Video Article

Patterning via Optical Saturable Transitions - Fabrication and Characterization

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Abstract

This protocol describes the fabrication and characterization of nanostructures using a novel nanolithographic technique called Patterning via Optical Saturable Transitions (POST). In this technique the chemical properties of organic photochromic molecules that undergo single-photon reactions are exploited, enabling rapid top-down nanopatterning over large areas at low light intensities, thereby, allowing for the circumvention of the far-field diffraction barrier.[4] Simple, cost-effective, high throughput and resolution alternatives to nanopatterning are being explored, such as, two-photon polymerization[5,6], beam pen lithography (BPL)[7], scanning electron beam lithography (SEBL), and focused ion beam (FIB) patterning. However, multi-photon approaches require high light intensities, which limit their potential for high throughput and offer low image contrast. Although, electron and ion beam lithographic processes offer increased resolution, the serial nature of the process is limited to slow writing speeds, which also prevents patterning of features over large areas. Beam-pen lithography is an approach towards parallel near-field optical lithography. However, the gap between the source of the beam and the surface of the photoresist needs to be controlled extremely precisely for good pattern uniformity and this is very challenging to accomplish for large arrays of beams. Patterning via Optical Saturable Transitions (POST) is an alternative optical nanopatterning technique for patterning sub-wavelength features[1-3]. Since this technique uses single photons instead of electrons, it is extremely fast and does not require high light intensities[1-3], opening the door to massive parallelization.

Video Link

The video component of this article can be found at https://www.jove.com/video/52449/

Introduction

Optical lithography is of key importance in the fabrication of nanoscale structures and devices. Increased advancements in novel lithography techniques has the ability to enable new generations of novel devices.[8-11] In this article, a review is presented of a class of optical lithographic techniques that achieve deep sub-wavelength resolution using novel photoswitchable molecules. This approach is called Patterning via Optical-Saturable Transitions (POST).[1-3]

POST is a novel nanofabrication technique that uniquely combines the ideas of saturating optical transitions of photochromic molecules, specifically (1,2-bis(5,5'-dimethyl-2,2'-bithiophen-yl))perfluorocyclopent-1-ene. Colloquially, this compound is referred to as BTE, **Figure 1**, such as those used in stimulated emission-depletion (STED) microscopy[12], with interference lithography, which makes it a powerful tool for large-area parallel nanopatterning of deep subwavelength features onto a variety of surfaces with potential extension to 2- and 3-dimensions.

The photochromic layer is originally in one homogeneous state. When this layer is exposed to a uniform illumination of λ_1, it converts into the second isomeric state (**1c**), **Figure 2**. Then the sample is exposed to a focused node at λ_2, which converts the sample into the first isomeric state (**1o**) everywhere except in the near vicinity of the node. By controlling the exposure dose, the size of the unconverted region may be made arbitrarily small. A subsequent fixing step of one of the isomers may be selectively and irreversibly converted (locked) into a 3rd state (in black) to lock the pattern. Next, the layer is exposed uniformly to λ_1, which converts everything except the locked region back to the original state. The sequence of steps may be repeated with a displacement of the sample relative to the optics, resulting in two locked regions whose spacing is smaller than the far-field diffraction limit. Therefore, any arbitrary geometry may be patterned in a "dot-matrix" fashion.[1-3]

Protocol

NOTE: perform all the following steps under cleanroom class 100 conditions or better.

1. Sample Preparation

1. Clean a 2" diameter silicon wafer with Buffered Oxide Etch (BOE) solution (6 parts 40% NH_4F and 1 part 49% HF) for 2 min (**Caution: Hazardous chemicals**). Choose this etch time to remove any organics or contaminants on the surface. Rinse with deionized (DI) water for approximately 5 min. Dry wafer with dry N_2.
NOTE: Never work alone when using HF. Always wears eye protection with face shield and personal protective equipment (PPE) in case of spills. Post guidelines for the use and handling of HF waste in the lab where the etching is performed.
NOTE: Steps 1.2 to 1.7 are for electrochemical *locking* only. If performing locking via dissolution proceed to Step 2.
2. To lay down the working electrode, sputter 100 nm of Platinum (Pt) onto the clean 2" diameter silicon wafer.
3. Before etching the platinum thin film, clean the RIE chamber of any impurities or leftover photoresist from previous dry etches.
4. Pump down the chamber until a base pressure of 1×10^{-5} Torr is achieved. Make sure that the RF power is set to 200 W and the flow rates for the oxygen and argon are set to 50 sccm and 10 sccm respectively. Ignite the Ar/O_2 plasma and run for at least 1 hr.
5. Turn off the Ar/O_2 plasma and allow the chamber vent for approximately 10 min.
6. To etch the platinum thin film surface, load the sample into the RIE chamber and pump the chamber down to a base pressure of 1×10^{-5} Torr. This time set the argon flow rate to 0 sccm. Ignite the O_2 plasma and let this process run for 30 min.
7. Turn off the O_2 plasma and let the chamber vent for 10 min.

2. Thermal Evaporation of Photochromic Molecule Using Custom Low Temperature Evaporator (LTE)

1. Fill AlO_2 boat with 30 mg of BTE and load into custom LTE source (**Figure 6**).
2. Load silicon wafer into sample mount.
3. Seal chamber ports and pump chamber down to a base pressure of 1×10^{-6} Torr.
4. Evaporate the BTE at a setpoint temperature of 100 °C, with a film thickness of 30 nm.
5. Immediately after evaporation, flood illuminate the sample to 5 min of UV to transform the BTE material to the closed form, **1c**.
6. In order to define the sample size, cleave a small piece of the wafer using a diamond scribe to scratch a line from the edge of the silicon surface. Grab the wafer on both sides of the scratch line and bend the wafer downwards until it breaks along the crystal plane.
7. Perform profilometer measurements to validate BTE thin film thickness. To do this, scratch the sample using a fine edge tweezers. Measure the step height from this scratch, which is the difference in height between the right and left cursor position.
NOTE: Inaccuracies in film thickness will result in discrepancies in exposure dose.
8. Store remaining sample in N_2 filled glovebox.

3. Exposures

NOTE: Perform all exposures under inert atmosphere conditions to prevent degradation of sample.

1. Cleave the sample by following the same procedure as outlined in step 2.6.
2. Load sample in inert atmosphere sample holder.
3. Mount inert sample holder on stage. Purge sample with N_2.
4. Expose the sample to the desired exposure time using an interferometer, such as the one shown in **Figure 8**.

4. Electrochemical Oxidation Using Three Electrode Cell

NOTE: Perform electrochemistry under inert atmosphere conditions to prevent degradation of sample.

1. Clamp a clean glass vial on top of the hot plate. Place a clean stirring bar in the vial. Turn on the stirrer.
2. Clean a new copper clip with methanol. Clean the platinum counter electrode with methanol.
3. Using a clean copper clip, clip the sample through one of the holes in the Teflon vial cap. Make sure to clip onto the exposed platinum only.
4. Place the Teflon vial cap onto the vial. Clip the red lead onto the platinum counter electrode and the black lead onto the copper clip holding the sample.
5. Using a clean syringe, fill the vial with filtered deionized (DI) water through the second hole in the Teflon vial cap. Fill as high without immersing any of the bare platinum on the sample.
6. Bubble nitrogen through the water for 3-5 min. Turn off the nitrogen.
7. Place the reference electrode in the second hole in the Teflon vial cap. Clip the white lead onto the reference electrode. Check to make sure none of the bare platinum on the sample is immersed.
8. Using a voltammograph, set the oxidation voltage to 0.5 V/sec.
9. After the desired oxidation time has elapsed, turn the power to the voltammograph off.
10. Remove the red, black, and white clips from the platinum counter electrode, copper clip, and reference electrode.
11. Expose the sample to UV for 5 min.

5. Sample Development — Electrochemical *Locking*

NOTE: Perform development under inert atmosphere conditions to prevent degradation of sample.

1. Develop the sample in filtered 5 (wt%) isopropanol, 95 (wt%) ethylene glycol for the desired amount of time. Note: Typically 50 nm samples are developed for 30-60 sec while 80 nm samples are developed for 60-180 sec.

2. Dry sample with dry N_2.
3. Immediately expose sample to 5 min of UV.

6. Sample Development — Dissolution *Locking*

NOTE: Perform development under inert atmosphere conditions to prevent degradation of sample.

1. Using 100 ml of ethylene glycol in a clean glass beaker, develop the exposed sample for the desired development time.
2. Dry sample with dry N_2. Immediately expose sample to 5 min of UV.

7. Multiple Exposures

1. If performing multiple exposures repeat steps 3-6 with a translation of the sample relative to the optics.

Representative Results

Fabricated samples:

Different oxidation times were characterized as illustrated by the atomic-force micrographs in **Figure 3** at an oxidation voltage of 0.85 V determined from cyclic voltammetry. The 50 nm-thick films were exposed to a standing wave at λ = 647 nm of period 400 nm for 60 sec at a power density of 0.95 mW/cm^2. As the oxidation time is increased from 10 min to 25 min, one can clearly see a loss of contrast as some of the regions comprised of **1o** get oxidized as well. The developer (5 (wt%) isopropanol: 95 (wt%) ethylene glycol) dissolves all oxidized portions. Larger oxidation times result in uneven line and increased surface non-uniformities after development. Therefore, a careful choice of the oxidation conditions is critical to patterning high-quality nanostructures.[2]

The higher dipole moment of the closed form of the molecule, **1c**, as compared to the open form, **1o**, allows for the closed form to be more soluble in polar solvents. This is represented in **Figure 4**, where half of the sample was converted to the closed form, **1c**, and the other half was converted to the open form, **1o**. The sample was then developed in 100 (wt%) ethylene glycol for several different development times and then the thickness of the film remaining was measured using a profilometer. From this graph the high selectivity of the dissolution *locking* step is seen. To remove the residual layer of the closed form, 1c, a reactive ion etching (RIE) process as used in nanoimprint lithography could be used.[13]

Since the photochromic film can readily recover to its original state upon exposure to UV, it is straightforward to extend the idea to multiple exposures. This is, of course, required for creating dense patterns. Here, the feasibility of this approach is shown by performing two exposures of the same standing wave, but with a ~45° rotation in between (**Figure 5**). Each exposure was conducted on the Lloyd's-mirror interferometer, with a standing wave of period, 540 nm at λ = 647 nm (incident intensity ~2.1 mW/cm^2) for 1 min. After the first exposure, the sample was immersed in 100 (wt%) ethylene glycol for 30 min and exposed to short-wavelength UV lamp for 5 min to convert the molecules to the original closed-ring isomer **1c**. The sample was then rotated approximately 45° relative to the optics, and a second exposure to the standing wave was performed. Again, the sample was immersed in 100 (wt%) ethylene glycol for 30 min. After each development, the sample was rinsed in deionized water and dried with N_2. The corresponding atomic-force micrograph resolves lines with spacing as small as ~260 nm or λ/2.5, which is less than half of the period of the standing wave.[3]

To verify the efficacy of the sample holder, several exposures were performed to see if the line edge roughness had improved. Assuming an incident sinusoidal illumination, the resulting feature size can be readily simulated. In **Figure 7**, this feature size is plotted as a function of the exposure time using the solid blue line. The experimentally measured values are shown using crosses. Using the exposure threshold as the only fitting parameter, it is shown that this simple model can accurately explain our experimental results. The smallest experimentally obtained feature size was ~85 nm, corresponding to a linewidth of ~λ/7.4. More precise control of the exposure time should enable even smaller features. Note that as the exposure time is increased, the simulation indicates that feature size should be reduced significantly below the far-field diffraction limit. From the scanning electron microscope (SEM) images, it is shown that the line-edge roughness has improved with the use of the inert atmosphere sample holder.
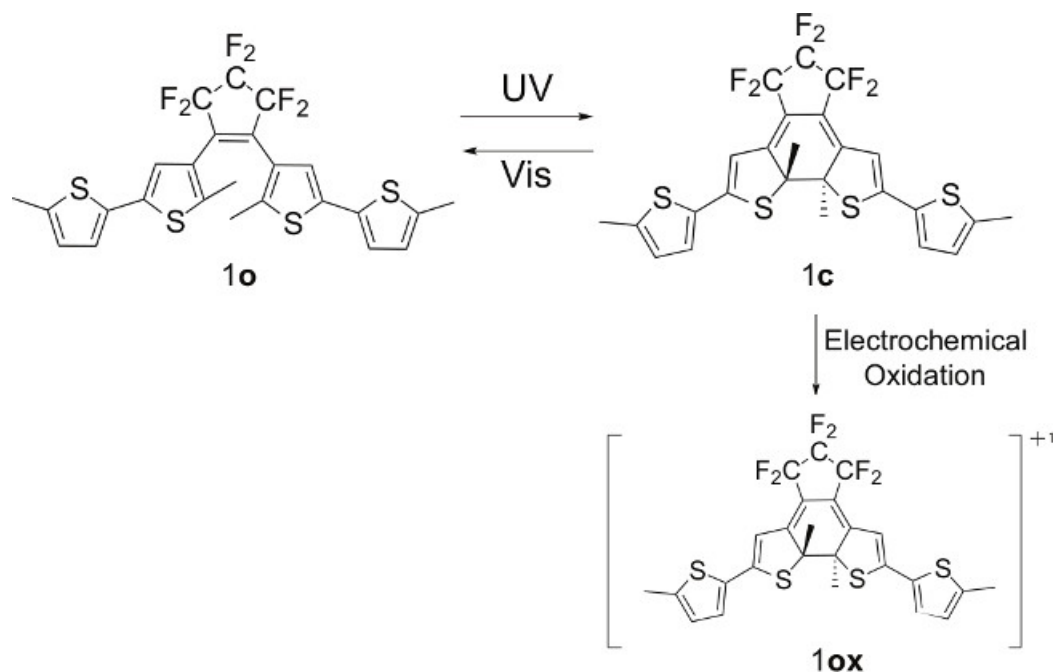
Figure 1. Organic photochromic molecule structure. Compound **1** exists in open form, **1o** and the closed form, **1c**. Electrochemical oxidation selectively converts **1c** to **1ox**.
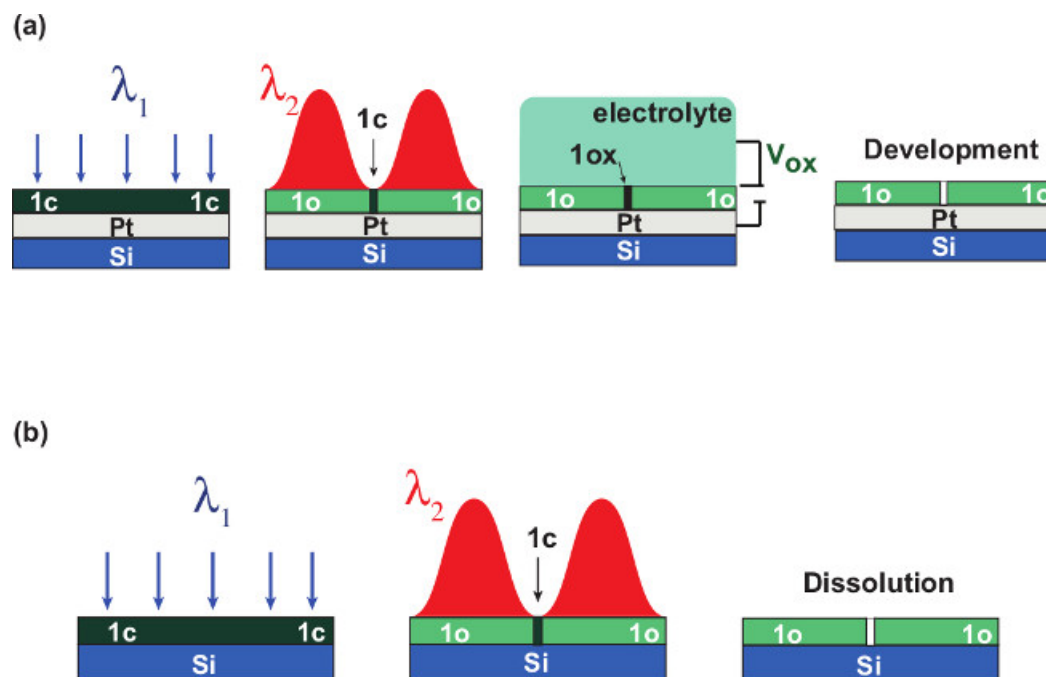

Figure 2. POST technique. Exposure and patterning "locking" steps required for recording feature. (**A**) Electrochemical oxidation. (**B**) Dissolution of one photoisomer.
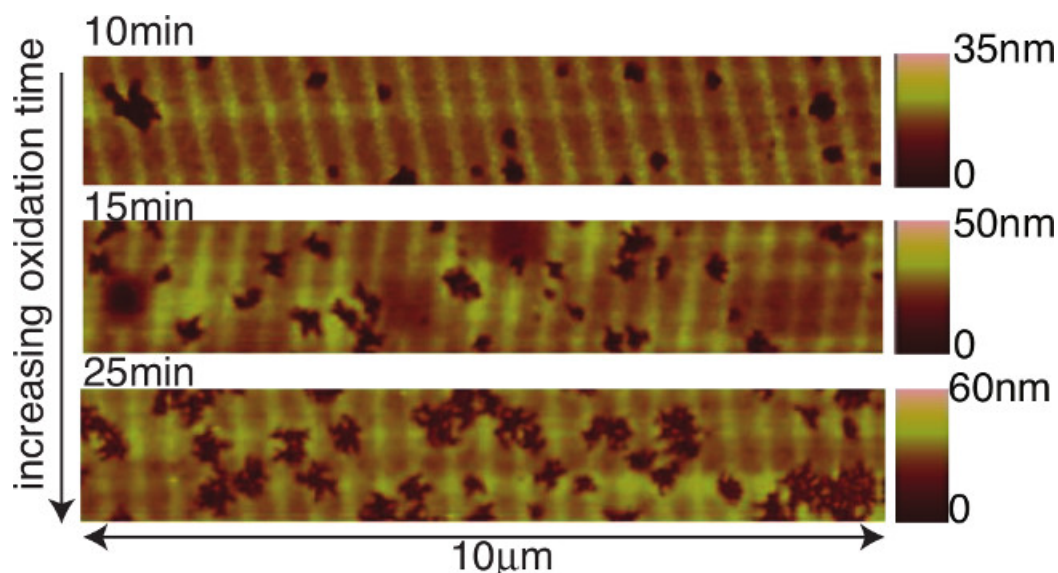
Figure 3. Isolated features. Atomic force micrographs of lines after development for samples at various oxidation times.[2] Thin-film thickness of ~50 nm. Reprinted with permission from [Cantu, P., *et al*. Subwavelength nanopatterning of photochromic diarylethene films. *App. Phys. Lett*. **100**(18), 183103]. Copyright [2012], AIP Publishing LLC. Please click here to view a larger version of this figure.
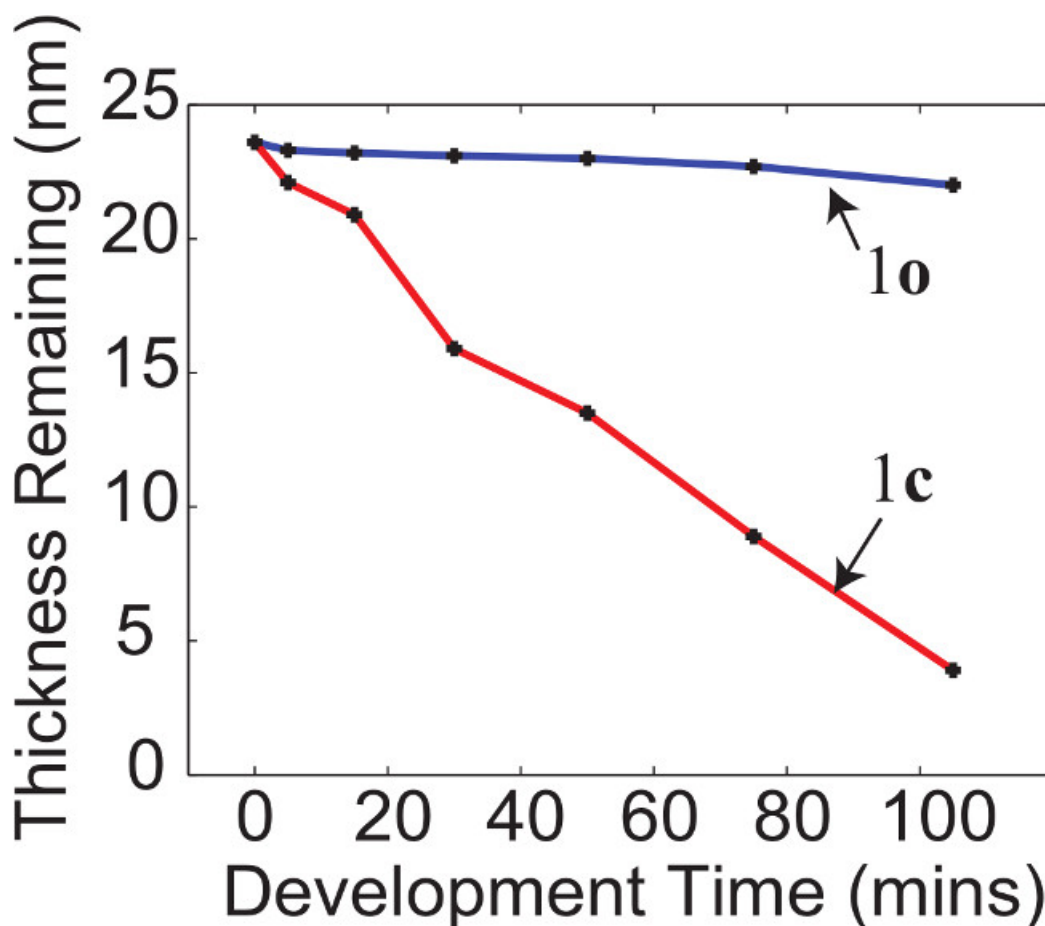
Figure 4. Dissolution rate. This figure shows the Macro-scale solubility of **1c** and **1o** in 100 (wt%) Ethylene glycol.[3] Thin-film thickness of ~29 nm. Reprinted with permission from [Cantu, P., *et al*. Nanopatterning of diarylethene films via selective dissolution of one photoisomer. *App. Phys. Lett*. **103**(17) 173112]. Copyright [2013], AIP Publishing LLC.
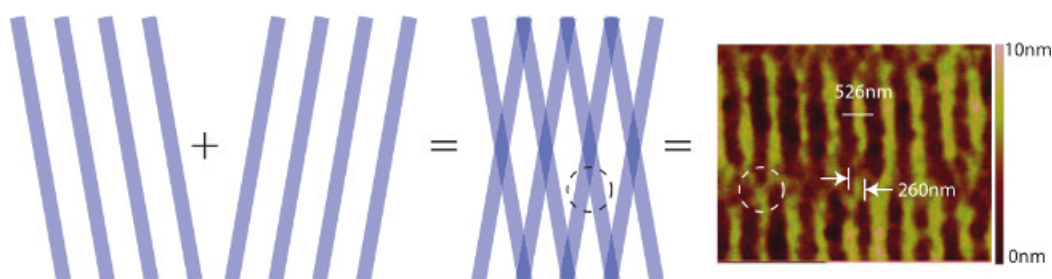
Figure 5. Experimental demonstration of a double-exposure. Left: Schematic showing orientation of sample for double-exposure using POST. **Right:** Atomic force micrograph of the resulting pattern. The atomic force micrograph reveals the smallest spacing between the features as ~260nm, which is approximately half the period of the illuminating standing wave.[3] Reprinted with permission from [Cantu, P., *et al*. Nanopatterning of diarylethene films via selective dissolution of one photoisomer. *App. Phys. Lett*. **103**(17) 173112]. Copyright [2013], AIP Publishing LLC. Please click here to view a larger version of this figure.
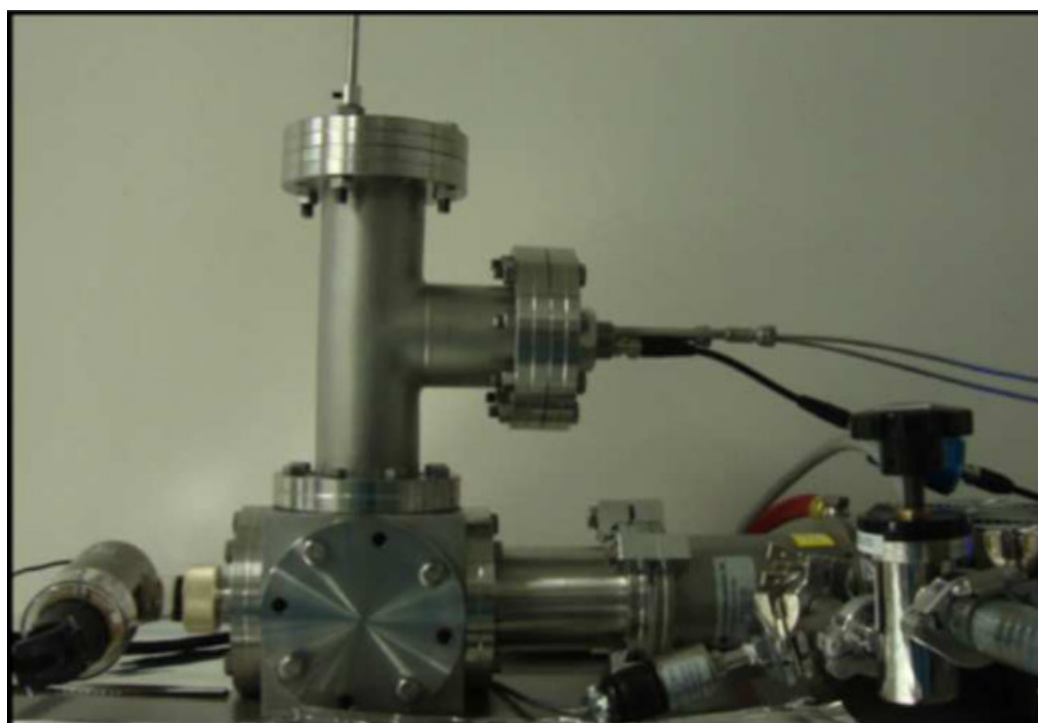

Figure 6. Custom evaporator. Image of the low temperature thermal evaporator (LTE) used in the POST technique.[2] Reprinted with permission from [Cantu, P., *et al*. Subwavelength nanopatterning of photochromic diarylethene films. *App. Phys. Lett*. **100**(18), 183103]. Copyright [2012], AIP Publishing LLC.
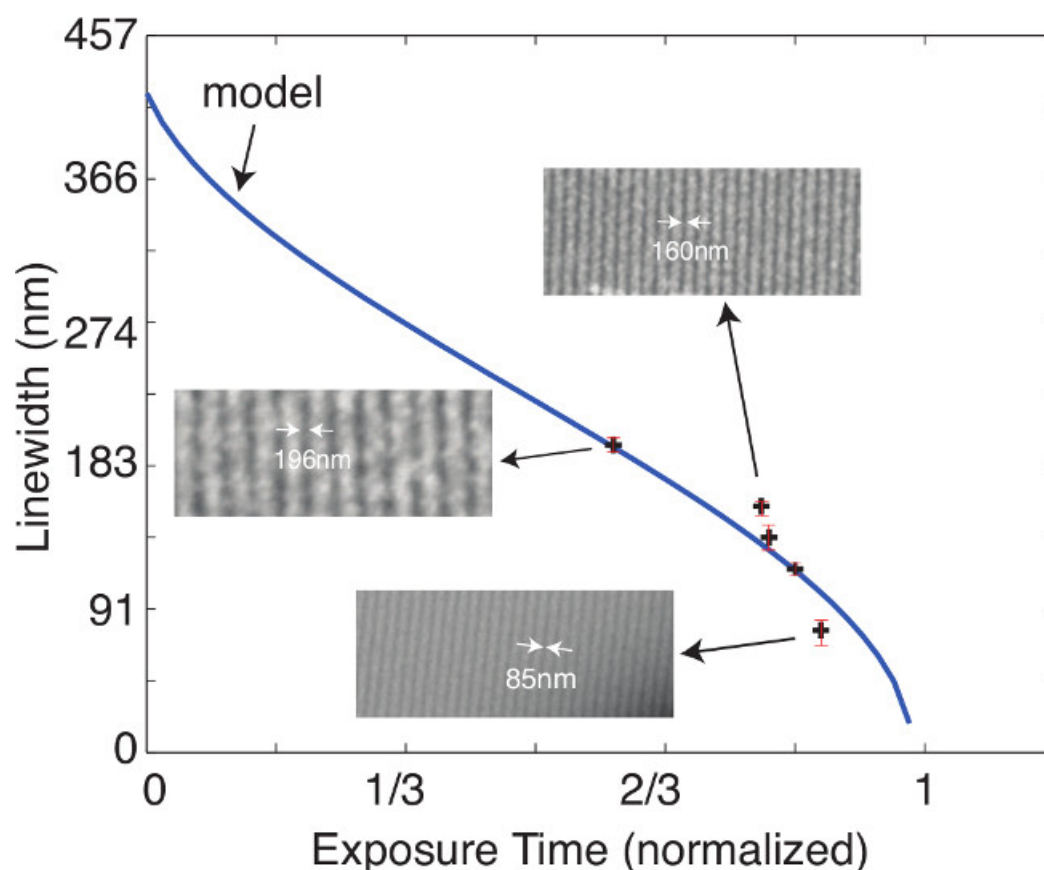
Figure 7. Linewidth vs exposure time for a single development and exposure. The incident simulated sinusoidal illumination is shown as a solid blue line, while the experimental data is shown using crosses. A sinusoidal illumination with period of 457 nm was assumed. Inset: SEM images. Please click here to view a larger version of this figure.
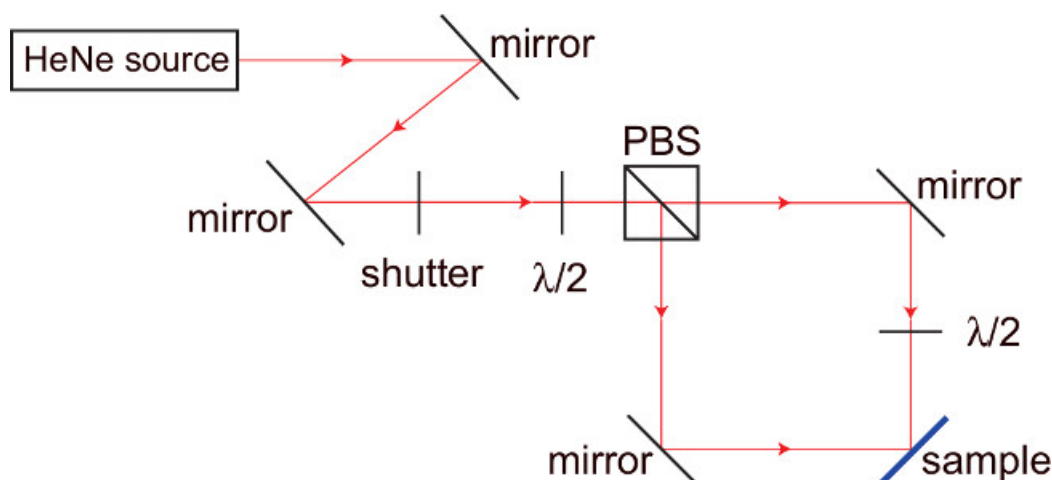
Figure 8. Schematic of the Mach-Zehnder interferometry setup used for exposures. The first half-wave plate is used to control the power in each arm. The second half-wave plate is used to control the polarization.

Discussion

The fabrication, experimental setup and related operational procedures of Patterning via Optical Saturable Transitions (POST) have been described. By exploiting the linear switching properties of thermally stable photochromic molecules, POST offers new perspectives on circumventing the far-field diffraction limit.[1-2,4]

Previously long-term storage requirement of the samples was solved by storing the samples under N_2, directly after the initial evaporation.[2] However, the significant line-edge roughness evident in the gratings, **Figures 3** and **5**, is likely due to the formation of oxidized products of **1c** in the presence of air.[2] Improving the uniformity of the patterns requires that the exposure and development process be conducted under an inert atmosphere. To address the exposures done in ambient conditions, a custom inert atmosphere sample holder was designed and fabricated. The

sample holder needed to provide a rigorous inert gas blanketing of the air-sensitive BTE in closed form, **1c** and maintain an excellent seal for sufficient time to obtain the appropriate exposure conditions. The holder was configured so that it could be easily modified for various optical configurations.

One way to address the exposure of the sample to atmosphere would be to design and fabricate an *in-situ* setup. The main goal of *in-situ* experimentation in both the electrochemical and dissolution method is performing the exposure, electrochemical oxidation, and development in an O_2 purged environment. Having the experiments performed *in-situ* would aid in the yield and quality of the desired nanostructures.

Currently the extension of this super-resolution technique, POST, to 3-dimensions, which would provide a promising approach to nanofabrication of nanoporous scaffolds, which act as supports for the initial cell attachment and subsequent tissue formation in biological tissue engineering (TE) is being investigated. The nanolithographic technique used to fabricate these initial scaffolds must produce a high yield and be at a low cost in order to produce any significant impact.[14]

There are, however, some limitations to the POST technique. The need for a separate locking mechanism (electrochemical or dissolution) requires an immersion-type setup. This could add associated complexities and cost if performed *in-situ*. Also, the need for a platinum layer for the electrochemical locking step (see **Step 1.2**) might preclude some already patterned substrates or devices. The organic compound (BTE), which is used as the recording medium, requires a relatively complex synthesis, which may add to the cost of the technique initially. However, with increased volumes, the cost should decrease.

Disclosures

The authors have nothing to disclose.

Acknowledgements

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