

Sub-Wavelength Optical Patterning via Optical-Saturable Transformations

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Abstract

The advent of scanning-electron-beam lithography (SEBL) has enabled the controlled manufacture of structures on the nanoscale in the past 20 years. However, SEBL is a serial process and hence unsuitable for patterning nanostructures over larger areas. Optical lithography, on the other hand, enables parallelism and hence is scalable; however, conventional optical lithography is limited by diffraction to feature sizes greater than about half the wavelength.

In the past, we demonstrated absorbance modulation to overcome this limit,¹ employing photochromic molecules that can be optically switched between two thermally stable states to form an optical nanoscale probe, the size of which is not limited by diffraction. Here, we report on an alternative approach that exploits a specific sequence of spectrally-selective reversible and irreversible photochemical transitions to achieve deep subwavelength resolution with potential extension to three dimensions. This approach, which we refer to as Patterning via Optical-Saturable Transformations (POST), involves only single-photon transitions and hence, has the potential for massive parallelism and high speeds.

Similar to absorbance modulation, POST utilizes photochromic molecules. But unlike absorbance modulation, POST requires an isomer-selective irreversible transformation to a “fixed” state as illustrated in Fig. 1. In this case, a film of molecules in an initial form B is exposed to a focused ring (node) at wavelength λ_2 . All regions of the film that receive non-zero intensity will convert to form A. In the vicinity of the node, a small population of molecules will remain in form B. A subsequent transformation can convert this population to the fixed form C. Next, uniform illumination at λ_1 brings all the molecules in form A back to form B while the molecules in form C retain their state. After translating the sample, the process is repeated to create complex geometries in a “dot-matrix” fashion. The pattern of molecules in form C can later serve as a resist for pattern transfer into an underlying substrate.

In this presentation, we will describe two diarylethene photochromes for POST. These molecules and their expected transformations are shown in Fig. 2. Due to the extended conjugation of the closed-form isomer, the oxidation potential of the closed-form is lower than for the open forms.² Thus, the irreversible “fixing” step is achieved by selective electrochemical oxidation of the closed-form isomer into either a stable dication (Fig. 2(a)) or into a quinoid structure (Fig. 2(b)). In both cases, the oxidized form can be selectively removed with appropriate solvents.

In order to demonstrate optical nanopatterning, we built a dual-wavelength Lloyd’s mirror interferometer, where the sample is illuminated either by a standing wave at λ_c or uniform beam at λ_o . The sample was mounted on a high-precision stage to enable multiple exposures. We will also describe our nanopatterning experiments and related results.

References:

[1] T. L. Andrew, H-Y. Tsai, and R. Menon, *Science*, **324**, 217 (2009).

[2] T. Saika, M. Irie, and T. Shimidzu, *J. Chem. Commun.* **1994**, 2123-2124 (1994).

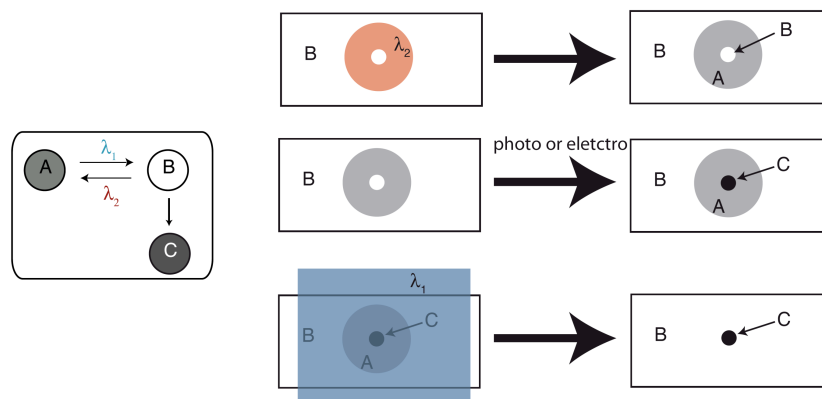


Fig. 1: (left) Molecular transformations required for POST. (right) Sequence of steps to create a deep-subwavelength region in a form C that is distinct from neighbors. The isomer-selective irreversible transformation from B to C may be electrochemical as indicated in Fig. 2 or photo-initiated.

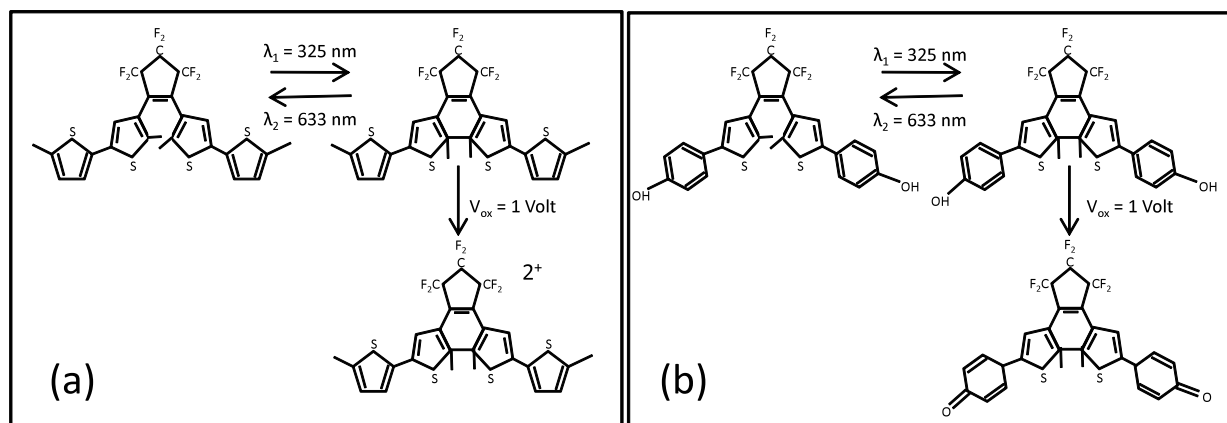


Fig 2: Two photochromic diarylethene molecules that we investigated for POST.