Highly tunable, high-throughput nanolithography based on strained regioregular conducting polymer films

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Atomic force microscopy (AFM) is now a standard imaging tool in laboratories but has displayed limited capability of nanolithography. We discover that an internal tensile strain exists in poly(3-hexylthiophene-2,5-diyl) (P3HT) films, and the physical effect is utilized to achieve highly tunable and high-throughput nanolithography. Trenches with widths spanning nearly two orders of magnitude from 40 nm to 2.3 μm are fabricated. We show that P3HT is also excellent for pattern transfer to inorganic materials. Furthermore, a lithography speed of 0.5 mm/s is achieved, which is a few orders of magnitude higher than other known methods of AFM-based nanolithography.


The enormous developments of nanoscience and technology have had a profound influence in many disciplines ranging from fundamental physics, chemistry, materials, and electronics to medicine and biology. In these disciplines, atomic force microscopy (AFM) has quickly become an indispensable tool for high-resolution imaging since its invention in 1985.1 An AFM works by scanning a fine tip over a surface in much the same way as a phonograph needle scans a record. The AFM tip has a diameter ranging from a couple of nanometers to tens of nanometers, and during imaging is kept very close to the sample surface to sense the force between tip and sample atoms. Compared with the well-established electron-beam lithography, AFM-based nanolithography enables much lower cost, nondestructive imaging of the resist before and after lithography by using the noncontact mode,2 potentially high throughput by using an array of tips,3 and the convenience of performing in situ electrical measurements.4 It is also desirable for nanolithography on certain biological materials and organic (semi-)conductors that are sensitive to vacuum or high-energy electron beams. As such, great effort has been made to extend AFM into a tool for nanolithography. A number of AFM-based lithography methods have been developed, such as mechanical modification,5,6 local anodic oxidation,7,8 thermal modification,9 erasable electrostatic modulation,10 low-energy electron exposure of poly(methylmethacrylate) (PMMA),11 and material deposition.12

Mechanical modifications by an AFM tip, referred to as nanoploughing, have been performed directly on semiconductor substrates and metal films.13–16 To reduce tip wearing that occurs when performing lithography directly on hard surfaces, nanoploughing is often carried out on a soft, thin polymer film such as photoresist17,18 or PMMA (Ref. 19–21) before being used as an etch mask for pattern transfer to the material below.22 Although simple to perform, nanoploughing is characterized by the build up of loose debris on the trench edges that may fall into the trench, which reduces yield and is regarded a general problem of this method.21,23,24 Furthermore, the ploughed trenches commonly do not form through the entire layer, requiring plasma etching to reach the substrate below.25 Perhaps the biggest difference between AFM-based nanoploughing and electron-beam lithography is the tunability; that is, the ploughed trench width is fixed by the AFM tip size and little tenability in the trench width has been achieved.26 For most nanostructures, particularly high-speed nanodevices, trenches with various widths are needed to provide insulation and/or to reduce the parasitic capacitance.27

Here we present a lithographic process of nanoploughing films of conducting polymer poly(3-hexylthiophene-2,5-diyl) (P3HT). The main difference from the polymers used in previous nanoploughing experiments is the regioregular nature; that is, the P3HT molecules are packed in a head-to-tail fashion. We show that this leads to a physical effect such that an internal tensile strain is sustained within spin-coated P3HT films. By varying the polymer film process conditions and lithography parameters we were able to fabricate trenches with widths spanning from 40 nm to 2.3 μm, nearly two orders of magnitude. The fabricated trenches have clean flat bottoms reaching the substrate below, which dramatically improves the yield and reproducibility. Pattern transfer to inorganic materials has also been achieved. These results may enable AFM to be tunable and reliable enough for practical lithography applications in research laboratories.

FIG. 1. (Color online) AFM micrograph of a 380-nm-wide trench and the molecular structure of P3HT. The trench has a flat bottom and is much wider than the AFM tip (about 40 nm in diameter) due to the internal tensile strain within the film. The cross section of the trench, shown by tilting the same AFM micrograph in the top left inset, illustrates the contrast between the trench width and the AFM tip size. The sketch shows that in situ electrical measurements can be carried out during nanolithography.
P3HT films were spun from solutions using either xylene or 1,2,4-trichlorobenzene (TCB) as the solvent. Samples were imaged before and after lithography, using intermittent contact (tapping) mode to avoid damage to the P3HT film. Figure 1 shows a three-dimensional (3D) AFM micrograph of a typical trench on a 15-nm-thick P3HT film which was ploughed by the AFM tip. The trench has a distinctive clean flat bottom. This is in strong contrast to previously reported nanoploughing lithography on, for example, photoresist or PMMA, where the trench profile was a replica of the shape of the tip and a plasma etch was often required to open up the trench bottom. Furthermore, the trench is about 380 nm wide, which is nearly one order of magnitude larger than the AFM tip diameter (40 nm). Separate experiments showed no obvious difference in the trench width when tips with a diameter of 10 nm were used. This independence is also in contrast to previous AFM-based nanoploughing lithography.

To study whether the trenches fully cut through the film, the conductive nature of P3HT was utilized and current-voltage (I-V) measurements were performed before and after lithography. After bisecting a P3HT Hall bar on a mica substrate, the current drops to the noise level of the measuring equipment as shown in Fig. 2. The result suggests a complete removal of the polymer inside the trench.

The flat, clean trench bottom and particularly the much larger trench width as compared to the AFM tip size strongly suggest that the trenches were formed by releasing the internal tensile strain of the film. The strain could be induced during the evaporation (drying) process of the solvent during and after spincoating the P3HT solution. Because strain-induced trench widening was not observed when regiorandom photoresist or PMMA was used, we conclude that the ordered head-to-tail coupling of molecules in the regioregular P3HT films caused the strain to be created and sustained during the drying process. As the film was cut by the AFM tip, the tensile strain caused the film to pull apart, resulting in not only much wider trenches than the tip diameter but also flat clean trench bottoms. The strain-relaxed trench edges were expected to be thicker than the bulk film, which was observed and is shown in Fig. 1. Since the solvent TCB has a higher boiling point than xylene, it takes a much longer time, tens of minutes, to dry the film and hence allows for more strain to be relaxed. Experimentally, trenches were indeed much narrower when TCB was used.

The final trench width was also determined by the film adhesion to the substrate, which acted against the released strain. As such, different trench widths were achieved either by varying the total internal strain by, for instance, varying the film thickness, or by modifying the film adhesion by substrate surface treatment. In general, the more hydrophobic the substrate surface, the less the adhesion of the P3HT film. Surfaces with an enhanced hydrophobicity were prepared by applying the self-assembled monolayer, octadecyltrichlorosilane (OTS). As seen from Fig. 3(a), a very wide trench, 2.3 μm, was produced on a treated substrate, which is nearly two orders of magnitude wider than the tip diameter and displays the dramatic effect of surface treatment. Such a...
wide trench is useful for insulation, particularly for microwave devices, which would be impossible to achieve with previous nanoploughing lithography. To illustrate the range of tunability of nanoploughing on P3HT films, Fig. 3(b) displays an AFM micrograph of a trench formed on a 2-nm-thick P3HT film on an untreated substrate. The trench is ~40 nm wide, which is nearly twice the thickness of the trench in Fig. 3(a).

Tunability of this lithography approach can be achieved by varying a range of film preparation conditions and lithographic parameters. With different solution concentrations, the P3HT film thickness was varied from a couple of nanometers to ~35 nm. In the simplest approximation, the total internal strain, and therefore the width of the trench, is proportional to the P3HT film thickness. Indeed, we found that 40- to 80-nm-wide trenches were created on films less than 3 nm thick, spun using TCB as the solvent on untreated substrates, whereas the trenches were always wider than 200 nm for films thicker than 30 nm.

Our AFM lithography on P3HT films was found to be highly reproducible. The tip did not have to cut all the way through the film due to the internal strain pulling the trench apart through the entire film to the substrate below. Hence the tip did not have to have any hard contact with the substrate and received little wear. Experimentally, we needed to change the tip only when it was accidentally broken.

Another useful result of the internal strain and regioregular nature of the P3HT material is that little debris was found to occur close to the trench sidewalls. Even if some debris were found at the end of a long or wide trench, the debris were tightly attached to the film and did not break into small pieces. This differs from previous nanoploughing lithography performed on, for example, thin photoresists films, in which debris was often formed on the edge of and could fall into the trenches causing poor yield. Similarly, we observed that the AFM tip was very rarely contaminated by debris from the P3HT film even after days of nanolithography and imaging.

To obtain tunability without changing the P3HT solution concentration, we prepared samples identically except for the varying spin speed. An additional sample was prepared by drop casting the solution, which caused a thick film to form and yielded trenches ~800 nm wide as shown in Fig. 4(a). At a higher spin speed, the film thickness decreases, as does the trench width. The result suggests that trench width is closely linked to the film thickness and therefore also to the total strain in the film, which is in agreement with the conclusions from changing the solution concentration.

To gain even greater tunability, different trench widths were achieved without changing the solution concentration or spin speed, but rather by altering the writing speed of the AFM tip. A range of trench widths were produced on a sample with writing speeds from 0.5 to 500 μm/s (the highest speed allowed by our AFM), as shown in Fig. 4(b). Tunability was therefore achieved within a single lithography step. We note that the maximum speed of lithography, 500 μm/s, is a few orders of magnitude higher than other known methods of AFM-based nanolithography. Even at the maximum speed, the obtained trenches still had a flat bottom and uniform edges, as shown by the AFM micrograph of three trenches in Fig. 4(c). The high speed was possible because the tensile strain pulling the film apart when the trenches were formed, and the tip did not need to drive very hard vertically to push into the polymer or horizontally along the trench direction to break the film. Hence the throughput of this approach could be very high, which is important as a general nanolithography tool for creating nanostructures covering large areas.

The above lithography allows direct fabrication of organic nanodevices without the need to use a resist as in photo- or electron-beam lithography. This is important since organic semiconductors are generally vulnerable to chemicals, UV light, and high-energy electron beams. We also further extended the method to fabricate nanostructures on conventional semiconductors by using nanostructured P3HT films as etch masks. We found that even very thin (a few nanometers) P3HT films could withstand standard etchants very well. The tunability and reproducibility of this lithography technique can therefore be harnessed to fabricate nanostructures on a wide range of materials.

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7E. S. Snow and P. M. Campbell, Science 276, 1639 (1997).