

Nanoscale Electromolecular Lithography (NEL)

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PIs: **Yong Chen,* Marya Lieberman,** Fraser Stoddart,* Xiang Zhang*****

*University of California, Los Angeles;

**University of Notre Dame;

***University of California, Berkeley

A new nanoscale manufacturing technique — nanoscale electromolecular lithography (NEL) is proposed for the fabrication of nanoscale patterns on resists by using an electric mask. In previous research, electron beam lithography (EBL) and atomic force microscopy / scanning tunneling microscopy (AFM/STM) probes have been used to generate nanoscale patterns on self-assembled molecular monolayers using electrochemical reactions. Although these techniques can reach molecular resolution, they can not be solutions for mass production due to their slow speeds. In NEL, we will develop high-speed and scalable top-down engineering techniques to create a practical, reliable, and robust nano-manufacturing technique for general application [1].

The NEL process is simple and straightforward: A layer of resist (pink) is coated onto a substrate-supported bottom electrode (blue), and then a mask with conductive metal patterns (blue) that are separated by insulating materials (sky blue) (**Figure 1a**) is pressed down toward a resist layer. An electric field is applied (**Figure 1b**) between the top and bottom electrodes. The resists residing between the electrodes will be configured (or “exposed”). After the top mask has been removed, the resist in the exposed areas can be eliminated selectively from the bottom electrode by washing (**Figure 1c**) with solvents. The patterned substrate can be further processed by chemical and/or physical methods to transfer the patterns from the resist onto other materials.

The EL mask was composed of metal patterns on an insulative substrate. The nanoscale metal patterns can be fabricated by e-beam and optical lithography or self-assembly technique. To transfer the fabricated mask pattern, the mask was first pressed onto the ER thin film to ensure direct contact between the mask and the ER film. Since electrochemical polymerization (“exposure”) happens only on the substrate surface, the mask surface is left intact and the mask can be easily separated from the substrate without contamination. Nanoscale patterns transferred from the mask to a resist layer are shown in **Figure 2**.

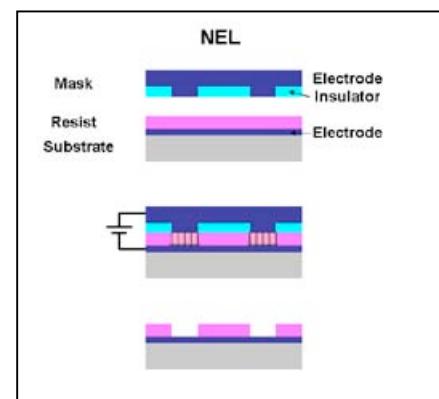


Fig. 1. Schematic diagrams showing the NEL process.

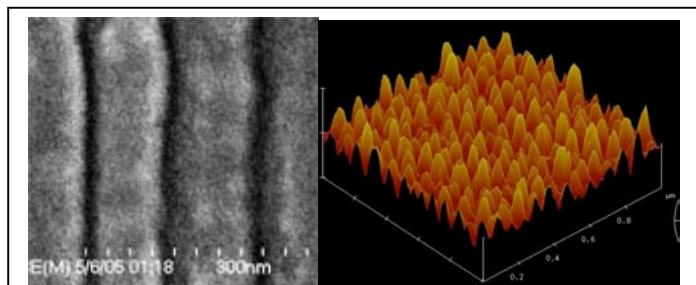


Fig. 2. (a) A SEM image of nanowire patterns generated by NEL on a resist layer. (b) An AFM image of nano dot patterns generated by NEL on a resist layer.

By selectively applying voltages to different conductive patterns on a mask, EL can also be used to generate on-demand patterns. As shown in **Figure 3(a)**, by applying a voltage to

particular lines, the linear patterns can be selectively transferred to the substrate as shown in **Figure. 3(b)**. Moreover, by controlling the amount of monomers polymerized during the electrochemical process via changes in the electrochemical voltage, current, and total charge flowing through individual conductive patterns, we can make 3D patterns with different heights on the substrate. **Figure. 3(c)** shows three linear patterns having different heights generated by applying a voltage with various durations (from the left to right in **Figure. 3(c)**) to the conductive linear patterns on the mask shown in **Figure. 3(a)**.

In order to achieve sub-10 nm resolution, we plan to use molecular resists that can be patterned subsequently using the NEL process. Self-assembled monolayers (SAMs) have been used as resists in previous AFM and EBL techniques at resolutions down to nanometers. Two classes of resist will be tested: (1) Traditional SAMs are structured like a lawn, with each molecule attached to the substrate like a blade of grass (**Figure 4**). We will re-engineer these SAMs so that the strong electrochemical field of the NEL stamp cleaves the molecules off at the base or at certain nodes along the molecule. This cleaving process will result in the exposure of useful chemical functional groups and/or in topographical changes. (2) The second kind of resist will consist of highly crosslinked two-dimensional arrays that are self-assembled onto electrode surfaces into simple pre-programmed patterns.

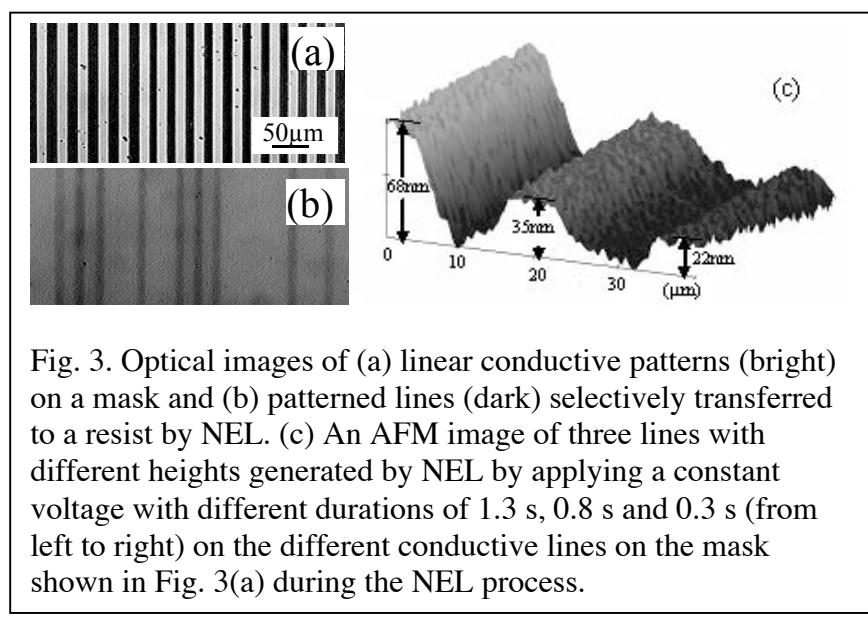


Fig. 3. Optical images of (a) linear conductive patterns (bright) on a mask and (b) patterned lines (dark) selectively transferred to a resist by NEL. (c) An AFM image of three lines with different heights generated by NEL by applying a constant voltage with different durations of 1.3 s, 0.8 s and 0.3 s (from left to right) on the different conductive lines on the mask shown in Fig. 3(a) during the NEL process.

The electrochemical field of the NEL stamp will break crosslinks and allow nanometer-scale regions to be “carved out” (**Figure 5**) of the molecular resist selectively. The advantages of the

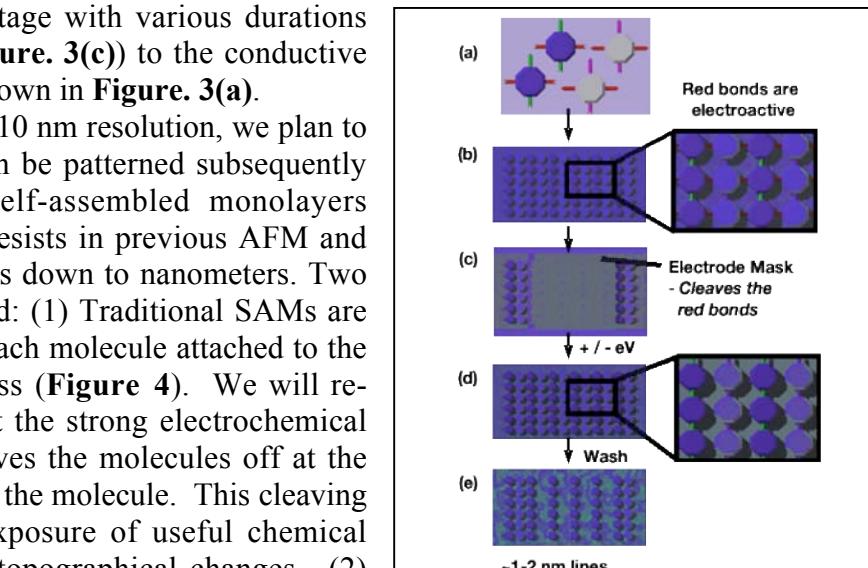


Fig. 5. Schematic representation of the NEL process showing (a) the molecular building blocks, (b) the self-assembly of the building blocks into a pre-programmed pattern on a surface, (c) an electrode mask placed over the self-assembled monolayer, (d) the surface after an applied voltage with the electroactive ‘red’ bonds permanently cleaved, and (e) the nanometer lines left on the surface after it has been washed with solvent.

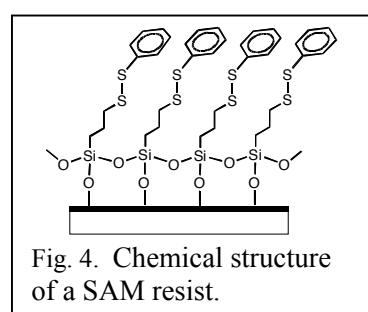


Fig. 4. Chemical structure of a SAM resist.

designed molecular resists are (1) the electrochemical method is a high-resolution, high-speed, low-defect lithographic process, (2) the molecular building blocks can create low-cost, low-defect, self-assembled films, and (3) the self-assembled structures allow for feature sizes of approximately one nanometer or potentially even smaller sizes to be achieved.

References

- [1] W. Shen, Y. Chen, and Q. Pei, "Electric lithography by electrochemical polymerization", Appl. Phys. Lett. 87, 124106 (2005).
- [2] Contact yongchen@seas.ucla.edu for further information.