

# Breaking the diffraction barrier in nanopatterning with optical saturable transformations

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

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

*Department of Chemistry, Massachusetts Institute of Technology,  
Cambridge, MA 02139*

*\*rmenon@eng.utah.edu*

Photons offer many advantages over charged particles for nanopatterning. For example, photon beams are easily parallelized and are not subject to placement errors due to stray electromagnetic fields. However, optical patterning is limited in resolution by the far-field diffraction barrier to about half the wavelength.<sup>1</sup> This barrier can be overcome in the near field,<sup>2</sup> but these approaches are typically difficult to parallelize. Far-field approaches that circumvent the diffraction barrier<sup>3,4,5</sup> have required high light intensities, which also limit parallelizability. Here we discuss a far-field nanopatterning technique that uses photochemical transitions to break the diffraction barrier using only low light intensities, opening the door to massive parallelization. We call this method Patterning via Optical Saturable Transformations (POST).

We demonstrate POST using a photochromic molecule, 1,2-bis(5,5'-dimethyl-2,2'-bithiophen-yl)perfluorocyclopent-1-ene, as the recording medium. POST is enabled by the 3 transitions of this molecule as indicated in Fig. 1 (left). Uniform illumination from a UV lamp first converts the photochromic film to the closed form. The film is then illuminated with a node at 633 nm. This converts the entire film to the open form, except for a diffraction-unlimited region near the node, which remains in the closed form. Because the closed form of this molecule exhibits extended conjugation, oxidizing this film at a low potential selectively converts the molecules in closed form to a 'fixed' form, *i.e.*, the stable radical cation. Repeating these three steps with intervening displacements of the sample, then selectively dissolving the oxidized form away in a polar solvent leads to nanoscale topography.

In this presentation, we will describe our recent experiments showing patterning beyond the diffraction limit (Fig. 2). We will also present simulations that demonstrate the potential of this approach.

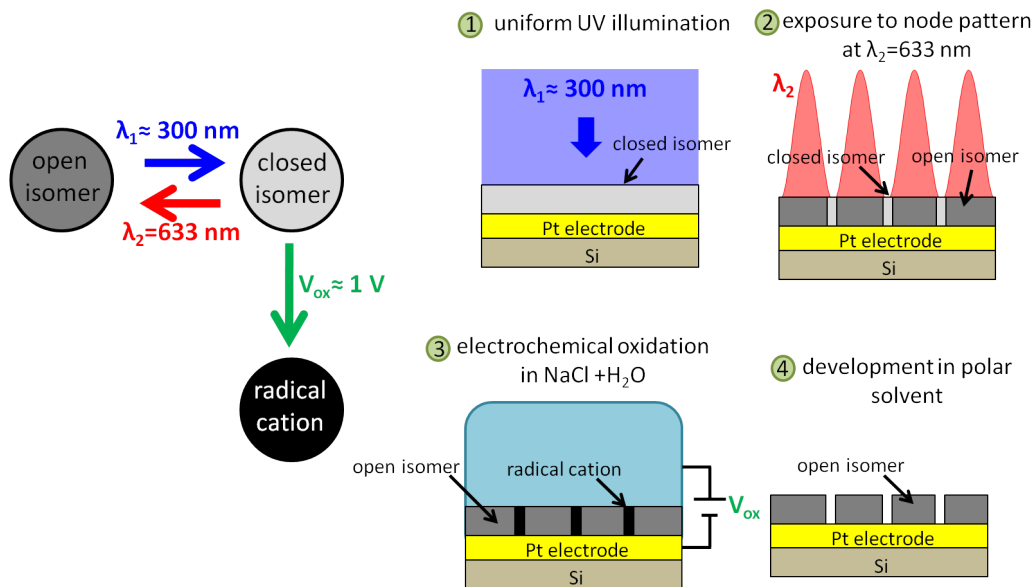
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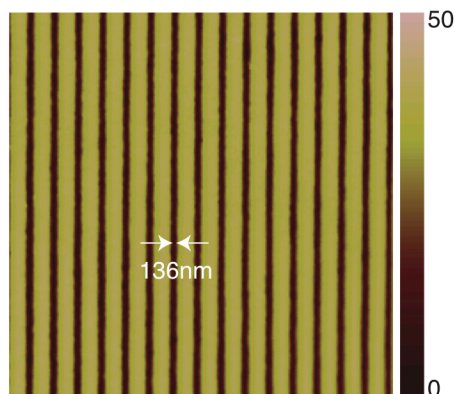
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**Figure 1:** (left) Scheme for the photochromic layer. (right) Sequence of steps for a single POST exposure. Uniform UV illumination converts all molecules to the closed isomer. A set of nodes at  $\lambda = 633 \text{ nm}$  converts all molecules to the open isomer except near the nodes. Electrochemical oxidation selectively converts the closed isomer to a stable radical cation. These three steps can be repeated with intervening displacements of the sample to create dense features whose spacing is smaller than the diffraction limit (not shown). A polar solvent selectively dissolves the radical cation, resulting in nanoscale topography.



**Figure 2:** Lines of width  $\sim 130 \text{ nm}$  patterned with  $633 \text{ nm}$  light. The sample was exposed to a red standing wave for 45 mins, electrochemically oxidized for 10 mins and developed in IPA:ethylene-glycol (95:5) for 60 seconds.