

Nanopatterned Organic Materials for Photovoltaic Devices

Stuart S. Williams^{*}, Meredith J. Hampton^{*}, Scott T. Retterer^{**}, Joseph L. Templeton^{*}, Edward T. Samulski^{*}, Joseph M. DeSimone^{*}

^{*}Department of Chemistry, University of North Carolina – Chapel Hill
Chapel Hill, NC. desimone@unc.edu

^{**}Center for Nanophase Materials Sciences at Oak Ridge National Laboratory, Oak Ridge, TN, 37831

ABSTRACT

In order to further increase the efficiency of current state-of-the-art photovoltaic devices, the interfacial architecture must be controlled at the nanoscale such that the donor/acceptor (D/A) blend results in an ideal morphology for maximizing charge collection efficiency. The ideal bulk heterojunction (BHJ) consists of an interpenetrating network such that every exciton formed is within a diffusion length of the D/A interface and there are straight pathways to the respective electrodes. In light of this ideal structure goal, we have fabricated patterned bilayer photovoltaic (PV) cells using a perfluoropolyether (PFPE) elastomeric stamp to control the morphology of the donor-acceptor interface within devices. Specifically, devices were fabricated using the Pattern Replication In Non-wetting Templates, or PRINT, process to have nanoscale control over the bilayer device architecture. This “top-down” approach allows for facile patterning over large areas. The low-surface energy, chemically resistant, variable modulus, fluoropolymer based molds used in PRINT provide a route to patterning a variety of materials. We have focused on patterning organic based materials systems which have been used in current BHJ devices. Ordered, sub-100 nm structures have been fabricated over large areas to investigate the effect of nanopatterning on PV-performance.

Keywords: nanopatterning, soft-lithography, organic photovoltaic, semiconducting polymers, organic electronics

INTRODUCTION

Recently soft lithography has developed into an important low cost fabrication method for pattern replication on the nanometer scale [1]. Soft lithography was first developed using embossing and stamping methods with applied forces to form patterns in photoresist materials as an alternative to photolithography for use in integrated circuits and other microelectronic devices. Embossing typically involves the patterning of materials into continuous arrays of features on an interconnected flash layer by using either ‘hard’ (such as silicon, quartz) or ‘soft’ molds [1-3]. Traditional soft lithography, pioneered by Whitesides, has been dominated by the elastomer

polydimethylsiloxane (PDMS) as a molding material to replicate micro- and nanosized structures for a variety of applications [4, 5]. Though PDMS has many advantageous properties for use in soft lithography, there exist several properties in the silicon based elastomers that hinder the use of PDMS molds for patterning some materials or applications; these properties include swelling in common organic solvents and residual silicone derivatives on surfaces being molded or patterned [6]. As an advanced alternative to PDMS molds, Rolland *et al.* reported the use of perfluoropolyether (PFPE) based molds for soft lithography and microfluidic devices [7, 8]. The PFPE based materials contain several distinctive properties compared to silicone based materials, such as (i) low surface energy (PFPE ~8-12 dynes/cm² vs. PDMS ~25 dynes/cm²) enables selective filling of micro and nanoscale cavities in the mold; (ii) the chemically resistant fluorinated molds are resistant to swelling in common organic solvents; (iii) the low surface energy allows for the mold to be easily released from the features being patterned; (iv) the modulus of the elastomer is easily tuned by changing the molecular weight between crosslinks of the precursor allowing for higher fidelity molds; and (v) the PFPE elastomers are formed via UV curing in several minutes compared to the thermally cured PDMS elastomers which can take up to an hour.

The unique properties of PFPE based molds such as chemical resistance, extremely low surface energy, high gas permeability, solvent resistance, high elastic recovery, and good mechanical strength allow for aqueous precursors and organic liquids to be patterned into isolated particles, arrays of particles, and arrays of patterned features for a wide variety of applications ranging from drug delivery to photovoltaics. These patterns and particles are formed using the fluoropolymer based molding technique developed in the DeSimone lab known as PRINTTM (Particle [or Pattern] Replication in Non-wetting Templates) and is shown schematically in Figure 1[9]. PRINT is different from traditional imprint lithography in that it exploits wetting phenomena to fill recessed cavities in the mold rather than relying solely on heat and pressure. Depending upon the material to be molded or patterned and the architecture of the mold, it is possible to form unique arrays of isolated particles using cavity filling concepts (Figure 1C-F and C-F’) or arrays of features on a substrate with an interconnecting flash layer

using more traditional imprinting techniques (Figure 1H- J).

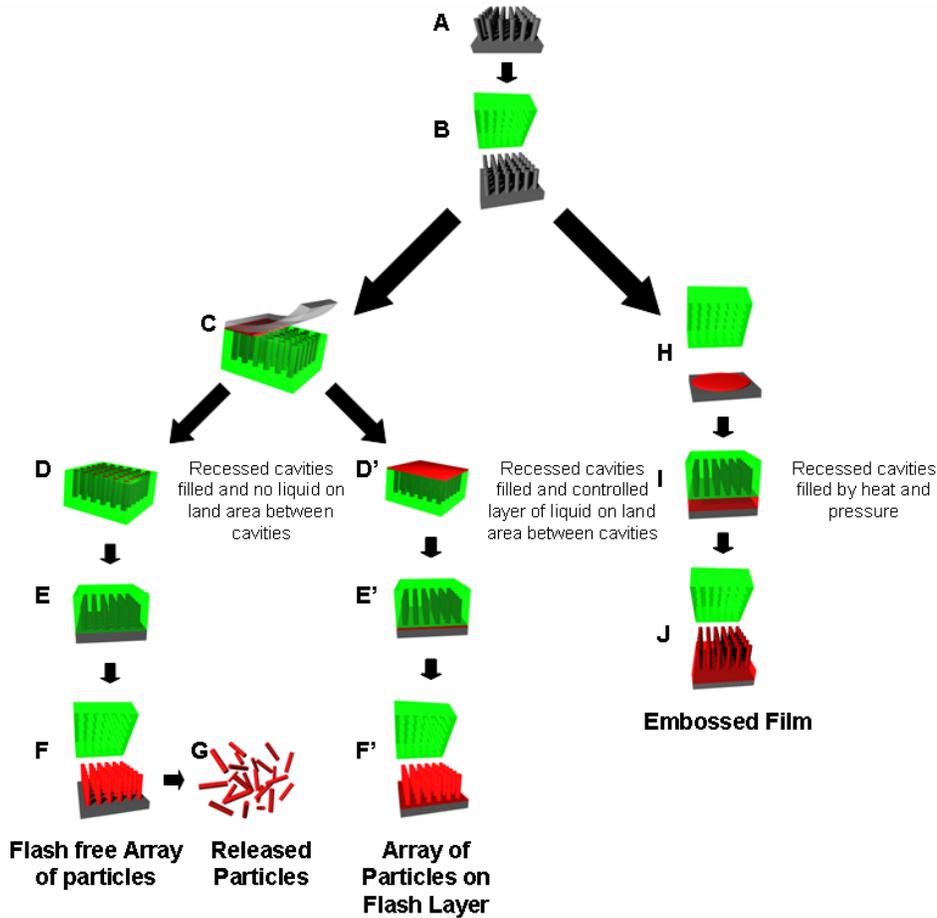


Figure 1. Schematic of PRINT™ process used to from isolated particles in solution (1G), arrays of particles on a flash layer (1F’), and an embossed array of features (1J).

The PRINT process starts with the formation of a master template, which is typically a silicon wafer fabricated using standard lithographic techniques (Figure 1A). The master template is then coated with a photocurable PFPE liquid, and cured ($\lambda_{\text{max}} = 365 \text{ nm}$) to form a low surface energy solid PFPE elastomer. The flexible, elastomeric PFPE mold can then be peeled off of the master template revealing an inverted pattern relative to the master template. To obtain isolated particles or arrays of particles, the cavities in the mold can be filled with a liquid via capillary action without wetting the ‘land’ area between the cavities (Figure 1C). The liquid can then be converted into solid by using a variety of solidification chemistries such as photochemical curing, thermal curing, solvent evaporation, or other liquid to solid phase transitions (Figure 1E,E’). The solid particles can then be removed from the mold to yield either an array of particles, free forming particles in solution, or particles arrayed on a controlled flash layer (1F,F’,G).

As a nanoparticle fabrication technique, PRINT gives unprecedented control over shape, size, and composition.

PRINT provides a route to high fidelity feature replication by being able to change the mesh density of the PFPE-mold, resulting in a resolution on the 1 nm length scale. In addition, the PFPE based molds are able to replicate ‘soft’ master templates such as polymers lying on a substrate [10]. Due to the ability of PRINT to be scaled up into a roll-to-roll, high throughput fabrication process, it is worth pursuing as a technology for patterning materials for use in organic-based photovoltaic cells.

PV applications

Organic photovoltaic (OPV) devices are a viable solution for the production of cost effective solar power. Conjugated polymers are promising materials for OPV’s for several reasons; (i) they are solution processable, (ii) absorb light strongly in the solar spectrum, and (iii) can be used to fabricate active devices on flexible substrates. Power conversion efficiencies (PCE, or η_{eff}) of conjugated polymer based OPV’s have reached upwards of 5%

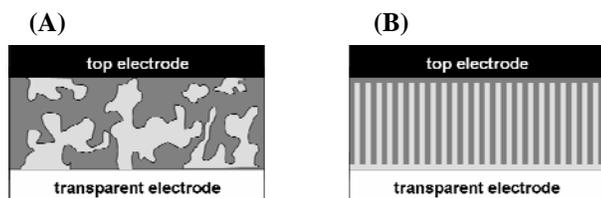


Figure 2. Cross-section schematic of (A) 'disordered' BHJ and (B) the ideal BHJ morphology. Adopted from [11].

utilizing a bulk heterojunction (BHJ) morphology shown in Figure 2a [12, 13]. The BHJ morphology typically involves a conjugated polymer as the donor material, mixed with a small molecule electron acceptor, such as the functionalized fullerene derivative phenyl C₆₀ butyric acid methyl ester, or PCBM. The donor-acceptor materials are mixed in one solution and deposited via spin casting onto a transparent electrode (typically indium tin oxide [ITO]), and the PV device is completed by capping the system with a metallic 'back' electrode (such as Al, Ag, Au). Upon post-fabrication annealing, the mixture phase separates into nanoscale domains which are on the order of the exciton diffusion length and will therefore increase the excitonic collection efficiency. The domain size of the morphological blend depends on many factors such as the polymer side chain length, molecular weight, regioregularity, and the annealing conditions [14, 15]. While most of these parameters can be tuned and optimized such that the phase separation occurs on the exciton diffusion length scale, there still exists charge mobility hindrances in the active area such as dead-ends, islands, and bottle-neck areas (Figure 2a) which can reduce device efficiency.

PRINT is a promising technology for patterning a wide variety of inorganic oxides into ordered arrays [16]. Nanostructured TiO₂ structures have been fabricated using the PRINT process, and infiltrated with P3HT to form solar cells [17]. The nanostructured devices showed a two-fold increase in short-circuit current relative to flat bilayer devices. In addition to the fabrication of nanostructured inorganic oxides as 'acceptor' templates, PRINT can be used to fabricate the ideal nanostructures for polymeric 'donor' materials.

Polymer Nanostructures and Devices

Poly(3-hexyl)thiophene-methanofullerene BHJ cells have shown the highest recorded efficiencies to date in solid state organic solar cells [18]. As stated in the introduction, these disordered networks have much room for improvement if the morphology of the donor-acceptor network can be controlled such that exciton splitting and charge carrier collection efficiencies are maximized by forming the ideal device architecture. There have been several attempts to fabricate ordered BHJ's in organic PV systems, in particular a promising technique is to use vapor phase deposition to control the crystal growth of a small molecule 'donor' used in OPV systems [19]. Kim *et. al.* have

patterned a deprotectable polythiophene to show how a surface area increase of the donor-acceptor interface can increase device performance [20].

Shown below in Figure 3 is a variety of patterns formed in a range of semiconducting polymers typically used in PV applications. These patterns are on the 200 nm length scale and over a large area (in.²). Though the length scale is large for phase separation in a heterojunction, this does prove that nanopatterns can be formed over large areas in a variety of polymers using the PRINT technique. It should be noted that nanostructures can be formed either using capillary filling techniques similar to that shown in Figure 1 D'-F' or using more traditional imprint techniques as shown in H-J.

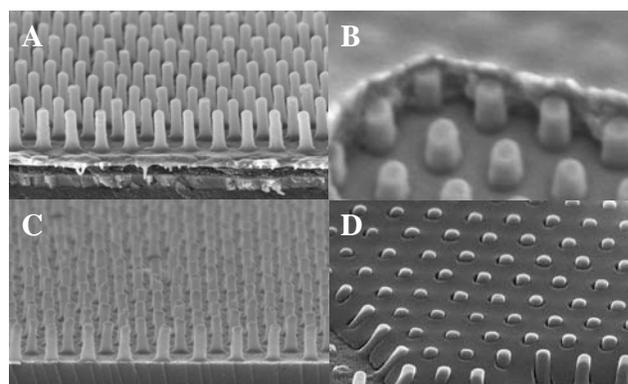


Figure 3. Scanning electron microscope images of (A) 200 x 600 nm cylindrical patterns of poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) (B) 200 nm x 200 nm cylinders patterned in PCBM with melted P3HT over the nanostructures (C) 200 x 600 nm cylindrical patterns of alternating poly(3-(2-methyl-2-hexylcarboxylate)thiophene-co-thiophene) (TDPTD) (D) 200 x 600 nm sodium poly[2-(3-thienyl)ethoxy-4-butylsulfonate] (Na⁺:PTEBS) cylindrical features coated with [(6)-1-(3-(methoxycarbonyl)propyl)-(5)-1-phenyl-[6,6]-C61] (PCBM).

Realizing that smaller length scales, yet large areas, are desirable for PV applications, we have also begun fabricating 'large-area' grating style master templates using e-beam techniques. Obtaining a large area master template with ordered, sub-100 nm features requires direct write e-beam which is quite time consuming to form patterns over cm² areas. However, once the master template is formed it is a permanent fixture of the PRINT process. We have focused on fabricating grating style structures with 120 nm periodicity and 100 nm heights. These nanostructures were successfully replicated in poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) as shown in Figure 4. Currently we are working to fabricate smaller nanostructures and on methods to control solubility of the polymeric nanostructures for subsequent solution deposition of accepting materials.

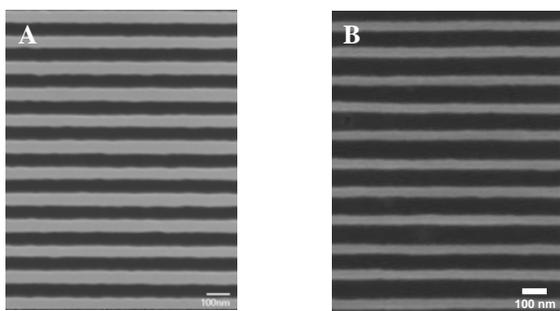


Figure 4. Scanning electron microscope images of (A) Si-master template with grating style features of 120 nm periodicity x 100 nm height (B) MDMO-PPV nanostructures formed from replicating master template in A.

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