DIO content is important in enabling soft lithography of polymer/fullerene blends, particularly when little or no pressure is applied (as is the case here).

Figure 3 presents the surface topography of PTB7-Th:PC$_{71}$BM films prepared with various amounts of DIO in the solution (0 – 5 vol.%) and then imprinted with the PDMS mold. Strikingly, the pattern on the mold is only reproduced in the polymer layer with a DIO content of 2 vol.% DIO or greater. The surface roughness values of the samples processed with 0, 1, 2, 3, 4 and 5 vol.% DIO are $R_q = 3.8$ nm, 1.6 nm, 23.6 nm, 29.2 nm, 28 nm and 30.9 nm respectively. For the case of the film processed without DIO, the round features observed in the AFM image of these films are large PC$_{71}$BM clusters which are known to form when DIO is not used. For the case of both 0 vol.% and 1 vol.%, the surface topography...
FIG. 3. AFM images of imprinted PTB7-Th:PC\(_{71}\)BM blends with (a) 0 vol.\%, (b) 1 vol.\%, (c) 2 vol.\%, (d) 3 vol.\%, (e) 4 vol.\% and (f) 5 vol.\% of DIO.

It is not clear why there is this discrepancy; however relaxation of the film after imprinting (enabled again by residual DIO) is a possibility. Given the relatively large peak heights in the masters (compared to the active layer thickness of devices) a reduced peak height in the imprinted films may be beneficial.

C. UV-Vis-NIR reflection spectroscopy

UV-Vis-NIR reflection spectroscopy was conducted with an integrating sphere to find evidence of improved light absorption within the imprinted device structures. Figure 4 presents the optical reflection spectra of complete device structures prepared with varying amounts of DIO additive. In general, imprinted films prepared with \( \geq 2\% \) of DIO additive show a significant reduction in reflected light over a broad wavelength range, improving light absorption especially in the range of 500 nm to 600 nm over which the active layer materials have low absorption. There is also a dramatic reduction in the reflection of light for wavelengths below the band-gap of the polymer, however light at these wavelengths may be absorbed more in the electrodes and interlayers than in the active layer.

D. Device performance

Figure 5 presents the device characteristics of control and imprinted cells prepared from 0 – 5 vol.\% DIO blend solutions. An active layer thickness of 120 nm was used which optimizes the performance of non-imprinted cells. Device performance parameters such as \( J_{SC} \), \( V_{OC} \), FF and PCE are summarized in Table I. In general, imprinted devices prepared from blend solutions containing \( \geq 2\% \) DIO additive showed improved device performance compared with control devices (non-imprinted devices), while devices prepared with \( \leq 1\% \) DIO experienced a reduction in device performance after imprinting was attempted. Examining the JV curves under simulated sunlight for the control devices first (Figure 5(a)),
$J_{SC}$ and FF are found to peak at around 3–4 vol.% of DIO while $V_{OC}$ is found to gradually decrease with increasing DIO content. With reference to the extracted performance parameters in Table I, the best control cell (4 vol.% DIO) has an overall power conversion efficiency of 10.7% with $J_{SC}$ of 19.8 mA/cm$^2$, $V_{OC}$ of 0.79 V and FF of 0.69. (Note that these quoted values are average values taken from the measurement of at least 16 cells.) For the imprinted cells, PCE is optimized for 2–3 vol.% DIO with a PCE of 10.8% to 10.9% achieved. Compared to the optimized control device, a higher $J_{SC}$ of 20.5 mA/cm$^2$ is achieved for the 2 vol.% imprinted cell. For the

FIG. 5. Device performance of control (a, c, e) and imprinted (b, d, f) solar cells prepared from 0–5 vol.% of DIO additive, (a, b) $J$-$V$ curves under 100 Mw/cm$^2$ AM 1.5G simulated sunlight, (c, d) $J$-$V$ curves taken in the dark, (e, f) external quantum efficiency (EQE) curves.
producing a flatter spectrum in the cells processed with ≥ that imprinting leads to a change in the shape of the EQE spectrum, the control (Figure 5(e)) and imprinted (Figure 5(f)) cells, it is clear prepared with 4 and 5 vol.% DIO. Comparing the EQE spectra of of control (Figure 5(c)) and imprinted (Figure 5(d)), imprinting is perform that of the control cells. Comparing the dark JV traces

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all) previous papers examining the effect of imprinting on device increased average active layer thickness. Furthermore most (if not 3 vol.% imprinted cell a similar JSC is obtained compared to the control device, however cell fill factor is found to be improved (0.69 vs. 0.66). The VOC of imprinted cells is also found to match or out-perform that of the control cells. Comparing the dark JV traces of control (Figure 5(c)) and imprinted (Figure 5(d)), imprinting is found to lead to a significant increase in leakage current, likely due to the increase film roughness, which may limit efficiency of cells prepared with 4 and 5 vol.% DIO. Comparing the EQE spectra of the control (Figure 5(e)) and imprinted (Figure 5(f)) cells, it is clear that imprinting leads to a change in the shape of the EQE spectrum, producing a flatter spectrum in the cells processed with ≥ 2 vol.% DIO, boosting EQE in the regions where light absorption by the active layer materials is weakest. There is also a small increase in EQE at the absorption onset, characterized by an apparent red-shift in the EQE curve. From the EQE data the highest EQE improvement results from the use of the 2 vol.% DIO with an absolute increase of 9% at 575 nm.

The fact that the JSC of the devices with an active layer thickness of 120 nm was not significantly enhanced by imprinting could be related to the fact that light absorption in the control device is already benefiting from constructive interference of light. Thus the optimum (average) active layer thickness for imprinted devices and control devices may not be the same, and imprinted devices with larger variations in local film thickness may benefit from an increased average active layer thickness. Furthermore most (if not all) previous papers examining the effect of imprinting on device performance only reference optimized imprinted devices to a control device of a single active layer thickness. Thus considering the efficacy of imprinting on cells with different active layer thickness was explored.

Figure 6 summarizes variations in key performance parameters (PCE, JSC, VOC, FF) with change in active layer thickness (thickness of the active layer before imprinting) for imprinted and control devices. (JV curves and EQE can be found in the supplementary material, Figure S4.) Control devices show optimum performance for active layer thicknesses of ~ 80 nm to 120 nm, with thinner devices less efficient due to inefficient light absorption and thicker films experiencing more recombination. As mentioned above, an active layer thickness of ~ 80 nm to 120 nm also optimizes optical interference effects in the control devices. In contrast to the control devices, the efficiency of imprinted devices systematically increases with increasing active layer thickness, with the efficiency of imprinted cells with an average active layer thickness of 190 nm outperforming the control devices. Indeed, the average PCE of imprinted cells with 190 nm average active layer thickness is 9.9% which is higher than the PCE of control cells of optimum active layer thickness (80 to 120 nm). (Note that a different batch of PTB7-Th was used for the thickness-dependent study resulting in slightly lower overall efficiency values compared to the results presented in Figure 5 and Table I.) Comparing the other cell parameters, the high PCE of the thick imprinted device is mainly due to its superior short-circuit current. The EQE curves (see supplementary material, Figure S4) show that the imprinted devices have flatter EQE profiles consistent with absorption being improved in the imprinted cells. These results therefore confirm that imprinted and non-imprinted cells indeed have different optimum active layer thickness, and thus it is important to compare imprinted cells to non-imprinted cells for a range of active layer thicknesses. These results also indicate that imprinting makes cells less sensitive to variations in active layer thickness which is attractive for manufactured (printed) cells where thicker films and less sensitivity to active layer thickness is desirable. The next section investigates the effect of imprinting and confinement on the morphology and microstructure of the active layer.

E. Morphology and microstructure

1. GIWAXS

Grazing-incidence wide-angle X-ray scattering measurements were performed to look for changes in thin film crystallinity as a function of DIO content, with and without imprinting. The GIWAXS data (see supplementary material, Figure S5-7) in general shows that the PTB7-Th:PC71BM films are characterized by weakly ordered PC71BM aggregates and weakly ordered PTB7-Th crystallites, consistent with previous observation. While there are changes in thin film microstructure with increasing amounts of DIO used (the polymer lamellar stacking peak at ~ 0.3 Å⁻¹ becomes sharper and intensifies with increasing DIO concentration, indicating an increase in polymer crystal size along the lamellar stacking direction) there is very little change in the scattering profile with imprinting. The lack of any change in the degree of crystallinity with imprinting is in contrast to the work of Jeong et al. who reported improved crystallization and multidimensional chain alignment with nanoimprinting based on an increase in the scattering intensity in imprinted films. However the scattering intensity measured by GIWAXS is exceptionally sensitive to the angle of incidence of the beam, with the scattering patterns in the manuscript of Jeong et al. showing no discernible change in shape with nano imprinting (as would be expected for an increase in crystalline order). In our experiments we have carefully aligned our samples with a Si crystal analyzer and measured GIWAXS patterns as a function of the angle of incidence to ensure that scattering intensities between samples are comparable. Of course, nanoimprinting can result in changes in polymer...
molecular orientation and crystallinity, especially when the length scale of imprinting is similar to or smaller than the contour length of the polymer. But for molds with periodicity of ∼ 500 nm as used here and by Jeong et al., nanoconfinement effects may not be expected. Control samples also show no change in mosaicity, indicating the confinement of the film during imprinting is not promoting the edge-on or face-on stacking of crystallites, but rather there remains an essentially random distribution of crystallites in the film.

2. R-SoXS

In order to understand the influence of DIO and imprinting on the nanomorphology of the blend (that is, the size/spacing of PC71BM domain before and after imprinting) resonant soft X-ray scattering (R-SoXS), measurements have been performed.\textsuperscript{33} Scattering is measured down to a $q$-value of $0.01 \text{ nm}^{-1}$ enabling structures of up to ∼ 600 nm in dimension/spacing to be probed. Figure 7 shows R-SoXS profiles of films prepared with 0, 3 and 5 vol.% DIO. The samples in Figure 7 had an average active layer thickness of 120 nm. Figure 7 shows scattering patterns acquired at both 284 eV and 270 eV. At 270 eV, only electron density contrast is active, while at 284 eV scattering contrast between PTB7-Th and PC71BM is achieved by utilizing differences in the near-edge optical constants of the two materials.\textsuperscript{34} For samples prepared with 0 vol.% DIO, the scattering profiles of the control and imprinted samples are essentially the same, see Figure 7(a). A broad peak at $q \sim 0.035 \text{ nm}^{-1}$ is seen consistent with the relatively large PC71BM domains seen in the AFM images which are a few hundred nanometers in size. For samples prepared with 3 vol.% DIO, Figure 7(b), both control and imprinted samples exhibit a peak located at $q \sim 0.11 \text{ nm}^{-1}$ corresponding to a center-to-center distance between PC71BM domains of ∼ 30 nm, consistent with previous reports.\textsuperscript{35} The position of this peak does not change with imprinting, indicating that the internal nanomorphology of the active layer is largely unaffected by these processes. At low $q$, the imprinted 3 vol.% DIO blend shows a prominent peak at $q \sim 0.01 \text{ nm}^{-1}$, corresponding to a ∼ 600 nm spacing that is absent in the control sample. This feature (which is also prominent in the scattering pattern acquired at 270 eV) is clearly

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**FIG. 6.** (a) PCE, (b) fill factor, (c) $J_{sc}$ and (d) $V_{oc}$ of control and imprinted devices as a function of average active layer thickness for a cells prepared with 3 vol.% DIO.
caused by imprinting consistent with the AFM images where an average peak-to-peak spacing of 689 nm was measured. These R-SoXS measurements have thus simultaneously captured both the small-scale nanomorphology (<50 nm) and photonic-scale (>200 nm) nanostructuring. For films prepared with 5 vol.% DIO, a broad at \( q \sim 0.01 \text{ nm}^{-1} \) is similarly observed in both samples, with a prominent peak at low \( q \) also present for the imprinted sample but absent for the control sample.

IV. CONCLUSION

By preparing and studying imprinted PTB7-Th:PC\textsubscript{71}BM solar cells prepared with different concentrations of the solvent additive DIO, we have shown that residual DIO is critical for enabling replication of features by soft nanoimprinting. A DIO content of 2 vol.% or higher was found to be necessary for effective reproduction of the master in the active layer film. From the thickness dependence of control and imprinted devices, we have further shown that control and imprinted cells have a different thickness dependence on PCE, with thicker imprinted cells outperforming thinner, optimize control cells. GIWAXS and R-SoXS studies also showed that soft lithography can be used to imprint on a photonic length scale without significantly altering the underlying nanoscale morphology and microstructure.

SUPPLEMENTARY MATERIAL

See supplementary material for the AFM section analysis of imprinted films; AFM images of control films prepared with different amounts of DIO; optical and AFM images of films imprinted with stamps with different Al thickness; JV curves, dark JV curves, EQE curves of devices with varying thickness; GIWAXS results.

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