Supramolecular NanoStamping: DNA at work as a printing type

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Abstract

Supramolecular NanoStamping (SuNS) is a novel printing technique for soft molecules, based on the selective interaction between complementary DNA pairs. SuNS is capable of reproducing patterns that may be composed of multiple DNA strands, fabricated with various lithography techniques. Also, it can be expanded to many different systems of substrates using relevant chemistries. Here, we will describe printing on PMMA, an acrylic polymer with a number of advantages, using SuNS.

Introduction

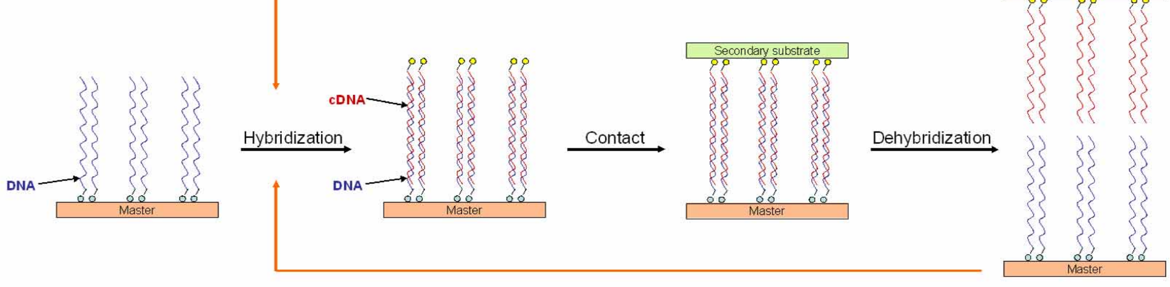
By definition, printing is the copying of a pattern from a master surface onto another surface in a parallel way. It offers the fastest and cheapest way to fabricate a number of identical patterns or products starting from a more expensive master or mold. For example, the spread of books to the public was driven by the development of Gutenberg's movable type. Also, the golden age of micro-devices couldn't be possible without the existence of optical lithography.

Recently, the research field of nanolithography has grown significantly since it is basic and essential part for manufacturing nano-devices materially. With the effort of many researchers, various nanolithography techniques such as electron-beam lithography or ion-beam lithography, have been successfully developed. However, in order to industrialize nano-devices, it is critical to find a relevant printing technique. Nanoimprinting (NIL)(1, 2) is a promising printing technique because it is capable of reproducing high-resolution patterns originally fabricated with the nanolithography techniques mentioned above. Unfortunately, it cannot be used to print organic/bio materials due to the use of mechanical forces or other generally harsh process involved in some of its variants. More in general there are few printing techniques that can print soft materials.

Supramolecular NanoStamping (SuNS) is a nanoscale printing technique for organic/bio molecules, in a sense the biological counterpart to NIL. It takes advantage of the selective supramolecular interaction of DNA pair. In SuNS, a master consists of a patterned surface where features are composed of a single strand DNA (ssDNA) monolayer. SuNS reproduces the original pattern in three steps: i) hybridization of master with complementary DNA (cDNA) that is functionalized with attachment group – ii) contact with another substrate, allowing cDNA to form a chemical bond with the secondary substrate – iii) dehybridization, leaving a copy composed of cDNA onto the secondary substrate (See scheme 1). Our group(3, 4)' and Crooks' group(5, 6) have developed this method in the last couple of years.

Among several advantages of SuNS, the most unique one is that SuNS is capable to print multiple kinds of DNA strands at once. That is SuNS is capable of transferring spatial information (size, shape and location) together with chemical information (the specific sequence of the DNA strands). This character potentially enables SuNS to print multi-component devices such as DNA microarrays.(7) Another unique character of SuNS is that a printed pattern can be used as another master to make more copies. Also, SuNS can be utilized to print onto many different substrates using a large variety of chemical interactions. As the first trial, gold substrates were used for printing thiolated DNA molecules.(3) However, gold substrates have a few drawbacks; they are too rigid to obtain a large printing coverage, not optically transparent and expensive. For these reasons, polymethylmethacrylate (PMMA) was tried as a new substrate material for SuNS.(4) PMMA is a popular substrate material because of its good optical property. It is often used as a substitute for glass. Additionally, since it has an intermediate glass temperature (T_g ~ 100°C), it is mechanically robust at room temperature but it can be easily softened by moderate heating.

Scheme 1



Results

In order to test the printing coverage when PMMA is used, two kinds of master were prepared. One is a silicon substrate containing various patterns fabricated with E-beam lithography on 2 mm X 2 mm area. The other is a grating pattern with 100 nm pitch fabricated with achromatic interference lithography (AIL) on silicon substrate (5 mm X 5 mm). Since the top of patterns on both masters were coated with gold, we could allow DNA monolayer on the pattern by dipping them into thiolated DNA solution. PMMA substrates were surface functionalized with aldehyde groups as described in ref (8).(8) After hybridization with amine terminated cDNA molecules, the master was placed onto a PMMA substrate followed by heating up to 75^{o}C for 15 min. At this temperature (relative temperature* 0.93), a conformal contact between the softened PMMA substrate and the master is expected, and also the imide bonds form due to the reaction between the terminal amines (cDNA) and the surface aldehyde groups (PMMA). The two attached substrates were separated by raising the temperature to 90 ^{o}C (dehybrization) and then imaged with Tapping mode AFM. (Fig 1) The printed patterns were detected on many different spots on the PMMA substrate. In AFM images, nearly defectless printed patterns were found on areas as large as 100 μm^2.(4)

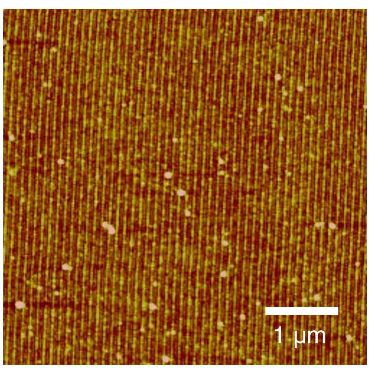


Figure 1. Tapping mode AFM image of printed AIL grating line with 100nm pitch on a functionalized PMMA substrate using SuNS.

Conclusion

In conclusion, here we have shown that it is possible to print a DNA pattern achieved by self-assembly onto a pattern fabricated by various lithography techniques onto a polymeric substrate. A pitch resolution of 100 nm and a point resolution of 50 nm can be achieved on an area bigger than 100 μm^2. We believe that the expansion of SuNS into PMMA system with many advantages will be helpful for fabricating inexpensive bio-devices.

References

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Arum Amy Yu is a graduate student in Prof. Stellacci's group in the Department of Materials Science and Engineering at MIT. She obtained a B.S. in both Materials Science and Chemistry at Korea Advanced Institute of Science and Technology in 2001.

Francesco Stellacci received his "Laurea" in 1998 at the Politecnico di Milano in Materials Science and Engineering with a thesis on photochromic materials with Prof. Giuseppe Zerbi. He then moved to the University of Arizona for a post-doctoral experience with Prof. J. W. Perry working on the two-photon microfabrication of metallic structures. Since 2002 he is an assistant professor in the Department of Materials Science and Engineering at MIT.

*Defined as the ratio of the temperature by the glass transition temperature both in Kelvin.