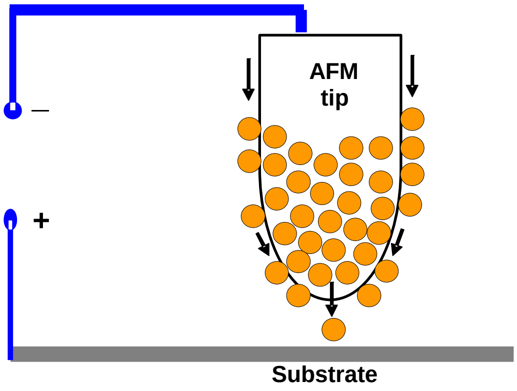
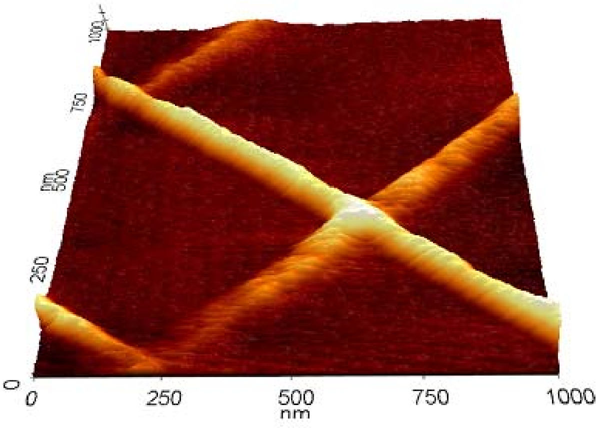
Field–assisted Nanopatterning (FAN) of Organic and Inorganic Species Including Polymers and Nanoparticles





Background and Introduction to Field Assisted Nanopatterning

The reliable fabrication of nanostructures with ever-smaller dimensions is of great importance for the development of nanoscale devices and molecular electronics. Tip-based fabrication methods are capable of creating a variety of nanostructures with nanometer-scale control over the size, orientation and position of each nanostructure. Methods involving the direct deposition of atoms or molecules at specified locations include field evaporation of metal atoms,[1] dip-pen nanolithoghraphy (DPN),[2] surface oxidation,[3] other tip-induced local surface reactions,[4] and more recently, field-assisted nanopatterning (FAN) developed in our group.[5,6] Using a conventional AFM with no alterations, we have demonstrated that FAN controllably patterns solid or liquid organic species (small organic molecules like N-methylpyrrole and naphthalene, large organic

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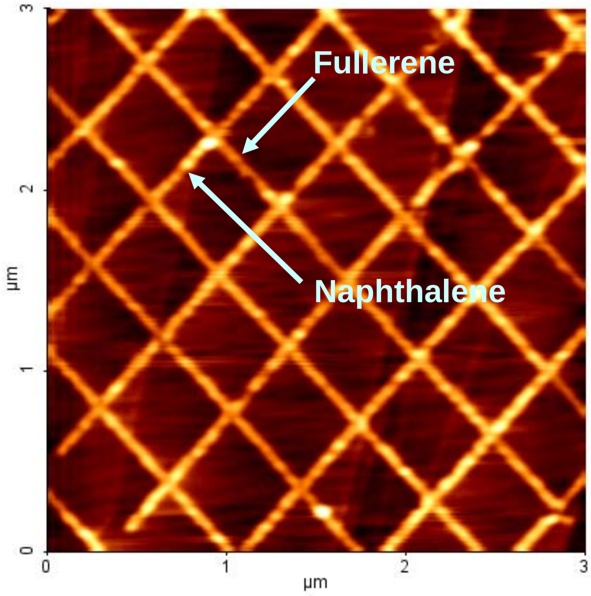
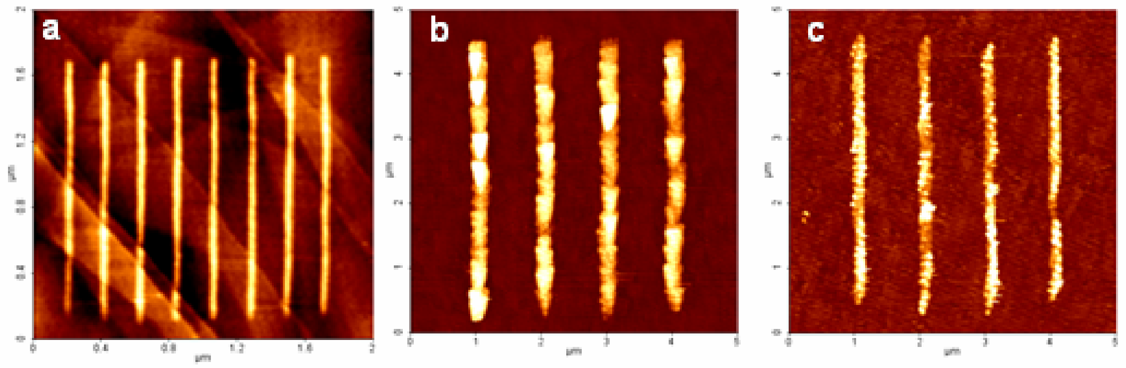
molecules like fullerenes and *meso*-tetraphenylporphyrin, polymers like poly-3-octylthiophene and polyaniline) and also inorganic species (metals, metal oxides, salts, nanoparticles) in the air under ambient conditions. In this way, organic nanowires and dots have been produced with feature sizes that range from tens of microns to sub-20 nm. FAN is achieved by applying a voltage (typically -6 to -10 V) between an AFM tip and a conducting or semi-conducting substrate. FAN is turned ON when a negative tip bias is applied, OFF when the tip bias is removed, back ON when the tip bias is re-established, etc. Nanopattern dimensions (i.e., feature sizes, gaps between features) can be tuned by varying the tip bias and fabrication (tip) speed, both of which are controlled by standard lithography software. FAN is performed in the contact mode using standard silicon tips (with native SiO_2 film) for both patterning and imaging. During fabrication, the tip force is maintained at ~2 nN.



Field–assisted nanopatterning of criss-crossing naphthalene and [60]fullerene lines on HOPG. The naphthalene lines were fabricated using a tip bias of –9 V and a fabrication speed of 100 nm/s. ***.*** *The [60]fullerene lines were patterned using a tip bias of –10 V and a fabrication speed of 100 nm/s.*

Mechanism for FAN

A mechanism for FAN involving field evaporation, a process of electric field-induced ionization and ejection of molecules from the Si tip, has been proposed.[5] According to this field evaporation mechanism, a threshold ionization and ejection potential exists for each molecule. The value of the threshold ejection potential depends upon several factors including tip geometry, the nature of the molecules to be deposited, the nature of the substrate, the gap between the tip and the substrate- if any, and the location of the molecule on the tip surface. At sufficiently negative tip bias values, electrostatic repulsions exist between molecules and also between the tip and the molecules. Ultimately, an ejection potential is achieved causing the molecules on the tip to be directionally deposited onto the electrostatically attractive substrate surface. The coatings on the tip are believed to be mobile under high electric field conditions, as has been suggested for DNA molecules under similar conditions.[7] Thus, the inorganic species

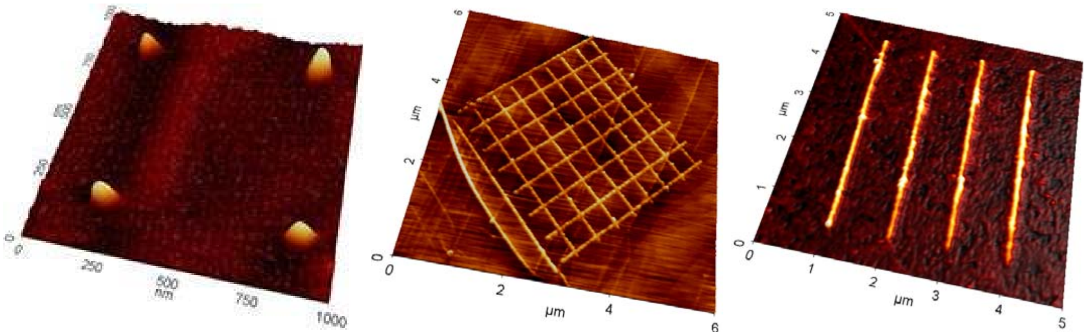


Field–assisted nanopatterning of (a) ZnO on HOPG, (b) Fe$_3$O$_4$ on ITO and (c) Fe on ITO. The lines were fabricated using a tip bias of -10 V and a fabrication speed of 100 nm/s. All line patterns were generated from top to bottom starting on the left and progressively moving to the right.

travel to the vicinity of the tip nadir before being directionally deposited onto the substrate.

Advantages of FAN over DPN

FAN has several important advantages over dip-pen nanolithography (DPN) and other tip-based nanofabrication techniques. These include: (a) a standard AFM with no alterations can be used for FAN; (b) the tip does not need to be lifted off the substrate to stop printing; (c) the deposition rates and feature size are independent of humidity; (d) the same tip can be used for both patterning and imaging; (e) a wide range of organic and inorganic molecules and materials including polymers and nanoparticles can be patterned using FAN; (f) a wide range of conducting and semiconducting substrates may be used with FAN; (g) FAN is amenable to material heterogeneity resulting in sophisticated architectures in which multiple different species are patterned onto a single substrate.



FAN of [60]fullerene on graphite (left), a heterogeneous grid of naphthalene and [60]fullerene on graphite (middle), and MnO_2 on ITO (right).

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