Nanoimprint-Induced Molecular Stacking and Pattern Stabilization in Small-Molecular Organic Compounds for Photovoltaic Applications

Xiaogan Liang,* Manuel Moritz, Teresa Chen, Yeon-Sik Jung, Yoshikazu Miyamoto, Gang Han, Biwu Ma, Stefano Cabrini, and Deirdre L. Olynick

Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720

Organic photovoltaic (OPV) are of great interest due to the potential for low cost solar energy conversion. OPV's based on small molecular weight organic compounds have additional advantages over polymeric PV materials, such as higher purity and thermal stability.[1] The carrier donor/acceptor interface morphology is continually being optimized to improve photo-generated exciton dissociation and thus energy conversion efficiency.[2, 3] Nanoimprint lithography (NIL) offers the potential for producing well-defined interpenetrating networks at the donor/acceptor (DA) interface and is compatible with roll-to-roll manufacturing for low-cost and high-throughput nanopatterning.[4, 5] Although nanoimprint with sub-20 nm pitch features has been widely demonstrated in polymeric materials, small-molecular weight organic compounds are difficult to pattern due to poor stability of imprinted nanostructures. Such instability is attributed to surface energy effects which enhance surface diffusion and self-faceting in small-molecular compounds, especially in the single-digit nanometer regime.[6] In this work, we systematically study the thermodynamic and kinetic behavior of imprinted features in small-molecular organic compounds and identify key processing parameters to create stable imprinted nanostructures.

As an example, Fig. 1 shows the thermal nanoimprinting of subphthalocyanine (SubPc), a very attractive OPV material. Before template removal, the SubPc can be molded conformally to the template (Fig. 1b). However, after room temperature separation of this template from the substrate, the imprinted features relax to a quasi-equilibrium aspect-ratio (or contrast) due to the surface diffusion, which is highly dependent on the imprinting temperatures (Fig. 2a). The highest feature contrast occurs at a specific window of imprinting temperatures (80 – 90 ^{o}C). X-ray diffraction (XRD) indicates that the nanoimprint at such a temperature-window can induce high-degree molecular stacking, which can help stabilize the imprinted features. In addition, other small-molecular weight materials, including methyl-acetoxycalixarene, copperphthalocyanine, and triphenylene, have been tested to compare the stability of the imprinted features to SubPc. Several similarities were found and dewetting played a critical role in the patterned film stability (Fig. 3).

Simulations show that surface anisotropy plays a critical role in the stability of low molecular weight organic nanostructures. The experimental approaches and theoretical models developed in this work can serve as a useful guideline for producing stable nanostructures in various small-molecular compounds and for improving the performance of OPV cells.

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* Email: xliang@lbl.gov

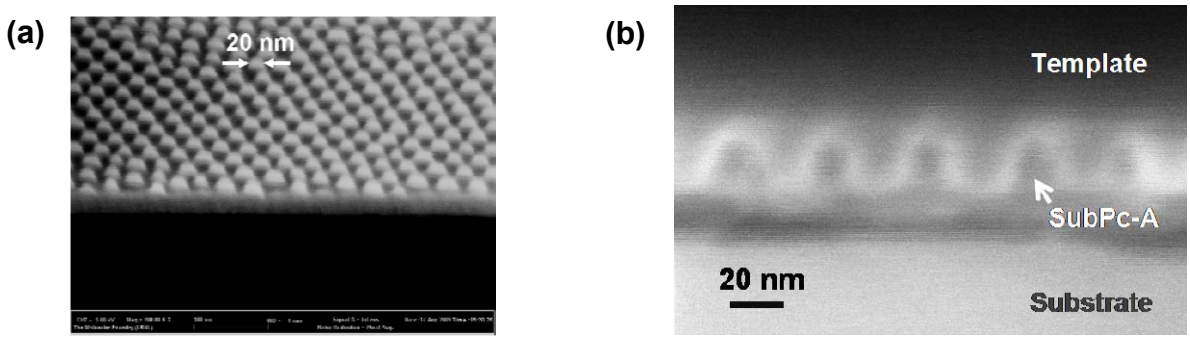

Fig. 1 (a) Tilted SEM image of a Si nanoimprint template bearing hexagonally-arranged posts with diameter of 20 nm and feature height of 22 nm. Features were fabricated with block-copolymer lithography (BCPL) followed with plasma etching of the silicon. (b) The cross-sectional SEM image displaying a representative imprinting process, which was achieved by mechanically cutting template/SubPc/substrate sandwich before template separation.

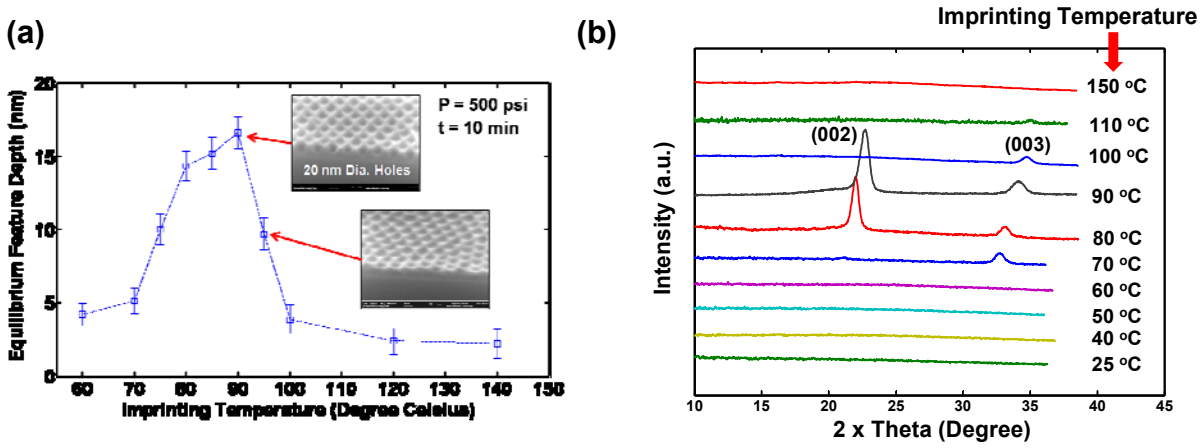

Fig. 2 (a) The imprinted feature depths were measured by using cross-sectional SEM and plotted as a function of imprinting temperatures. The insets shows representative cross-sectional SEM images of imprinted SubPc-A. (b) XRD spectra of SubPc samples (represented in (a)) imprinted at various temperatures.

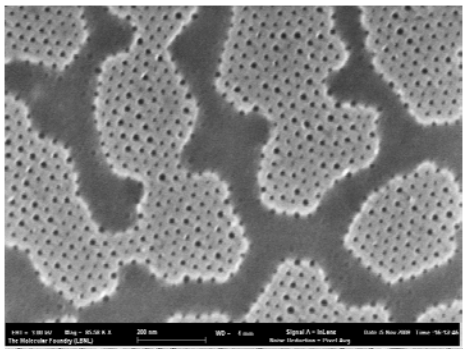

Fig. 3 An SEM image of imprinted calixarene at 150 ^{o}C using silicon imprint template bearing hexagonally-arranged 20 nm dia posts (patterned by BCPL). Hierarchical structures were formed including 20 nm dia. hexagonal holes and island-like domains 100's of nm in size. These are attributed to the dewetting process initiated by Rayleigh-like instability. [7]

* Email: xliang@lbl.gov