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High performance printed organic transistors using a novel scanned thermal annealing technology

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ABSTRACT

Printed organic thin film transistors (OTFTs) are a key component for the realization of low-cost, flexible electronics applications such as printed RFID tags or flexible displays. In recent years, great advances have been made in developing higher performance organic semiconductors. Many of these new materials show strongly process-dependent performance characteristics. The development of novel processing techniques is thus a key step towards utilizing the full potential of these semiconductor materials. Here we demonstrate a novel directional crystallization technique using a scanned thermal gradient to significantly improve the performance of printed OTFTs. A heat source is translated relative to the sample to induce the crystallization of the semiconductor. This scanned annealing creates a moving thermal gradient and thus develops a moving solvent evaporation gradient. Compared with uniform annealing on a hotplate grain size increases markedly and shows a clear directionality due to the separation of grain nucleation and growth. With this technique, mobility is boosted by about one order of magnitude. Mobilities close to 2 $cm^2/V\,s$ can be achieved. Off-state performance is likewise improved as evidenced by a 3× improvement in subthreshold swing.

1. Introduction

Printed organic electronics has been suggested as an enabling technology for a variety of novel applications such as printed RFID tags [1,2], flexible displays [3], low-cost sensor networks [4,5] and smart packaging on paper [6,7]. One of the key devices for any such system are printed transistors. Performance of organic thin film transistors (OTFTs) has been improved significantly in recent years [8–12]. This includes improvements in both printing technology [13,14] and semiconductor materials [15–17]. However, many of these materials show strongly process dependent characteristics; as a result, while high performance devices have been demonstrated on idealized silicon-based test structures, performance has generally lagged in real printed devices on plastic. In particular, the semiconductor morphology in printed devices is generally much poorer than that achieved on smooth silicon substrates, resulting in degraded performance. Here we demonstrate a novel scanned thermal annealing technology that can be applied to plastic substrates to facilitate significant performance improvements. We employ a state of the art commercial organic semiconductor that has been shown to hold great promise for printed organic devices and circuits [18–20]. Similar acene based organic semiconductors have been studied extensively by John Anthony and co-workers [21–23]. Here we show that the directional crystallization resulting from scanned annealing of this solution processed, printable organic semiconductor can be exploited to significantly improve the performance of printed OTFTs, and demonstrate that high performance can indeed be achieved in printed devices on plastic substrates.

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Directional crystallization techniques have been shown to significantly enhance the performance of inorganic semiconductors. Amorphous silicon can be crystallized into polysilicon by selective laser heating [24–28]. The crystallization mechanism involves melting and crystallization on solidification. By scanning the laser heat source, very large grains can be grown. This mechanism cannot be applied directly to solution processed semiconductors where the crystallization mechanism relies on the solvent being driven out of the film. This cannot be done repeatedly unlike melting and solidification of silicon, although there have been some reports for thick organic semiconductor films [29,30]. Multiple techniques have been reported to achieve directional crystallization of solution processed organic semiconductors. However, many of these techniques such as off-center spin coating [17] and crystallization on a tilted substrate [31] are incompatible with roll-to-roll fabrication and have not been shown to work well in realistic flexible substrates. Others, such as solution shearing [32,33] and zone casting [34–39] have shown great promise to leverage directional crystallization for improved electrical performance. However, most reports on solution sheared or zone cast films operate at very low speeds on the order of tens of micrometers per second. Our method operates at 1 mm/s, which still requires further improvement, but is orders of magnitude faster than previous reports. A stationary thermal gradient has been used to enhance the performance of solution processed TIPS-pentacene transistors [40]. This work demonstrates the benefit of thermal gradients for the crystallization of solution processed organic semiconductors, however, does not allow sufficient control due to inherent temperature variations across the sample, particularly when using flexible substrates and printed electronics processes.

Here we demonstrate a novel technique, which utilizes a scanned thermal gradient to induce the directional crystallization of a solution processed organic semiconductor. A plastic substrate is translated relative to a heated metal bar that is in contact with the bottom side of the plastic substrate (see Fig. 1(a) for an illustration of the technique); since the scanning process inherently exploits the relative motion of the substrate, it is very compatible with roll-to-roll processing. The top side contains devices with the solution deposited semiconductor. A thermal gradient is induced within the plastic substrate at the edge of the heated bar. This leads to a gradient in solvent evaporation rate and thus a gradient in the crystallization driving force. This gradient is scanned across the substrate as the heated bar is translated. The effect of this technique on crystallization is illustrated in Fig. 2(a). To understand this, it behooves us to first summarize the kinetics of crystallization. Crystallization is typically described by two phenomena, nucleation and grain growth. Nucleation describes the process by which initial crystallites are formed, while grain growth describes the process by which these crystallites enlarge. Typically, the activation energy for nucleation exceeds that of grain growth; as a consequence, once grains nucleate, they typically grow to fill the available space between nuclei. As a consequence, grain size is typically limited by the density of initial nuclei. Uniform heating as conventionally used leads to the uniform nucleation of grains, which will then grow

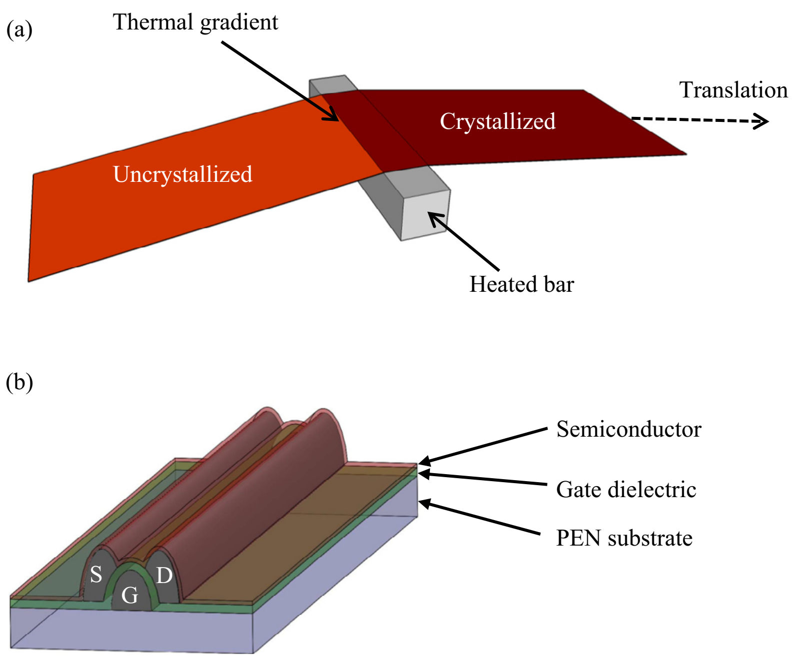

Fig. 1. (a) Scanned thermal annealing method. A plastic substrate is brought in contact with a heated metal bar and translated to the right relative to the bar. OTFTs with the organic semiconductor are located on top of the plastic substrate. A thermal gradient and thus solvent evaporation gradient exists inside the plastic substrate at the leading edge of the heated bar. Crystallization occurs at the location of the gradient. The semiconductor material to the left of the thermal gradient has not crystallized yet whereas material to the right of it has already crystallized. (b) Device structure of printed OTFTs.