

Solid-Phase Deposition: Conformal Coverage of Micron-Scale Relief Structures with Stretchable Semiconducting Polymers

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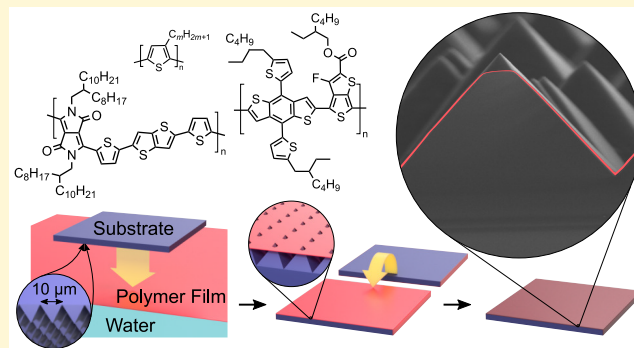


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Supporting Information

ABSTRACT: There are a variety of methods available for forming thin films of electronic polymers, but very few of them are applicable to surfaces bearing relief structures on the micron scale. Of the methods that are capable of conformal coverage of such topography, most are applicable only to coatings that can be polymerized in situ—for example, by chemical vapor deposition—and are, thus, not amenable to polymers with complex molecular structures, such as π -conjugated (semi-conducting) polymers. This Letter describes a method termed solid-phase deposition (SPD). The SPD process is a variant of water transfer printing whereby a thin film of a semiconducting polymer is suspended on water and taken up by a substrate bearing micron-scale relief structures (in this case, sharp pyramids etched in silicon). Under ambient conditions, solid films that are sufficiently compliant (thin, ductile, or of low modulus) can coat these surfaces readily. Stiffer films comprising higher modulus polymers can be made amenable to the process by the application of heat or solvent vapor. We successfully formed coatings from films of poly(3-alkylthiophenes) spanning the range from glassy (alkyl = butyl) to rubbery (alkyl = heptyl), along with the low-bandgap polymers DPP-DTT and PTB7-Th, on textured silicon and indium tin oxide (ITO) surfaces.



The manufacturing of semiconductor devices is enabled to a large extent by techniques that produce uniform thin films of polymeric materials. For example, spin-coating, slot-die coating, and various forms of chemical vapor deposition (CVD). However, just a small subset of these methods can coat substrates bearing topographic (relief) structures in a conformal manner. Meaning, few methods can form coatings in such a way that the thin film is uniform in thickness and the surface features are preserved with a high degree of fidelity. Moreover, methods that have this capability—for example, polymer CVD—are limited to materials that can be polymerized in situ, and thus, the diversity in the molecular structure of the deposited film is limited.^{1,2} That is, there are currently no methods available to form conformal coatings of materials, such as low-bandgap semiconducting polymers. Development of such a process would be useful, for example, in the field of photovoltaics, where silicon, perovskite, and organic semiconductors are commonly structured with relief as a means of trapping light.^{3–6} Here, we describe a process inspired by water-based transfer printing, whereby a solid polymer film initially supported atop the surface of water can then be taken up by

a topographically patterned substrate. This process—solid-phase deposition (SPD)—relies on plastic deformation of the polymer film to adhere to the relief structures in a conformal, defect-free way. It is applicable to a wide variety of polymers of varying complexity and function to form conformal coatings of nanometer-scale thicknesses on surfaces with micron-scale relief features. In this work, we used silicon textured with random pyramids with heights on the order of 10 μm . Such substrates were chosen both to demonstrate the capability of SPD to coat features, which are much larger than the coatings are thick, as well as because prior work has shown that the reflectance of textured silicon surfaces significantly increases if the pyramids are too small (less than approximately 2 μm).⁷

Thin polymeric films are ubiquitous in science and technology. Along with photoresists—which have enabled

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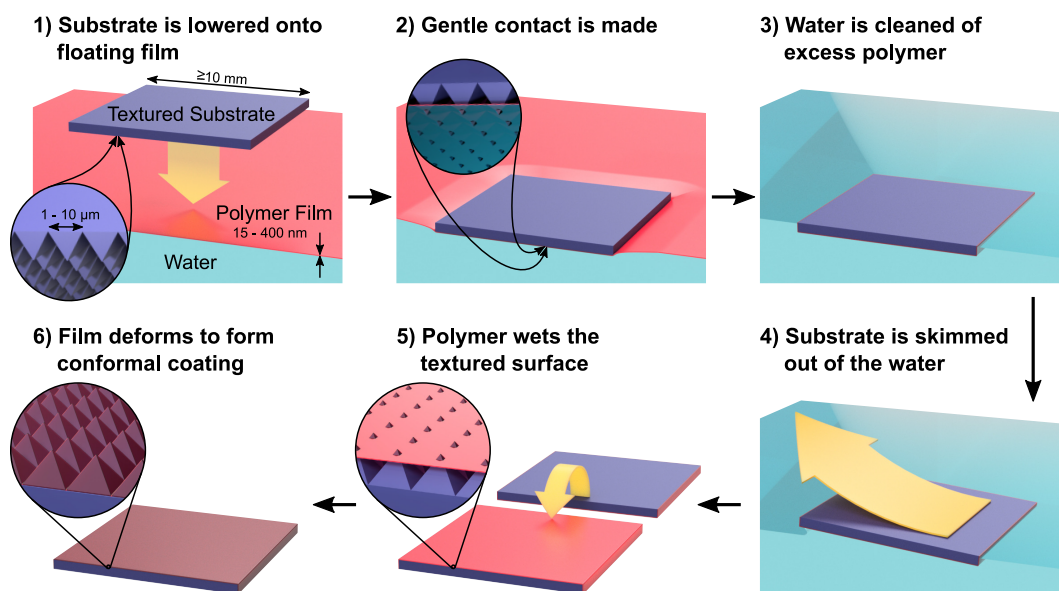


Figure 1. Summary of a solid-phase deposition process, taking place in ambient conditions. A polymer film suspended on water is taken up by a textured substrate with high-energy surfaces, enabling the necessary deformation of the polymer as it conformally coats the substrate.

essentially all of modern electronics—familiar examples in consumer electronics are antireflective⁸ and antimudge coatings.⁹ In biotechnology, polymeric films are used as mimics of cell surfaces,¹⁰ and chemical patterning of surfaces is ubiquitous in commercial genomics.¹¹ In the next generation of thin-film photovoltaics, polymeric thin films can serve as electron- and hole-transport layers. However, to maximize light absorption in thin-film solar cells,¹² it may be necessary to use surface relief structures, as is common in silicon solar cells.¹³

Conventional techniques such as spin-coating and spray-deposition can be used cover micron-scale topographic features. However, these techniques generally either have a planarizing effect for thick films, obscuring the surface features, or lack uniformity for thin films, as solution tends to pool in concave features and leave convex features bare. Polymeric coatings can be applied to relief structures with high uniformity using a number of techniques, which can be categorized as either “graft-to” or “graft-from” approaches.¹⁴ In “graft-to” processes, preformed polymers can be covalently or electrostatically bound to surfaces which bear reactive groups (or intrinsic reactivity to end groups on the polymers¹⁵) or bound charges.¹⁶ For example, fluorinated monolayers terminating in silane groups are used to coat touch screens.¹⁷ Layer-by-layer assembly is a process by which polyanions and polycations are coated onto surfaces in an alternating manner.¹⁸ Electrostatic forces ensure the formation of uniform layers.

In “graft-from” processes, the polymerization occurs directly on the surface.¹⁹ Well known examples include various forms of controlled radical polymerization, notably atom-transfer radical polymerization (ATRP).²⁰ In surface-initiated ATRP, an alkyl bromide serves as the site of initiation of the chain-growth process. Surface-initiated ATRP proceeds in the solution phase. In contrast, polymers formed by polycondensation reactions can be formed on-surface in a vapor-phase process known as molecular-layer deposition (MLD).²¹ In this process—applicable only to AB-type polymers—A and B monomers are alternately reacted with the surface in an iterative fashion. Lack of self-reactivity of like monomers ensures uniform thickness of a monodisperse coating. A

solution-phase process, which is otherwise analogous to MLD, termed molecular layer-by-layer deposition, has also been demonstrated.²² Other than MLD, relevant vapor-phase processes fall under the general category of polymer CVD.¹ Like MLD, polymer CVD is applicable to a variety of substrates, including topographically complex surfaces such as textiles.²³ Significant advances have been made in reactive vapor deposition of relatively simple conjugated polymers such as polythiophenes and poly(phenylenevinyls).²⁴ However, polymer CVD is generally limited to reactive monomers or those with a low molecular weight.

While powerful, these techniques are not applicable to polymers that can only be polymerized using conventional, solution-phase chemistry. For example, polymers whose formation requires heating (and possibly reflux), heterogeneous catalysts, redox processes, and harsh solvents may not be amenable to coating by existing methods. These polymers include essentially all low-bandgap π -conjugated (semiconducting) polymers used in research in photovoltaics, thin-film transistors, light-emitting devices, and biosensors. New methods are thus needed for the deposition of preformed polymers on surfaces bearing micron-scale relief features.

Our laboratory has had a long interest in the mechanical properties of conjugated polymers, especially in ways to combine mechanical deformability with good charge-transport properties.²⁵ For example, we have previously demonstrated the ability to transfer stretchable bulk heterojunction films to hemispherical surfaces,²⁶ though these surfaces did not impose the greatest possible mechanical demands on the films. We, thus, sought to develop a method whereby physical transfer and subsequent deformation of a presolidified film could be used to obtain conformal coverage of topographic surfaces—even those bearing sharp features—with substantially more uniformity than it was previously possible to achieve. We were inspired by the work of Rogers et al. in the area of kinetically controlled transfer printing²⁷ and also by the common industrial process known as water transfer printing.²⁸

The SPD process is shown schematically in Figure 1. Unless otherwise noted, this was the process used throughout this

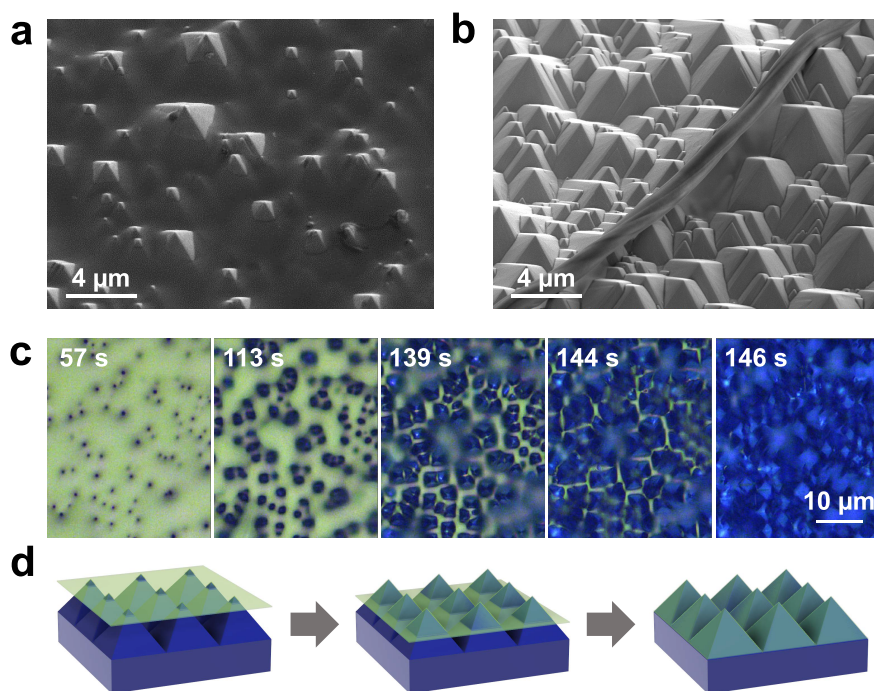


Figure 2. Evolution of the wetting process. (a) Scanning electron micrograph (SEM) of a polymer film which partially coated the pyramidal peaks of a textured silicon substrate (b) SEM of another polymer film that has wetted a textured silicon substrate. The top left region shows bare pyramids, while the bottom-right region has been conformally coated, leading to the contrast between the two regions. The feature crossing the SEM diagonally is a rolled-up portion of the film, the continuation of which can be seen immediately below the roll as the film joins with the surface. (c) Still frames with time-stamps from an optical microscopy video showing the same sample area as a polymer film progressively wets the surface of a pyramidal silicon substrate. (d) Schematic illustration showing the progression of the wetting process after the film has been transferred.

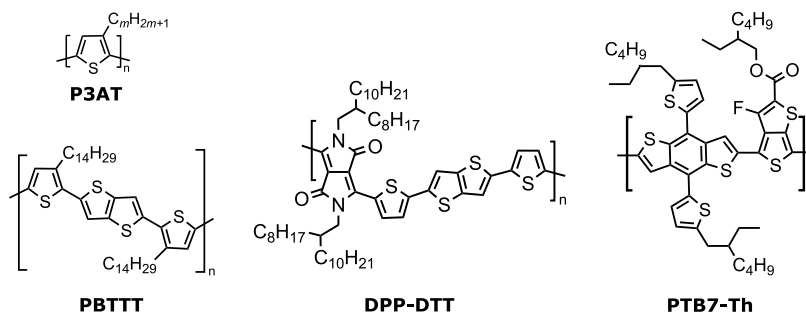


Figure 3. Chemical structures of the conjugated polymers discussed in the text.

work. SPD begins by suspending a presolidified polymeric film on the surface of water, in a process known as solution spreading.²⁹ The process of transferring this film to a substrate is independent of the method used to produce the film, but we chose solution spreading for its simplicity. Solution spreading relies on the Gibbs–Marangoni effect to drive the spreading of a polymer solution atop the surface of water. Evaporation of the solvent results in the formation of a solidified polymer film, which remains suspended at the water–air interface. The process of transfer begins by pressing the substrate into the floating film with the relief structures (pyramids) oriented downward (step 1). Upon contact with the polymeric film (step 2) and before lifting the substrate from the surface of the water, excess polymer was manually cleared from the perimeter of the substrate using a tool (step 3). The substrate (bearing the polymeric film underneath) is skimmed from the surface (step 4) and inverted (step 5). Given favorable ductility of the polymeric film and adhesion to the substrate, the conformal

coverage takes place spontaneously (step 6). Various stages of the wetting process are shown in [Figure 2](#); footage corresponding to [Figure 2c](#) can be found in [Video S1](#).

We found that the ability to obtain conformally coated films was a product of the surface energy of the substrate as well as the dimensions and mechanical properties of the polymeric films. In our experiments, we found it necessary to render the substrates hydrophilic using an air plasma. In contrast, treating the substrates with a hydrophobic silane monolayer led to poor transfer. The cause for this effect is 2-fold: The hydrophilic surface promotes wetting by the polymer film itself, but it also allows for the intrusion of water into the polymer–substrate gap by capillary action. Entry of the water occurs from the edges when the excess polymer is removed (step 3 in [Figure 1](#)). In a way that will be described in more detail later, the presence of the water facilitates the conformal coating on a topographic substrate. Because the film is initially planar, the deformation it must undergo is significant. Thus, films with low

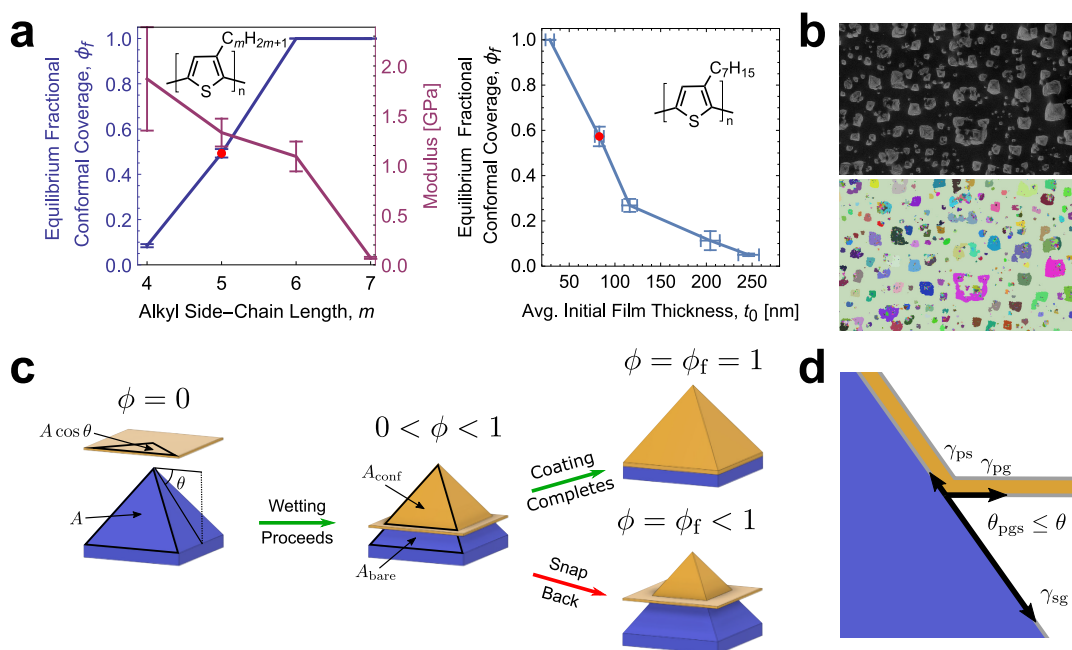


Figure 4. Fractional conformal coverage. (a) SPD was performed using various P3AT films. (Left) ϕ_f was measured for films stamped with P3ATs of different side-chain lengths, m . Also shown are literature values of the moduli for the same P3ATs, as measured by the buckling technique.³⁰ (Right) ϕ_f was measured for P3HpT films of varying initial thickness, t_0 . The red data points indicate conditions which led to some samples of a “mixed state,” where snap-back occurred over part of the sample, but completed over the rest. Only regions of the former were used in calculating the point value. (b) Sample of raw SEM data (top) and the same data after image segmentation (bottom) used to perform a measurement of ϕ_f . (c) Schematic diagram of the possible evolutions of the wetting process. The films were either observed to complete coverage (top fork) or undergo “snap-back” and stop (bottom fork.) (d) Cross-sectional diagram of the polymer–substrate–gas interface. The vectors show the relative magnitudes of the interfacial energies, as estimated from contact angle measurements. The represented system has P3HpT as the polymer, air-plasma treated/oxidized silicon as the substrate, and air as the gas. $\gamma_{sg} = 76.3 \text{ mJ m}^{-2}$, $\gamma_{pg} = 28.6 \text{ mJ m}^{-2}$, and $\gamma_{ps} = 11.5 \text{ mJ m}^{-2}$.

stiffness, low yield strength, high ductility, low thickness, or a combination of these properties, produced conformal coatings with the fewest defects. Good results were obtained for many semiconducting polymer films under ambient conditions. Nevertheless, for films of polymers with greater stiffness, yield strength, brittleness, or thickness, it was possible to use solvent vapor or other means to induce plasticization and permit conformal coating. We will discuss these “assisted” methods of SPD later.

To investigate the roles played by the extensive and intensive properties of the polymeric films on the SPD process, we performed experiments using a variety of poly(3-alkylthiophenes) (P3ATs; Figure 3) as the model materials. In particular, we varied the length of the side chain (m) to tune the intrinsic deformability, while keeping the pretransfer thickness (t_0) constant. We also varied t_0 while keeping m constant ($m = 7$). In these experiments, P3AT films were transferred onto comparable, plasma-treated substrates and SPD was allowed to proceed in ambient conditions until no further evolution of the coating process was observed. The end point of each experiment was measurement of the “equilibrium fractional conformal coverage”, ϕ_f . We define the fractional conformal coating of the system as

$$\phi = \frac{A_{\text{conf}}}{A} \quad (1)$$

where A is the total pyramidal area in view and A_{conf} is the pyramidal area, which has been coated. Measurement of ϕ_f was done by collecting top-down scanning electron micrographs (SEMs) of the samples and using image analysis methods to

segment the image, allowing for determination of A_{conf} . The results of these experiments and a sample of the SEM data used are shown in Figure 4a and b, respectively.

The cause for the incomplete conformal coverage ($\phi_f < 1$) in these experiments was the occurrence of a what we will refer to as “snap-back.” Snap-back is characterized by the rapid recession of the film from the underlying substrate surface after wetting has already occurred, as depicted in Figure 4c. Once snap-back has happened in a given region, further wetting of the substrate surface was not observed. Snap-back was also observed to nucleate and then propagate throughout the rest of the sample. This nucleation is seen in Video S2, along with additional optical microscopy footage of the snap-back behavior taking place.

The extent of snap-back is quantified by ϕ_b and the observed dependencies of ϕ_f on m and t_0 can be explained by considering how the total strain energy of the polymer, U , is expected to vary across the samples. In general

$$U = \int_{V_p} u \, dV \quad (2)$$

where u is the strain energy density and V_p is the total polymer volume. Additionally, it is well understood that all else being equal, the mechanical properties of P3ATs vary monotonically as a function of m . An increase in m results in a decrease of tensile modulus, yield strength, and ultimate tensile strength and an increase in fracture strain.²⁵ In short, P3ATs with a larger m are more compliant, will show a lower u for a given strain, and u will grow less rapidly as the strain occurs. Given that the films are much thinner than the pyramids are tall, it

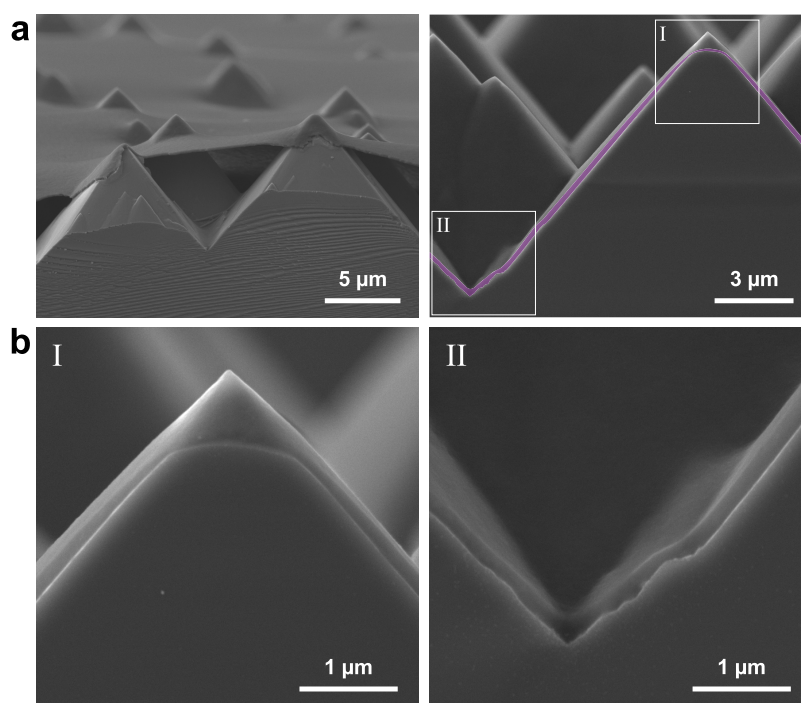


Figure 5. Results of the SPD process when assisted by solvent vapor. (a) (Left) Cross-sectional SEM of a thick P3HpT film, which underwent snap-back after evolving in air and (right) an analogous sample, which was exposed to chloroform vapor (60 °C for 10 min) immediately after film transfer. The polymer cross-section is shown in false color for clarity. (b) Magnified regions of the right frame from section a; the micrographs show how the film thins at the pyramid apex but otherwise remains uniform throughout.

may be reasonable to assume that different films will display similar overall strain distributions for a given ϕ as the film makes its initial descent. If so, it follows that the strain energy required to trigger snap-back will be reached at lower values of ϕ for less compliant polymers because of a more rapid increase of u or for thicker films due to a larger V_p . On the basis of this analysis, it is logical to put forward that SPD is facilitated when the polymer is above its glass transition temperature, as is the case for P3HpT and P3HT in ambient conditions. However, it should be emphasized that film thickness, as well as other factors, such as the geometry (e.g., the complexity of the topography), are likely to influence the quality of the coated film.

It is evident that the mechanical properties of the polymer films play a significant role in facilitating (or frustrating) the SPD process, but the driving mechanism remains unexplained. Given that successful coatings have only been observed when the substrate is rendered hydrophilic, it may appear that SPD is driven by a reduction in interfacial free energy. Indeed, the interfacial tensions between the substrate, polymers, and air (as estimated by contact angle measurements) indicate that the advancement of the triple interface down the slope of the pyramid is energetically favorable. This scenario is depicted in Figure 4d, where the restricted geometry at the triple interface is expected to ensure an imbalance of interfacial tensions. However, dry films transferred directly onto the substrates (i.e., without being suspended on water), do not show significant wetting. This result indicates that the simple description above is incomplete, and implies that water is playing an active role in SPD.

As previously mentioned, SPD involves the presence of water between the polymer film and the substrate. The presence of water was verified by performing a series of coatings where, partway through the wetting process, a dry

cleanroom swab was used to wipe away half of the film. For every sample examined in this way, wiping away the film revealed a thin layer of water which visibly evaporated. The evaporation of water was shortly followed by completion of the coating on the other half of the substrate (where the film had not been wiped away), indicated by a visible change in color. Sample footage of this process can be found in Video S3. We believe the film deformation involved in SPD is primarily driven by this water, which is adhered to both the polymer film and the substrate, and fills the void between them. As water molecules enter the gas phase after diffusing through the film, the volume of water is reduced. It is generally unfavorable to form a gas–liquid interface, and so the water continues to adhere to the film as its volume decreases, pulling the film down and deforming it. However, if the strain energy stored in the film is sufficiently high, then a gas–liquid interface will form, resulting in a “headspace” as the water and film de-adhere, which manifests as “snap-back.” This final point is supported by the second clip in Video S2, which clearly shows how the film dramatically changes color once a region has snapped back. The change in color indicates a change in the index of refraction of the medium backing the film, which goes from water to a gas.

For sufficiently compliant polymeric thin films, the SPD process can complete unassisted, with fractional conformal coverage approaching unity. However, to make the process amenable to stiffer films, we explored various methods of *in situ* plasticization. The aim of these methods is to soften the film so that the stored strain energy is dissipated quickly, thereby making snap-back or mechanical failure less likely. One of these methods is to transiently plasticize a transferred film by exposing it to the vapor of a low-boiling-point solvent (e.g., chloroform) in an enclosed chamber. This solvent-vapor assisted process proved effective in enabling conformal transfer

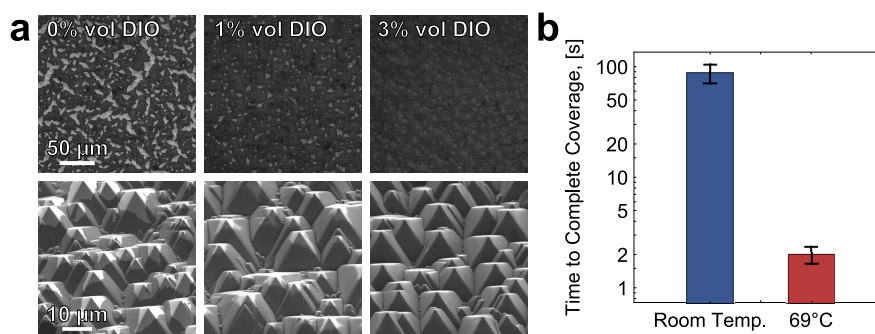


Figure 6. Use of cosolvent additives and increased temperature to increase the fractional coverage and speed of the coating process. (a) (Top row) Top-down micrographs of DPP-DTT coating bare pyramidal silicon and exposed to chloroform vapor after transfer. From left to right, there was an increasing amount of DIO included in the polymer solution used to derive the film. Lighter regions show bare silicon. These micrographs were captured with an in-lens detector. (Bottom row) Same samples at higher magnification and viewed from an angle. (b) Chart showing the measured time from initial transfer to complete coverage for samples allowed to evolve at two different temperatures. The substrates were bare silicon, coated with a thin P3HpT film ($t_0 \approx 25$ nm), and allowed to evolve in air.

of various polymeric films at a wide range of thicknesses. Figure 5 shows cross-sectional scanning electron micrographs taken of two comparable samples stamped with thick P3HpT films. For one sample, SPD was allowed to evolve in air and snap-back occurred. For the other, the sample was exposed to chloroform vapor immediately after film transfer. The vapor was supplied from a heated source (60 °C) and exposure was done for 10 min. The resultant coating is generally uniform, though the film was consistently observed to thin near the apexes of the pyramids, presumably due to a concentration of force at those sites. It is possible that this thinning could be reduced or avoided by using pyramidal substrates with peaks of larger radii of curvature. Pyramids of decreased sharpness are already standard in the silicon photovoltaics industry, as overly sharp pyramids cause issues relating to dopant diffusion, among other problems. Additional micrographs showing the thinning at the apex can be found in Figure S1. For comparison, cross-sectional micrographs of pyramidal substrates, which were spin-coated with P3HpT using several conditions can be found in Figure S2. These samples display various defects, such as pooling between pyramids as well as uncoated peaks and sidewalls, which arise with such an approach.

In addition to the use of solvent vapor as a means of temporary plasticization, it is possible to achieve a similar effect by including high-boiling cosolvents in the solutions from which the films are solidified. These minimally volatile additives function as traditional plasticizers, and some have the added benefit of improving the performance metrics of thin-film transistors and solar cells. This method was explored with the addition of 1,8-diiodooctane (DIO) to solutions of DPP-DTT (Figure 3), a low-bandgap polymer. DPP-DTT is a donor–acceptor polymer of technological interest due to its low bandgap, air-stability, and exceptionally high hole mobilities.³¹ However, attempts to coat this polymer from a neat solution, whether in air or assisted by solvent vapor exposure, resulted in significant fracturing of the films. For the bare silicon substrates we tested, these defects occurred at the apexes of the pyramids. Interestingly, when tested on ITO-coated pyramids, the films were observed to fracture at the valleys between pyramids. In both cases, the inclusion of small quantities of DIO ($\leq 3\%$ by premixed volume of solution) significantly reduced the occurrence of these defects. Figure 6a shows these results for DPP-DTT on bare silicon. It should be

noted that DIO, while facilitating SPD, actually makes the films more prone to fracturing under rapid mechanical insults. To accommodate this fragility, the method of polymer transfer differed from the others in this work in that the substrate was dipped directly into the water and used to scoop the polymer up from below.

Lastly, SPD can also be assisted by heating. Heating can accelerate the coating process by increasing the rate at which water is expelled from the polymer–substrate gap and is also expected to soften otherwise stiff or brittle films. Figure 6b shows the results of an experiment where thin P3HpT films ($t_0 \approx 25$ nm) were transferred onto bare silicon substrates. Coating was allowed to evolve either at ambient conditions or on a heated surface (69 °C). The average time to coating completion was reduced by almost 2 orders of magnitude for the heated samples compared to those at room temperature from 87 ± 17 to 2.0 ± 0.3 s.

We have found these methods to assist SPD to be suitable in most scenarios, but some polymers remain too brittle for successful transfer (e.g., PBTTT, Figure 3). The side-chains of PBTTT are known to interdigitate, resulting in exceptionally high crystalline fractions.³² This degree of crystallinity makes the PBTTT films exceptionally brittle, and they have never survived the transfer process in our hands. The polymer still adheres to the pyramid walls, but fractures at the single micron scale, creating completely discontinuous coatings (Figure S3). All of the polymers with which we have attempted to form SPD coatings, along with the methods that have been successful, are detailed in Table 1.

Two possible use cases of SPD, which are of particular interest to us, include the application of charge-selective layers in silicon/perovskite tandem cells as well as enhanced light management in organic photovoltaic (OPV) devices. The majority of this work pertains to neat polymer films and is, therefore, most applicable to the former use case. On the other hand, use of SPD in OPV poses unique challenges. The efficiency and stability of OPV cells is highly dependent on the morphology of the bulk heterojunction (BHJ) active layer, in which a polymeric donor and an acceptor are combined in an interpenetrating network. Moreover, BHJ films generally have poor mechanical properties, particularly when using fullerene acceptors. The poor mechanical properties would most likely require the use of one of the assisted methods to form high-quality coatings. However, these methods (meaning, the

Table 1. Polymers with Which SPD Has Been Attempted, the SPD Methods Used Which Were Successful^a, the Type of Pyramidal Silicon Substrate Used (Bare or ITO-Coated), and the Previously Published Values for the Modulus and Crack Onset Strain^b

| polymer | successful methods | silicon substrate | modulus [GPa] | crack onset strain [%] |
|---------|--------------------|---------------------|---------------|------------------------|
| P3BT | sv | bare | 1.87 | 6 |
| P3PT | SPD, sv | bare | 1.33 | |
| P3HT | SPD, sv | bare and ITO-coated | 1.09 | 9 |
| P3HpT | SPD, sv, h | bare | 0.07 | 65 |
| DPP-DTT | sv + cs | bare and ITO-coated | | |
| PTB7-Th | sv | bare | | |
| PBTTT | | ITO-coated | 0.879 | <2.5 |

^a“SPD” corresponds to no assistance, “sv” to solvent vapor, “cs” to cosolvent, and “h” to heated. ^bAs measured by the so-called “buckling technique” and assimilated in ref 30.

application of heat, solvent vapor, or cosolvents) are often what is used to arrive at a desired morphology. Therefore, employing SPD, particularly one of its assisted variations, could have a negative impact on the BHJ morphology. One possible approach to account for this issue could be to devise a means to slow SPD down such that the BHJ film can undergo very slow relaxation, thereby preventing snap-back while minimally disturbing the film morphology. However, the slowing of a manufacturing process is generally not desirable, and therefore, the more likely approach to integrating SPD into the manufacturing of OPV cells would be to merge SPD with another step (such as thermal/solvent annealing) such that this single hybrid step produced a BHJ coating that was both conformal and possessed the desired morphology. Micrographs of a BHJ film (P3HT: PCBM in 1: 1 ratio) applied to ITO-coated pyramids can be seen in Figure S4.

In summary, a novel process by which to apply uniform and conformal polymeric coatings to topographically complex surfaces has been introduced and explored. This process necessitates the formation of a presolidified film, here formed and suspended on the surface of water. The film is, then, mechanically taken up from the water surface by an activated substrate, and the process proceeds by leveraging or enhancing the plasticity of the film as the polymer wets the substrate surfaces. By appropriate tuning of the system parameters and materials selection, it is possible to form functional coatings in a range of thicknesses, in minutes or less, in or near ambient conditions. Moreover, the process is applicable to a wide range of polymers not otherwise possible to coat with using solution or vapor-phase processes. This process is not without its limits, as it appears to be incompatible with exceptionally brittle polymers and is unlikely to be applicable to substrates with reentrant surfaces (i.e., those with undercuts). It has also not been demonstrated over large areas, though solution spreading has been shown to be compatible with roll-to-roll processing,³³ and so, the compatibility of SPD with textured, flexible substrates seems likely. Regardless, because of its simplicity, expediency, and flexibility, we believe SPD could impact a wide range of fields, such as sensing, medicine, and energy. Our interests lie in how it may be used to enhance and enable novel photovoltaic devices. The past decade of work has signified both a resurgence in organic photovoltaics, as well as a massive surge in interest for hybrid organic/inorganic materials and

devices. As the photovoltaics community continues to strive in enabling tandem cells for the next generation of utility-scale solar power production, we believe further developments in SPD may position it as a viable processing method in the manufacture of these devices.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00213>.

General material processing, profilometry, fractional conformal coating, image analysis, solvent-vapor-assisted SPD, cosolvent-assisted SPD, heat-assisted SPD, surface energy measurements, and additional electron micrographs for samples coated with neat polymers using SPD and spin-coating and samples coated using bulk-heterojunction films (PDF)

Optical microscopy footage showing SPD taking place in air (MP4)

Optical microscopy footage of snap-back occurring on several samples (MP4)

Video showing the evaporation of a thin layer of water after the film is partially removed from a sample (MP4)

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Notes

The authors declare no competing financial interest.

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