Direct Nano Patterning of Anisotropic Conjugated Polymer

Azusa Miyagawa
Materials Science, Japan Advanced Institute of Science and Technology, Ishikawa Prefecture, Japan

NNIN iREG Site: Lurie Nanofabrication Facility, University of Michigan, Ann Arbor, MI
NNIN iREG Principal Investigator: Dr. Jinsang Kim, Materials Science and Engineering, University of Michigan
NNIN iREG Mentors: Dr. Pilar Herrera-Fierro, Lurie Nanofabrication Facility, University of Michigan;
Kyeongwoon Chung, Materials Science and Engineering, University of Michigan
Contact: s1340015@jaist.ac.jp, jinsang@umich.edu, pilarhf@umich.edu, kychung@umich.edu

C H E M

Abstract:

Conjugated polymers with a one-dimensional p-orbital overlap exhibit optoelectronic anisotropy. Their unique anisotropic properties can be fully realized in device applications only when the conjugated chains are aligned. To align chains, we directly drew conjugated polymer lines via dip pen nanolithography (DPN) using a NanoInk DPN 5000. As the first step, poly(3-hexylthiophene) was used as a polymeric material and patterned lines on a gold (Au) surface, changing the solution concentration and writing speed. The line quality was evaluated by fluorescence microscope and atomic force microscope. Our results indicated that solution concentration was not important, but writing speed was critical for writing continuous lines. There are more factors to be considered to write fine lines. However we also revealed that nanoscale lines can be written by DPN technique.

Introduction:

Conjugated polymers (CPs) are active materials for various optoelectronic applications, such as organic solar cells, thin film transistors and light-emitting diodes. Their highly anisotropic optical and electronic properties are owing to the one-dimensional p-orbital overlap along the conjugated polymer backbone. However, these properties of conjugated polymer cannot be fully realized in device applications unless CPs are molecularly and macroscopically assembled and aligned with a well-defined structure. In reality, the directed assembly and particularly macroscopic alignment of CPs is a challenging task, because CPs do not have good self-organization owing to their non-planar structure in solution.

In our previous work, we could obtain well-defined conjugated polymer films by setting of molecular-design rules for improving the directional alignment of CPs under the application of shear stress [1]. In this study, to further improve the CPs alignment, the dip pen nanolithography (DPN) technique was used to make well-aligned CP lines in nanoscale, which is known to be potentially capable of patterning in the nanometer range [2-4]. The DPN process uses a scanning probe tip (the "pen") to directly deposit a material ("ink") with nanoscale onto a substrate. The influence of writing speed and solution concentration on the line continuity was investigated.

Experimental Procedure:

The polymeric material used in this study was poly (3-hexylthiophene) (P3HT) purchased from Rieke Metals. P3HT was dissolved in a mixture of o-dichlorobenzene and 1.8-octanedithiol (10:1) and filtered through a 0.45 μm PTFE filter before use. Solution concentrations were 2.5 and 10 g/l. Silicon wafers with a gold (Au) top layer were used. Au substrates were cut into pieces of 1 cm × 1 cm and cleaned by immersion in acetone. The substrates were treated with oxygen plasma.

DPN was carried out using a DPN 5000 (NanoInk, Inc.) in an atmosphere control chamber. Lithography was performed at a temperature of 25°C and 50% relative humidity. The writing speed were 1.0 and 0.001 mm/s. Silicon nitride single pens (Type A, NanoInk, Inc.) were used. The ink was filled in an Inkwell (IWL-0031-01, NanoInk, Inc.). Image analyses were done with the Olympus BX-51 fluorescence microscope (FM) and Nano Man atomic force microscope (AFM).

Results and Conclusions:

Fluorescent Microscopy. Figure 1 shows the FM image of the line written with the ink of 2.5 g/l concentration and the writing speed of 0.001 mm/s. Changing concentrations did not show any noticeable changes in the line continuity. However, continuous lines were not generated via a writing speed of 1.0 mm/s, even though that writing speed was critical for line quality. Furthermore, it was found that lines could be written more than 1000 μm on a one-time ink loading.

Atomic Force Microscopy. The AFM topography image of generated lines with the ink of 10 g/l concentration and the writing speed of 0.001 mm/s is shown in Figure 2. Changing concentration also does not show a difference even in AFM images, indicating that the solution concentration does not affect the line continuity. The AFM image of the cross section reveals that the generated line width and thickness was 0.8 μm and 20 nm, respectively (Figure 3).

Comparing direct writing processes, whereas inkjet printing is limited to feature sizes of some tens of microns [5], generated lines in this study are the nanometer range. However, even written in the same condition, continuous lines are not obtained constantly. This indicates that there are more parameters to be considered to write continuous lines. For instance, ink amount of the probe [3], probe conditions [4], humidity [2], writing force and surface conditions are also important to writing patterns and we have to consider them.

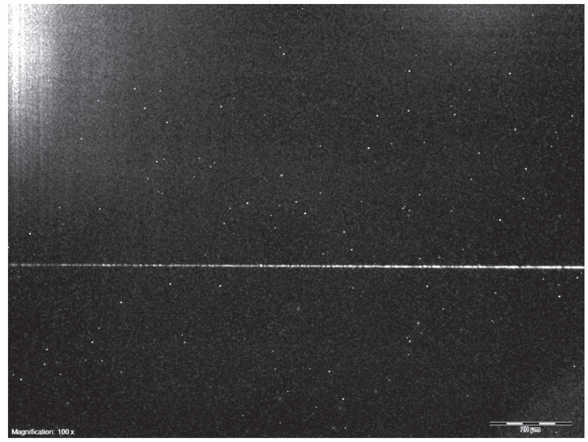

Figure 1: The FM image of P3HT line written with 2.5 g/l concentration ink.

Future Work:

The most important is to write continuous lines constantly. We need to write lines with changing other properties such as ink amount, writing force and humidity.

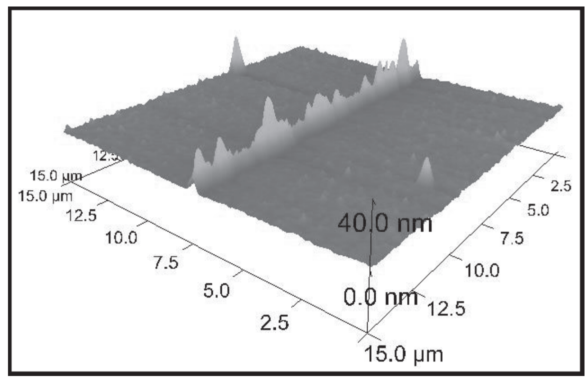

Figure 2: The AFM image of P3HT line written with 10 g/l concentrations ink.

Acknowledgements:

I would like to thank the National Nanotechnology Infrastructure Network International Research Experience for Graduates (NNIN iREG) Program, the National Science Foundation, Nanotechnology Platform, Japan, the Lurie Nanofabrication Facility and staff, Dr. Jingsan Kim, Dr. Pilar Herrera-Fierro, and Mr. Kyeongwoon Chung.

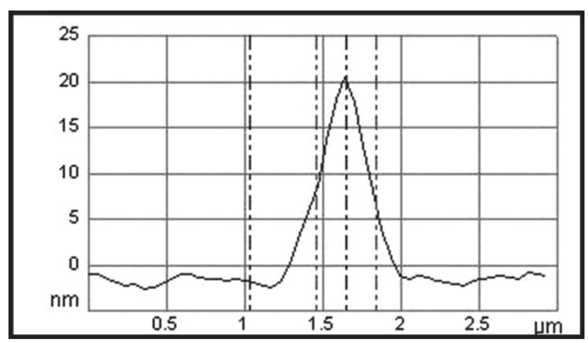

Figure 3: The AFM image of the cross section for Figure 2.

References:

[1] Kim, B., Jeong, E., Chung, J. W., Seo, S., Koo, B., Kim, J. "A molecular design principle of lyotropic liquid-crystalline conjugated polymers with directed alignment capability for plastic electronics." Nature Mater. 12, 659 (2013).

[2] Wang, H. T., Nafday, O. A., Haaheim, J. R., Tecaarwerk, E., Amro, N. A., Sanedrin, R. G., Chang, C. Y., Ren, F., Pearton, S. J. Toward conductive traces: Dip Pen Nanolithography of silver nanoparticle-based inks. Appl. Phys. Lett. 93, 143105 (2008).

[3] Kramer, M. A., Ivanisevic, A. Parallel dip-pen nanolithography using spore- and colloid- terminated cantilevers. Small 8, 3791 (2012).

[4] Lenhert, S., Sun, P., Wang, Y., Fuchs, H., Mirkin, A. Massively parallel dip-pen nanolithography of heterogeneous supported phospholipid multilayer patterns. Small 3, 71 (2007).

[5] Calvert, P. Inkjet printing for materials and devices. Chem. Mater. 13, 3299 (2001).