

# Patterning via Optical Saturable Transformations via Solubility Rate Difference

P. Cantu,<sup>1</sup> T. L. Andrews,<sup>2</sup> and R. Menon<sup>1\*</sup>

<sup>1</sup>*Department of Electrical and Computer Engineering, University of Utah,  
Salt Lake City, UT 84112*

<sup>2</sup>*Department of Chemistry, University of Wisconsin-Madison,  
Madison, WI 53706*

\**rmenon@eng.utah.edu*

The ability to pattern sub-wavelength features on various substrates with high throughput, accuracy, and uniformity has become increasingly important as technology continues to push the limits of feature size to the nanometer scale. Patterning via Optical Saturable Transitions (POST) is a high-throughput, low-cost, novel nanopatterning method proposed and demonstrated recently<sup>1,2</sup>. This approach circumvents the far-field diffraction limit<sup>3</sup> by exploiting the switching properties of novel organic photochromic molecules, Scheme 1. Previously, an electrochemical oxidation “locking step”<sup>1,2</sup> was used to pattern isolated lines as both positive tone and negative tone resists as narrow as  $\lambda/8$  and  $\lambda/16$ , respectively, with resolved spacing between features as narrow as  $\lambda/4$ , where  $\lambda$  is the exposure wavelength. In contrast with other diffraction-limited methods, POST does not have the restriction of high light intensity to achieve these nanoscale resolutions.

Here, we report an electrode-free technique as a highly selective “locking step” that bypasses electrochemical oxidation by exploiting difference in solubility between the two thermally stable photoisomer states of the molecule, Fig 2. In the POST process, a thin film, of a novel photochromic diarylethene derivative, namely, 1,2-bis(5,5'-dimethyl-2,2'-bithiophen-yl) perfluorocyclopent-1-ene, is thermally evaporated onto a substrate (i.e. silicon wafer). Upon uniform irradiation with short-wavelength UV,  $\lambda_1$ , the open-ring isomer, **1o**, converts to the closed-ring form, **1c**. A subsequent illumination with a node,  $\lambda_2$ , at 633nm converts the molecules back to the open-ring form, **1o**, except in the near-vicinity of the node. By optically saturating this transition, the molecules in the closed-form, **1c**, remain in a region that is far smaller than the far-field diffraction limit. It is at this stage that the solubility difference “locking step” is applied by developing the sample in a polar solvent (100% ethylene glycol). This highly selective solubility “locking step” opens the door to an inexpensive, scalable nanopatterning technique.

An experimental demonstration of POST technique using the solubility difference “locking step” is shown in Fig. 3.

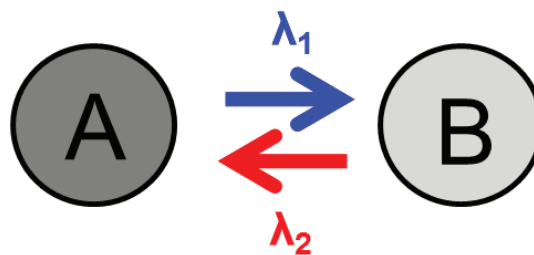
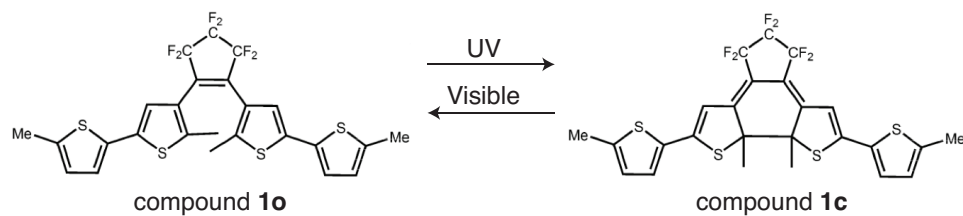
In this presentation, we will describe our experiments to improve the robustness of the process as well as present preliminary patterning of complex 2D geometries with POST.

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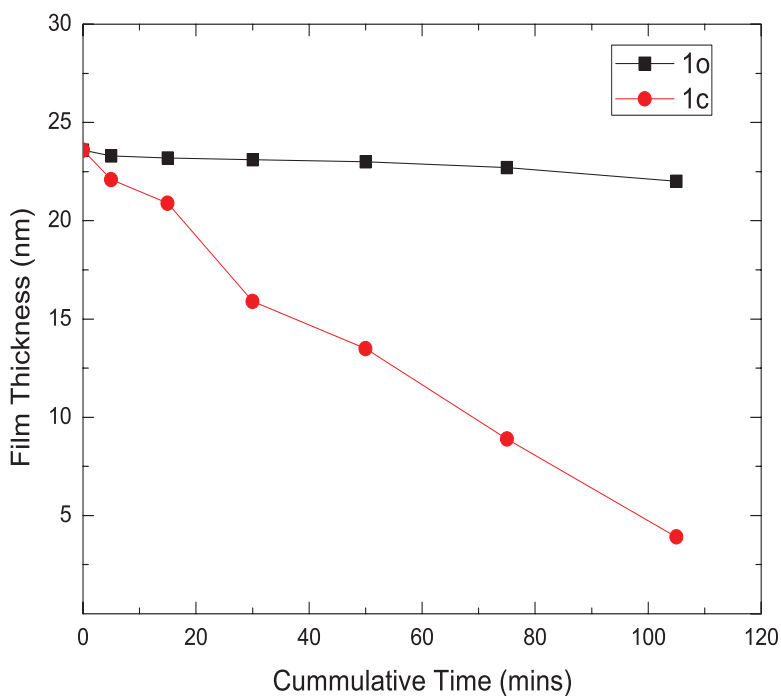
[1] N. Brimhall, et al, *Breaking the Far-Field Diffraction Limit in Optical Nanopatterning via Repeated Photochemical and Electrochemical Transitions in Photochromic Molecules*, Physical Review Letters. 107, 205501 (2011).

[2] P. Cantu, et al, *Subwavelength nanopatterning of photochromic diarylethene films*, Applied Physics Letter. 100, 183103 (2012).

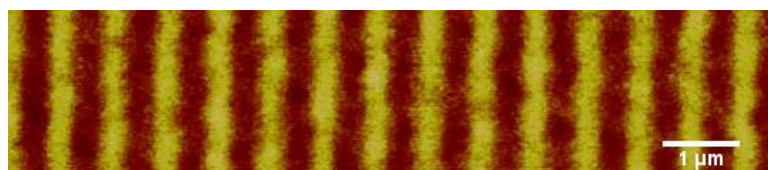
[3] E. Abbé, Arch. Mikrosk. Anat. Entwicklungsmech. 9, 413 (1873).



**Scheme 1:** A novel diarylethene based nanopatterning system based on photochromism and solubility. The suffix “o” or “c” after the compound number refers the ring open (e.g., **1o**), ring closed (e.g., **1c**) of the diarylethene component.



**Figure 2:** Dissolution of ~25nm thin-film of open form (**1o**) and closed form (**1c**) organic photochromic molecule (BTE) in 100% Ethylene Glycol solvent over various times.



**Figure 3:** Lines of width ~140nm patterned with 633nm light. The sample was exposed to a red standing wave for 5 hrs 14 mins, and developed in 100% Ethylene Glycol for 60 seconds.