

# Electron Beam Lithography and Liftoff of Molecules and DNA Rafts

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**Abstract** — Electron beam lithography patterning of polymethylmethacrylate (PMMA) is a versatile tool for defining molecular structures on the sub-10 nm scale. We demonstrate lithographic resolution to about 5 nm using a cold development technique. Narrow trenches are used to pattern Creutz-Taube molecules with resolution to about 15 nm. In addition, DNA rafts are patterned with high fidelity at linewidths of about 100 nm. This technique can be applied to molecular patterning in general, and quantum-dot cellular automata (QCA) in particular.

**Index Terms** — DNA tiling, electron beam lithography, molecular electronics, nanofabrication, nanotechnology, QCA.

## I. INTRODUCTION

The International Technology Roadmap for Semiconductors predicts integrated circuits with gate lengths of 9 nm by the year 2016 [1]. Given the amazing progress by industry, including the tendency to perform even better than forecasts, as well as recent results of gate lengths approaching 10 nm [2], it is reasonable to assume that future predictions will be realized. Nevertheless, issues of overhead on total transistor area and power dissipation leave some room for continued evolution and miniaturization, although not necessarily in the Si domain. The ultimate size scale for future computing devices lies in the domain of molecular electronics. However, the conventional paradigm of gating molecules seems impractical. Recognizing that the whole field of molecular electronics is in a nascent phase, one of the most promising uses of molecules for computing is that of quantum-dot cellular automata (QCA) [3]. In this paradigm, molecules are capacitively clocked and field-coupled to neighbors, so that most individual contacts are not necessary. With QCA, it is predicted that high speed and low power can be achieved.

In general, “top down” lithographic methods have difficulties in satisfying the requirements of both resolution and throughput. In the other hand, self-assembly has shown the capability for patterning nano components, such as nanoparticles and nanocrystals on the molecular scale [4]-[7] and creating an extraordinary level of structural complexity [7]. However, the manufacturing of bottom-up assembled systems with such stereochemical complexity would be extremely difficult. A possible

solution to this manufacturing challenge is an appropriate combination of top down lithography combined with self-assembly.

The ultimate goal here is to construct molecular quantum-dot cellular automata (MQCA) by allowing molecules or DNA (deoxyribonucleic acid) tiles as QCA cells to self assemble on templates formed by electron beam lithography (EBL)-formed trenches involving one step of removal of poly(methylmethacrylate) (PMMA) by liftoff. This technique has proven viable for both Creutz-Taube molecules and larger DNA nanostructures. This work on DNA patterning is a preliminary study of the combination of lithography and self-assembly. We have begun the investigation of using self-assembly to build functional molecular sub-systems on DNA rafts and EBL and molecular liftoff to position the rafts into macroscopic architectures.

EBL is still the most versatile of the high-resolution patterning techniques, but is not generally capable of writing below the 10 nm required of molecular structures. Since even large molecules do not approach this size, it is important to be able to define patterns well below 10 nm. Here we report a cold-development technique used to break the 10-nm barrier with good control over patterning properties, to about 5 nm. At this scale, perhaps a few, or even one large molecule can fit laterally within a PMMA trench. Based on the chosen chemistry, self-assembly of the molecules within the trenches will guarantee coherent pattern formation suitable for quantum-dot cellular automata (QCA).

## II. EXPERIMENTAL

EBL is performed using our 30-kV cold-cathode field emission Hitachi S-4500 scanning electron microscope converted to EBL. The spot size is about 1 nm. One advantage of using this system is the ease of achieving optimum beam parameters prior to exposure, assuring that the best possible lithography results can be reliably achieved. We have used this system to investigate the effects of varying the developer temperature on ultimate lithographic resolution, and found that cooling the developer yields noticeable advantages. Figure 1 shows contrast curves for developer temperatures to 4 °C. The significant feature is that the tail usually present in these

curves is closer to the final exposure dose (where the straight portion of the curve extrapolates to zero), so less overdose is necessary to ensure clearing of the patterns, and higher resolution results. Figure 2 shows resist coated with 2 nm of Cr, developed with the cold-development process. The linewidths approach and perhaps surpass 5-nm width for 40-nm thick PMMA.

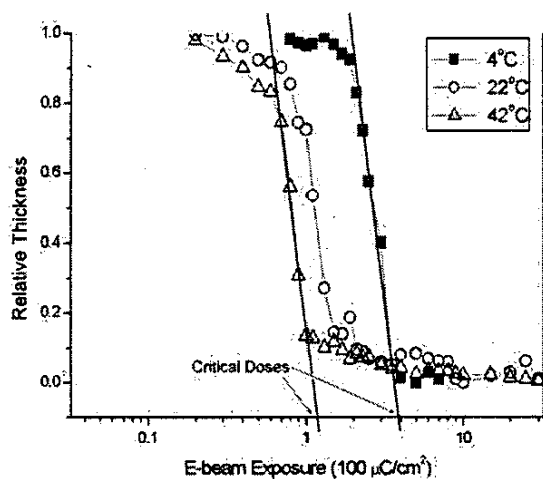


Fig. 1. The PMMA contrast curves at development temperatures of 4 °C, 22 °C, and 42 °C, measured by AFM.

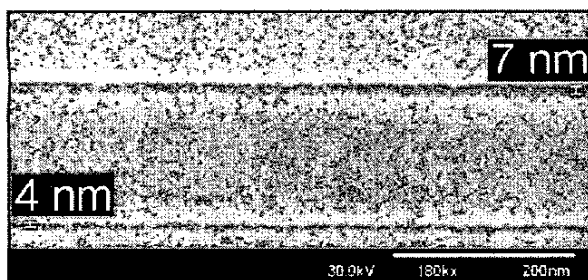


Fig. 2. PMMA trenches sputter-coated with 2 nm Cr developed by cold development.

We have used such PMMA masks to perform a molecular lift-off technique wherein hydrophilic molecules preferentially stick to a SiO<sub>2</sub> surface. Upon removal of the PMMA mask, the molecules are left behind and imaged in an AFM. The most important feature of the cold development process is that the bottom of the narrow trenches must be clean of resist residue. To test this, we deposited 5-nm negatively charged gold particles into the positively charged trenches (trench bottom was coated with polylysine after development). As can be seen in Fig. 3, a line of single particles is

obtained, which would not be possible without a clean oxide surface at the bottom of the trench since the particles do not stick to PMMA residue.

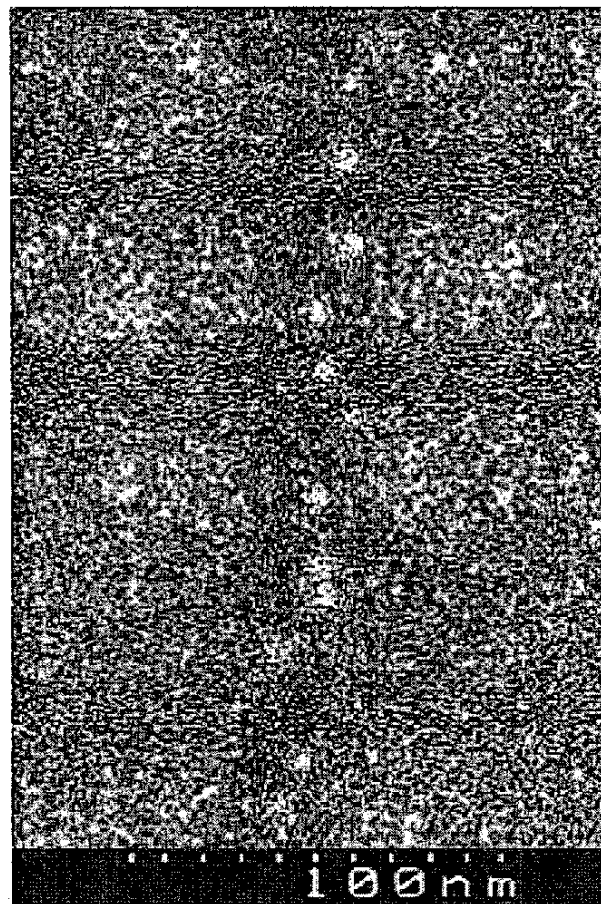


Fig. 3. Lifted-off line of 5-nm Au nanoparticles

Figure 4 is an AFM image of a lifted-off line of Creutz-Taube ion  $[(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5](\text{o-toluenesulphonate})_5$  (CT5) molecules with an apparent width of 22 nm. Upon deconvolution of the AFM tip, assumed to have about a 10 nm radius, an actual linewidth of about 15 nm is achieved.

In order to effect controlled deposition of DNA rafts without damage, we performed a two-step attachment process. The lift-off process is illustrated in Fig. 5. First, we performed lift-off with PMMA of APTES (3-Aminopropyl-triethoxysilane) with CH<sub>2</sub>Cl<sub>2</sub> for 3 minutes [8]. Next, 20 μl of DNA raft solution (1 μM) was deposited on the surface. After 4 hour attachment, the surface was rinsed with water, dried with nitrogen, and then imaged in AFM. Figure 6 shows the APTES attachment lines, and then DNA attached to these lines.



Fig. 4. AFM image of a lifted-off line of Creutz-Taube ion  $[(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5](\text{o-toluenesulphonate})_5$  (CT5) molecules with a calculated width of about 15 nm.

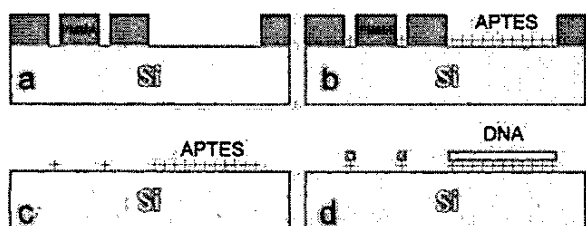


Fig. 5. Molecular lift-off of APTES for DNA attachment.

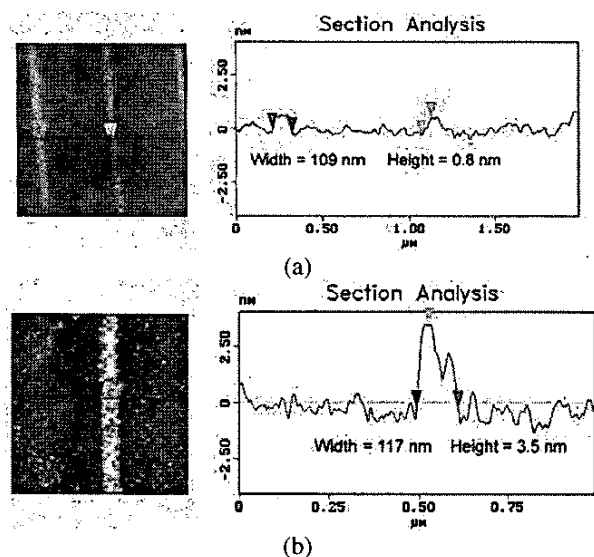


Fig. 6 AFM images and profiles of a) APTES lines by lift-off and b) DNA rafts attached to the APTES lines.

### III. CONCLUSION

It is not likely that a completely self-assembled circuit of sufficient complexity can be achieved, but some self-assembly would be used to connect molecules together within a pattern. Such patterns would likely be on the order of one to a few molecules in width. Furthermore, it is likely that a large fraction of a conventional CMOS chip would be patterned with molecules to interface with conventional CMOS. Using EBL with a sufficiently small beam, even with the brightest source, it would take several hours to pattern a single chip, but techniques such as nanoimprint lithography may serve as an intermediate step from the EBL techniques demonstrated here and future manufacturing technologies.

### ACKNOWLEDGEMENT

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