Deep-subwavelength patterning with photoswitchable molecules

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The prospect of circumventing the diffraction barrier[1] by using photons with only low light intensities, allowing direct and massively parallel nano-patterning of a silicon surface is an exciting one. This would, however, previously require decreasing the wavelength, λ, used, increasing the numerical aperture, NA, or scaling of the process dependent parameter, k, which brings complexity to the optical systems and increased costs. Nevertheless, for relatively small wavelengths, 13.5nm (Extreme ultra violet), it has already been possible to pattern sub-10nm features, λ/4, using EUV interference lithography[2]. However, the delay in wide spread industry adoption of EUV lithography is not only the cost of the complex optical system, but also the sensitivity of the photoresist material[3], as they rely on the availability of ultra-high resolution lithography tools.

Here, we present large-area sub-wavelength resolution in optical nano-lithography: 1D periodic-gratings and 2D periodic nanostructures of sub-wavelength dimensions by exploiting photochemical transitions of photochromic thin films. We call this method Patterning via Optical Saturable Transformations (POST). A novel photochromic diarylethene derivative, namely, 1,2-bis(5,5′-dimethyl-2,2'-bithiophen-yl) perfluorocyclopent-1-ene, is used to demonstrate POST, Scheme 1. Upon irradiation with short-wavelength UV, the open-ring isomer, 1**o**, converts to the closed-ring form, 1**c**. A subsequent illumination with a node at 633nm converts the molecules back to the open-ring form, 1**o**, except in the near-vicinity of the node. By optically saturating this transition, the molecules in the closed-form, 1**c**, remain in a region that is far smaller than the far-field diffraction limit. Then, by selective-oxidation of the closed-ring form, 1**c**, into a stable radical cation, 1**ox**, the patterning is complete. Finally, the cations are dissolved in a polar solvent, leaving behind a nanoscale topography. The proposed fabrication technique is fast and straightforward, providing an attractive alternative of circumventing the diffraction barrier. We experimentally demonstrate large-area 1D and 2D nanostructures with an illumination of 633nm (red light) and obtain a resolution several times beyond the diffraction limit. The POST technique, for which we recently demonstrated a proof of concept[4], as well as theoretically treating the "optical node" in the creation of features[4], relies on saturating the optical transition of a novel photochromic thin film and coupling this with a "fixing" step in order to create dense features beyond the far-field diffraction limit, not dependent upon the wavelength of light used. This work paves the way for high-volume optical nano-patterning of dense patterns down to sub-wavelength resolution without costly optical equipment, depending only on the quality of the optical node. For example, POST could considerably improve optical lithography resolution at low light intensities with high parallelizability, without the need for complex optical systems. An experimental demonstration of the POST technique is shown in Fig. 2.

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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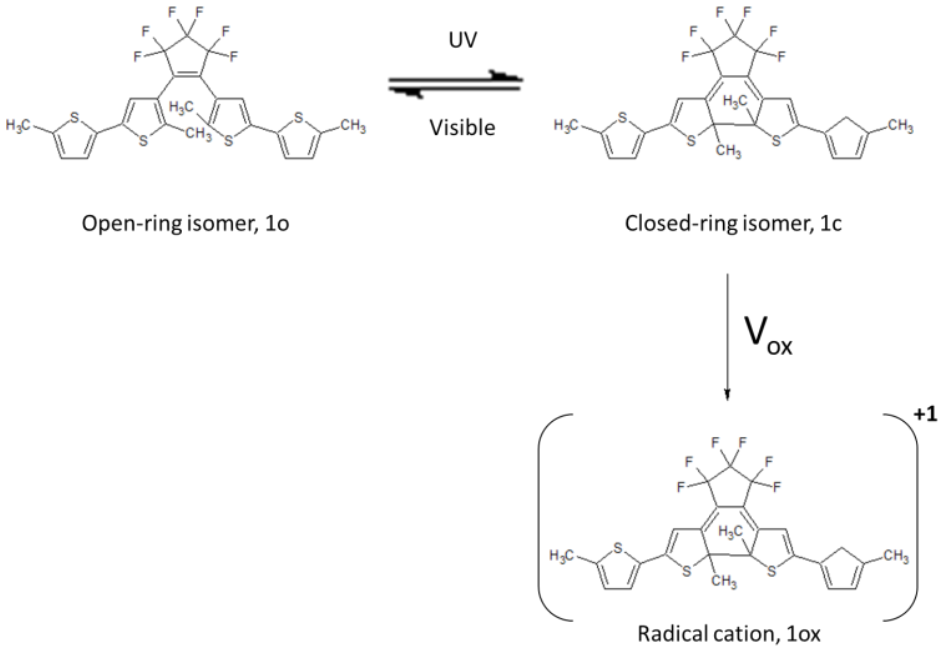

Scheme 1: *A novel diarylethene based nanopatterning system based on photochromism and electrochemistry. The suffix "o", "c", or "ox" after the compound number refers the ring open (e.g., 1**o**), ring closed (e.g., 1**c**) or radical cation state (e.g., 1**ox**) of the diarylethene component.*

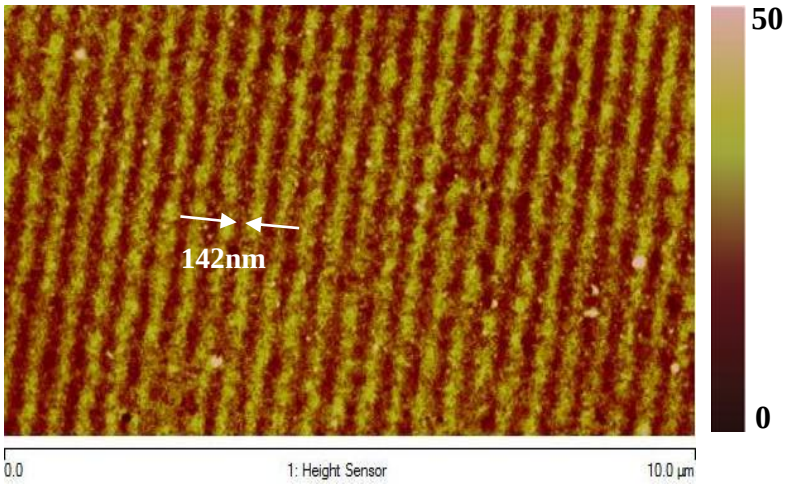

Figure 2: *Lines of width ~140nm patterned with 647nm light. The sample was exposed to a red standing wave for 15 mins, electrochemically oxidized at I_{peak}/8 and developed in IPA:ethylene-glycol (95:5) for 60 seconds.*