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Extrusion on-demand pattern coating using a hybrid manufacturing process

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ABSTRACT

Roll-to-roll (R2R) solution processing of thin film devices offers savings to cost, time, and material waste. Emerging technologies in electronics, optoelectronics, and microfluidics could potentially benefit from these manufacturing advantages. However, the associated complex pattern requirements are difficult to attain with traditional solution-based methods, barring significant concessions to device performance and process scalability. In this paper, we present and implement a novel hybridization of continuous (*e.g.*, slot die) and on-demand (*e.g.*, inkjet) techniques designed to address these shortcomings, wherein outflow from localized regions of an extrusion die is actuated in real time to produce patterns. Pattern features were produced with aqueous solutions of poly(vinyl alcohol) (PVA), and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), and deposition phenomena were observed *in situ* using a specialized roll feed imaging system. Minimum feature size is shown to be directionally dependent, with transient flow effects dominating along the axis coincident with substrate motion, and sensitive to several process inputs as well as coating material properties. Strategies for managing residual fluid in the die cavity and beneath the die lip are illustrated, through flow actuation mechanisms and exploitation of deposition phenomena, to optimize pattern fidelity.

1. Introduction

Fluid deposition-based techniques for thin film production have long been noted for their suitability for roll-to-roll (R2R) production, low material waste, and potential for high throughput at low cost [1]. Slot die extrusion, the most widely-utilized of these methods, has been used for a range of emerging devices including batteries [2–4], organic photovoltaic (OPV) cells [5–8], organic light emitting diodes (OLEDs) [9,10], and electrochromic displays [11]. Other state-of-the-art processing methods used for similar devices include doctor blade extrusion [12], gravure and flexographic printing [13–17], screen printing [18–20], and inkjet printing [17,21–31]. Many of these devices, which represent significant progress in energy efficiency and environmental sustainability, have emerged only recently. However, fluid deposition-based techniques for their fabrication have remained fundamentally unchanged for several decades.

For wide-area solution processing of thin films, slot die extrusion has been favored for its high throughput, efficient material utilization, and suitability for a broad range of coating fluid viscosities [6]. As a pre-metered method where the rate of inflow matches the rate of deposition with no loss, slot die extrusion also enables precise control of film thickness, decoupled from processing speed. Discrete continuous lines have been produced by slot die extrusion, using a segmented shim to define the internal slot geometry along the land that separates multiple local menisci during the extrusion process [7,8]. While additional processing steps are necessary to achieve patterns of greater complexity, numerous studies have employed slot die extrusion for select steps during fabrication of organic and polymer thin film devices [1,5–11].

In pursuit of more complex pattern capabilities, extrusion coating has been extended to coat grids of quadrilateral patches. For this purpose, various methods and apparatuses incorporating periodic cessation of flow into traditional slot die designs have been proposed. Choinsky designed a variable-volume chamber for dispensing fluid patches of variable size and uniform thickness [32]. Previous studies have described and characterized phenomena associated with patch extrusion coating, including the raised features at the lateral edges [33,34] and tapering of the patch width at the leading and trailing edges [35–37]. Diverter valves and recirculation mechanisms have also been integrated into the fluid delivery system in order to optimize control over the sharpness of

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the final pattern [38–40]. While methods for coating intermittent patches are useful for some steps in fabricating OPV and battery devices, the pattern requirements in many of the other applications mentioned previously are more substantial.

Rotogravure techniques have garnered interest for large-area solution processing of arbitrary 2D patterns. Offset gravure was used by Leppävuori et al. to deposit metallic inks in discrete lines as narrow as 500 μm [13]. Gravure coating of the OPV materials, poly (3-hexylthiophene):phenyl(C61 butyric acid methyl ester) (P3HT: PCBM) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on poly(ethylene terephthalate) (PET) substrate, was demonstrated by Kopola et al. [14] and subsequently with industrial-scale tooling by Yang et al. [15]. However, the material requirements for gravure have been shown to be demanding. Voigt et al. investigated the role of various solvents and additives for P3HT:PCBM and PEDOT:PSS inks gravure coated on ITO-treated PET, and observed significant film quality and device performance dependencies on surface tension, shear-dependent viscosity, evaporative rate, and substrate pre-treatment [16]. Furthermore, the tooling and hardware reconfiguration required for each pattern makes gravure coating less attractive for manufacturing operations requiring a high degree of flexibility.

Nano-imprint lithography (NIL) has also been utilized as a lab-scale technique across multiple studies spanning thin-film transistors (TFTs) [41], nanolithography diffraction gratings [42], and drug delivery [43]. In conjunction with non-patterned deposition methods, NIL can be used to define nanoscale 2- or even 3-dimensional structures. As with gravure and screen printing, however, process flexibility of NIL is limited by the need for tooling specific to each unique pattern.

Where digital configuration of patterns is required, inkjet printing is the current state-of-the-art. Inkjet printing has been demonstrated for the partial or complete manufacture of complex pattern applications, including OLED devices [21,25], rectifying diodes [24], TFT arrays [26–29], and microfluidic channels [30,31]. However, inkjet printing is limited for scalable manufacturing due to its relatively low throughput and restrictive requirements for ink viscosity [6]. Furthermore, uniform topology is inherently difficult to achieve with methods based on discrete droplet deposition, since physical properties must be tuned for leveling across droplets as well as deposition dynamics [44]. In the absence of proper leveling, the contact edges of each droplet define a periodic topographic feature. Depending on the fluid-substrate wetting dynamics and curing conditions, these features range from convex to concave, and are exemplified in the familiar coffee ring effect at the edges of isolated droplets [22,45]. While additives and solvents are instrumental in tuning the physical properties of coating fluids to meet these requirements, consideration must also be given to the performance characteristics of the materials deposited.

As an alternative to patterned fluid deposition, patterned substrate pre-treatment has been explored in a number of studies. Sirringhaus et al. achieved a minimum feature size of 5 μm for inkjet-printed PEDOT:PSS transistor electrodes by selectively altering the surface energy of a glass substrate prior to deposition through photolithography and O_2 plasma etching [26]. Subsequent interest in selective plasma etching as a pre-patterning technique has included a method for mask-free patterned plasma etching [46]. Precursory deposition of lyophobic layers has also been used to induce pattern de-wetting in subsequent deposition steps [47]. However, while pre-treatment strategies offer clear improvements to pattern quality, they also add cost and complexity in the form of additional manufacturing steps.

The inherent limitations of conventional methods outlined above are significant. Additionally, published comparisons of these deposition methods demonstrate that no single contemporary technique encompasses all requisite performance characteristics for additive manufacturing of patterned films [6,48,49]. Thus, the true potential of solution deposition techniques to enable highly scalable and waste-free manufacturing of thin film devices remains unmet. The development of new solution processing methods is one approach to overcoming this disparity.

In this paper, we demonstrate the viability of an innovative deposition method for thin film patterning using an extrude-on-demand (EOD) approach. As a hybridization of continuous and intermittent coating techniques, this method is capable of producing 2D printed patterns by local extrusion of fluid on-demand. Solutions of polyvinyl alcohol (PVA) and PEDOT:PSS are deposited in thin films with pattern features with widths as low as 377 μm. The operability of the coating tool is characterized in relation to flow behavior, demonstrating a unique combination of advantages intended to address the need for scalable solution processing of patterned thin films across a wide range of coating fluid material properties.

2. Extrusion on-demand operating principles

The hybrid thin film coating system introduces an *extrude-on-demand* (EOD) coating system. Independent on/off flow control at discrete localized extrusion regions (DLERs), as illustrated in Fig. 1, is the mechanism used to generate 2D patterns. In contrast to conventional coating and extrusion-based methods such as knife-over-edge and slot die, patterning is achieved within the deposition step, without additional pre-treatments or post-deposition patterning processes.

EOD deposits an array of contiguous fluid patches of fixed width and variable length. Analogous to discrete droplets in inkjet deposition, these patches approximate a given 2D pattern. As shown in Fig. 1c, this method of fluid delivery circumvents flow interruptions within the contact line that defines the pattern, in contrast to inkjet. EOD is also distinct from existing extrusion methods for discrete line and intermittent patch coating. While these existing methods feature limited flow control at localized regions, EOD includes the additional capability of independent, on-demand actuation.

Patterned thin film applications demand fine control over feature size with respect to both pattern axes, as well as film

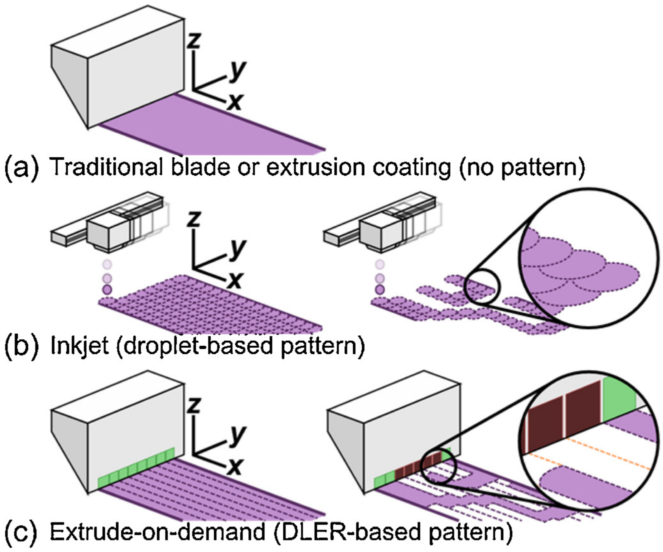

Fig. 1. Comparison across (a) traditional blade or extrusion coating, which coats continuously but is unsuitable for producing 2D patterns on demand, (b) droplet deposition (*e.g.*, drop-on-demand or continuous inkjet), and (c) EOD, wherein flow control at discrete sections of the outlet region produces patterns on demand.