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Scanning Probe Microscope Based Nanolithography on Conducting Polymer Films

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We demonstrate successful nanolithography to pattern organic semiconductor films by using the oscillating tip of an atomic force microscope (AFM). The nano-indentation technique, which was previously used to create trenches on materials including thin photoresist and metal films, has now been systematically studied and applied to the most commonly used semiconducting polymer, regioregular poly(3-hexylthiophene) (P3HT). We discover that the internal tensile strain in the films and the long P3HT molecules have actually enabled us to eliminate all major common problems of the nano-indentation method to date, namely the refilling of the trenches by debris, tip contamination by debris, and the short AFM tip life time, which have so far seriously hampered and limited the practical applications of the nano-indentation technique. The trenches that we have created are generally formed through the entire P3HT film, with a clean bottom virtually free from debris. Successful pattern transfer to the underneath inorganic semiconductor has been achieved by a wet chemical etch with the created organic nanostructures as the etching mask. Furthermore, no obvious degradation of the AFM tip either by debris contamination or mechanical wearing is observed after many days of nanolithography. This allows nanostructures over tens of microns in length to be reproducibly fabricated in large numbers. [DOI: 10.1143/JJAP.45.2095]

KEYWORDS: atomic force microscope, nanolithography, conducting polymer, nano-indentation, poly(3-hexylthiophene), thin film, organic semiconductor

1. Introduction

The development of organic thin film transistors (OTFTs) and organic light emitting diodes (OLEDs) has been very rapid in recent years. This has even led to some preliminary commercialization which takes advantage of the unique combination of electronic and mechanical properties of organic (semi-)conductors.[1] However, the operation speed of OTFTs is currently around KHz or even lower, which obviously has to be improved for vast majority of practical applications. It is therefore essential to tailor transistor channels and reduce gate dimensions to at least a few microns. Patterning of organic semiconductors is also needed in order to isolate between individual devices to avoid cross talk and improve on/off ratios.[2,3] In recent years, several approaches to pattern organic materials have been developed such as screen printing,[4] ink-jet printing,[5,6] soft lithographic stamping,[7] and photochemical cross-linking.[8] Despite much effort on these methods, the organic semiconductors in the OTFTs reported to date were mostly not patterned, largely because of the lack of the nonstandard equipment needed in these lithography approaches in ordinary research laboratories. Even though ink jet printing is a most promising choice for future organic electronics, achievable dimensions are limited by the size of the ink droplets which is typically tens of microns. This is insufficient to improve the speed of OTFTs significantly even considering possible developments of ink jet printers in the near future.[9]

Among the possible ways to achieve micron- or submicron-sized structures, UV photolithography has been used to fabricate organic semiconductor structures,[4,10] but it is limited because organic semiconductors are generally sensitive to UV exposure and necessary measures have to be taken.[11] Recently, Austin and Chou developed a nanolithography approach based on the nanoimprint technique,[12] and fabricated 70 nm structures on poly(3-hexylthiophene)-2,5-diyl (P3HT) film, which is the soluble semiconducting polymer with the highest reported carrier mobility so far.[13,14] Rather than patterning P3HT directly, the nanolithography was performed on the SiO_2 deposited on top of the P3HT film, followed by reactive etching to remove SiO_2 and P3HT in desired areas.

In addition to its well-known capabilities in imaging and spectroscopy, atomic force microscope (AFM) has been developed into a convenient and flexible tool for patterning of material structures at the nanoscale. AFM-based nanolithography involves two basic technologies: mechanical[15–18] and electrochemical means.[19–23] In the former, trenches or holes are formed on the material by either direct tip scratching (applying a constant force to the tip) or dynamic indentation (pressing an oscillating tip into the material). Despite the simplicity and a number of experiments performed on thin photoresist and metal layers, such nanolithography techniques suffer from three serious drawbacks: the refilling of the trenches by debris (causing incomplete pattern transfer), tip contamination by the debris, and the short AFM tip life time (resulting in a high cost and poor reproducibility). These issues, to a large extent, have made this approach hardly useful in practice.[24]

In this work, we demonstrate a novel AFM-based nanolithography technique to pattern organic semiconductor materials. We show that the combination of internal tensile strain, inter-molecule regioregularity, and long molecules in the P3HT films can eliminate these three major problems of the nano-indentation lithography. The created trenches are generally formed through the entire P3HT film, with a clean bottom virtually free from debris. This has enabled successful pattern transfer to the inorganic semiconductor underneath by wet chemical etching. No obvious degradation of the AFM tip is observed after many days of nanolithography, showing remarkable reliability and promising potential in patterning both organic and inorganic nanostructures.

2. Experiments

Regioregular P3HT (more than 98.5% head to tail

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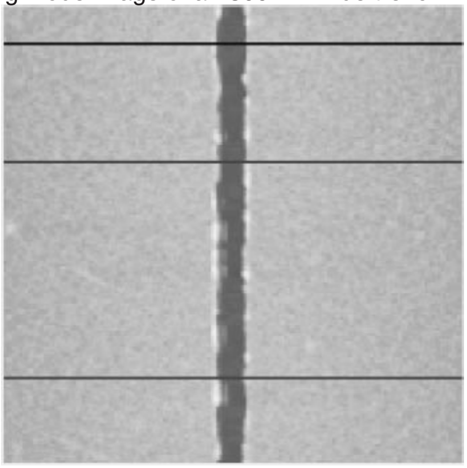
*Corresponding author. E-mail address: A.Song@manchester.ac.uk coupling) was obtained from Aldrich and used without further purification. A P3HT solution of about 1% weight in a common solvent (chloroform, trichlorobenzene, or xylene) was filtered through a 0.2 μm PTFE syringe filter, to remove insoluble particles and impurities. Before spin coating P3HT on a substrate (silicon, silicon oxide, mica, or GaAs), a layer of hexamethyldisilasane (HMDS) or octadecyltrichorosilane (OTS) was normally deposited to improve the interface between the substrate and P3HT.[25)]

A VEECO CP-R Research AFM is used in our experiments. μmasch Si_3N_4 tips are adopted for both imaging using the tapping mode and nano-indentation. The tips have radii < 20 nm, with angles $< 30°$ and typical force constants of 14 N/m. Different types of tips, such as ultra-sharp STING probes with <5 nm radii, have also been used, but no obvious difference in the created trenches was found. This, as will be shown below, differs from the earlier nano-indentation lithography, in which the resulted trenches had a width solely determined by the tip diameter.

Figure 1(a) is a tapping-mode atomic force micrograph of a single trench created by nano-indentation on a thin P3HT film. From the depth profiles along the three horizontal lines in Fig. 1(b), the trench is shown to have a flat bottom. This is in contrast to previous results of nano-indentation experiments on photoresist and metal films, in which the obtained trenches typically had a curved profile, reflecting the actual shape of the AFM tip, and the trench bottoms typically did not reach the substrate reliably so that a short plasma etching was generally needed in order to clean them up. Also differing from the previous results is that the trench in Fig. 1(a) is about 300 nm wide, much larger than the AFM tip diameter.

a) Tapping mode image of a ~300 nm wide trench



b) Depth profiles along the three lines in a)

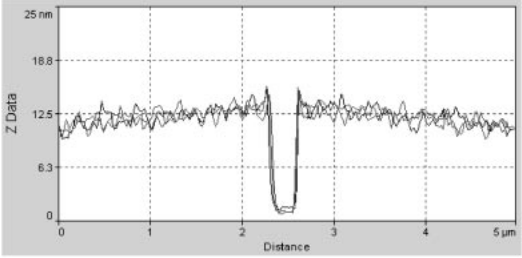


Fig. 1. (a) A $5 \times 5\,\mu m^2$ AFM image of a single trench created by nano-indentation on a thin P3HT film, and (b) the depth profiles along the three horizontal lines. The flat bottom of the trench shows that the internal tensile strain effectively pulls the film apart during the lithography, resulting in a trench much wider than the diameter of the AFM tip.

To determine the reason behind this, we have also performed nano-indentation on a thin layer of photoresist, and obtained tip-wide trenches. We therefore conclude that the wide trenches on P3HT films are because of the internal strain that is intrinsic to the film. Tensile stain can be formed during the fast drying process of the P3HT solution. The regioregular nature, i.e., molecules are aligned in a head-to-tail fashion, also allows the stain to be held during the quick evaporation process of the P3HT solvent by limiting the reorganization of the molecules, which, otherwise, may relax the strain. It is the internal tensile strain that actually pulls the film apart during the lithography, resulting in a trench much wider than the diameter of the AFM tip. Because of this mechanism, the actual trench width is determined by the strength of the stain and the adhesion force between the P3HT and substrate. By choosing different substrate surface treatment conditions to obtain different adhesion forces, we have verified the mechanism as well as obtained the ability to tune the trench width (details to be published elsewhere). Since heating normally relaxes strain in a material, we have performed annealing experiments on P3HT films. Indeed, we find that the fabricated trenches become narrower than on films that have not been heat treated, which is expected because of the reduced strain in the film. This enables a certain degree of tunability.[26)]

Whereas a narrow trench may be desirable in certain applications to fabricate ultra small structures, a wide trench is very useful in practical nanodevices where good insulation between different parts, particularly in high-speed nano-devices, has to be achieved reliably.[27–29)] This technique is hence not only a reliable but also a flexible method to fabricate nanodevices and circuits in research laboratories.

Figure 2 shows an array of 90 holes on a 7-nm-thick P3HT film fabricated using the nano-indentation method. The indentations are performed at the centre of each site, but with different nominal vertical scanner displacements from

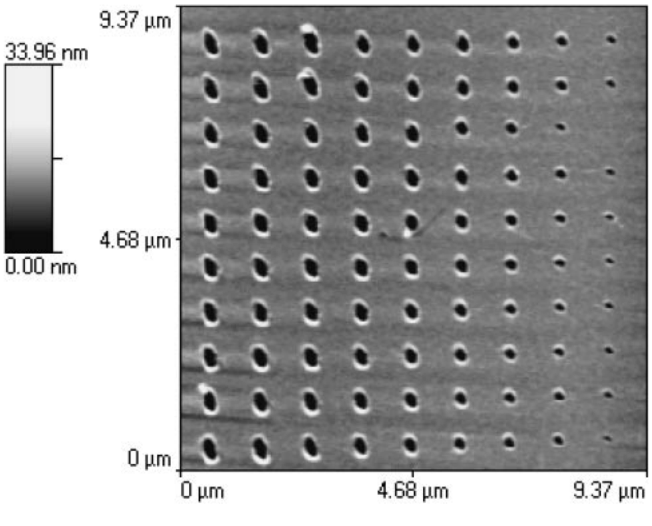


Fig. 2. An array of holes on a P3HT film fabricated by nano-indentation with different nominal vertical scanner displacements from 0.1 to 0.7 μm. This results in different mechanical impacts that loosen the P3HT film around the holes from the substrate and therefore different hole diameters.

0.1 to 0.7 µm. The estimated peak value of the force on the film is from 1.4 to about 10 µN (in other experiments on thinner films, a much lower peak force around 100 nN was sufficient). This results in different mechanical impacts that loosen the P3HT film around the holes from the substrate and therefore leads to different hole diameters. The slight derivation from the perfect round shape of the holes is due to the slight tilt of the substrate. Good reproducibility is achieved. The missing hole in the right column is likely due to local inhomogeneity of the film, since the neighbouring one in the next column also has a slightly smaller diameter than would have been expected.

The presence of the strain also means that the tip does not need to punch through the entire film, because the strain can pull the film apart once it is cut to a certain depth. Since the substrate is typically much more rigid than organic films, this allows for a very long tip lifetime. Because the trenches always open up entirely to the substrate surface and have flat bottoms, the film thickness can be easily determined by AFM imaging after the lithography.

We believe that the same mechanism makes the tip free from debris-induced contamination, which often results in losing imaging capability in previous nano-indentation lithography on photoresist and metal films. Typically, we observe no obvious tip damage or contamination after many hours of continous nano-indentation lithography. This is crucial in fabrication of complex structures or devices, where, for instance, any tip contamination would interrupt the lithography and cause a restart to be necessary. Figure 3 shows four trenches fabricated on a P3HT film by nano-indentation at a speed of 1 µm/s, which we have performed in large numbers in our experiments but had hardly any tip contamination problem.

With the trenches all the way through the P3HT film and having a clean bottom, pattern transfer by wet chemical etching onto the substrate underneath has become very easy and reproducible. Figure 4 is an AFM micrograph of a nanostructure made by pattern transfer onto the GaAs substrate by wet chemical etching, immediately after the fabrication of circular trenches on a P3HT film. In comparison with earlier experiments where the nano-indentation was performed on a thin layer of photoresist, no plasma etching was needed to remove the residue of photoresist inside the trenches after nano-indentation. This is important for patterning organic nanodevices, since any plasma etching would seriously damage the organic semiconductor because they are generally extremely sensitive to oxygen.

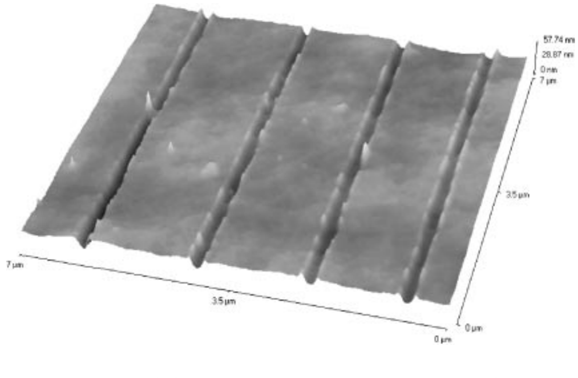


Fig. 3. An array of four trenches created on a P3HT film by nano-indentation at a speed of 1 µm/s. The area of the image is $7 \times 7\,\mu\text{m}^2$.

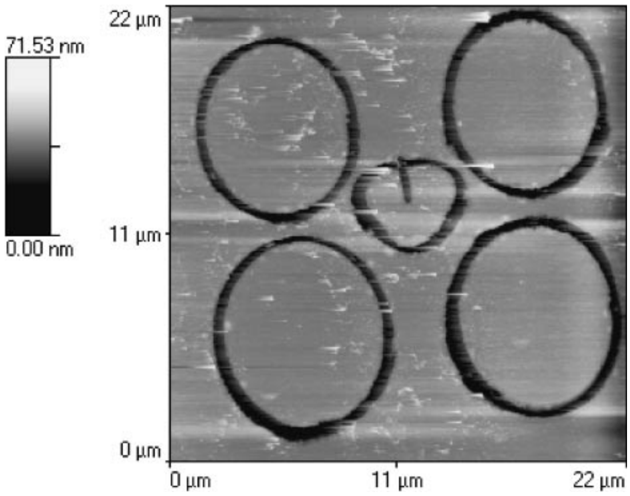


Fig. 4. An AFM micrograph of a nanostructure made by pattern transfer onto a GaAs substrate by wet chemical etching, immediately after the fabrication of the circular trenches on a P3HT film.

Because of the good reliability of the lithography, we have also fabricated organic nanodevices. Figure 5 shows that a narrow channel is formed between two semicircular trenches, each about 60 µm long. Electrical insulation has been achieved between two sides of the trenches as shown in our electrical measurements (to be reported elsewhere). This technique can therefore be applied to fabricate a range of organic devices, including making insulating trenches to isolate individual devices. Work is in progress to tailor OTFT channel dimensions and reduce gate lengths to the micron or even sub-micron region, in order to significantly improve the speed of OTFTs, as well as to avoid cross talk and improve on/off ratios.

3. Conclusions

To conclude, we have demonstrated successful nano-indentation lithography on organic semiconducting P3HT films with an atomic force microscope. Previous drawbacks of nano-indentation on photoresist and metal films are largely solved by taking the advantage of the internal strain, regioregularity, and long molecules in the P3HT films. Well defined trenches and good pattern transfer have been achieved without obvious damage to the AFM tips. Such a method can be used to fabricate both organic nano-devices by direct lithography on an organic semiconductor film, and inorganic devices by using the patterned organic film as a mask for pattern transfer. As such, the combination of nano-indention and conducting polymer films provide a simple, reliable, and low-cost way of nanolithography, which can be applied in research laboratories for a broad range of organic and inorganic device research.

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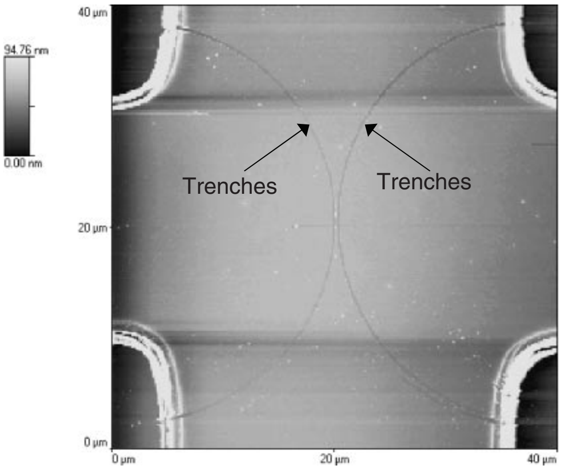
a) Fabrication of 60- m-long curved trenches



b) Zoomed image of the central part

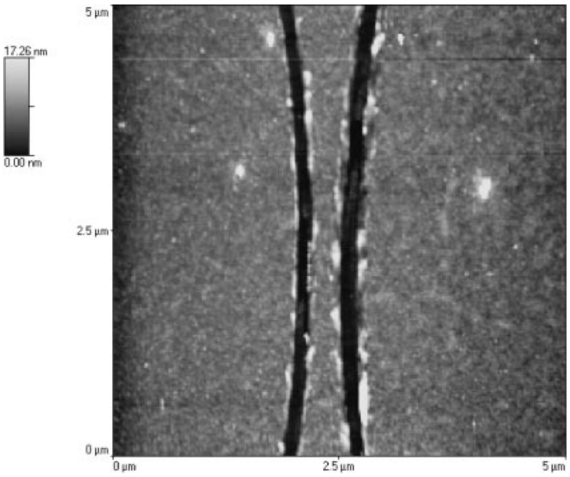


Fig. 5. Long insulating trenches fabricated by nano-indentation on a cross junction of a thin P3HT film. Each of the semicircular trenches is around 60 µm long, showing good capability of fabricating structures over a long spatial distance.

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