Nanostructure Fabrication Using Dip-pen Nanolithography

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In the field of nanoscience and nanotechnology, the development of lithographic methods for fabricating submicrometer and more recently sub-100 nm features is of great interest for both fundamental and technological purposes. Many structures when miniaturized to the sub-100 nm length scale possess architecture dependent chemical and physical properties. The ability to print such structures and interface them with larger architectures is opening applications in electronics,[1] optics,[2] catalysis,[3] and biosensing.[4] Examples of lithographic methods for making micro and/or nano scale patterns include photolithography,[5] microcontact printing,[6] e-beam lithography,[7] nanoimprint lithography,[8] and dip-pen nanolithography (DPN).[9]

The development of DPN as both a nanofabrication research and production tool has been the topic of significant interest over the past five years. DPN, which is a direct-write scanning-probe-based lithography, utilizes a cantilever tip to deliver various reagents to nanoscopic regions of a target substrate with high resolution and registration. Although the bulk of the effort in utilizing DPN has focused on its use as a serial process, the use of multiple scanning-probe microscopy (SPM) cantilever probes as pens has been shown to increase patterning speed and array density.[10] Another attribute of DPN is its substrate generality, and its ability to interface soft matter with hard inorganic substrates. A wide variety of substrates, from metals to insulators, have been explored in combination with many types of inks including small organic molecules, metal ions, biomaterials, sol gels, nanoparticles, and polymers.[11]

The ionic layer-by-layer (LBL) assembled films, introduced by Decher,[12] have been widely studied because of their potential applications in electronic materials[13] such as photovoltaics and electrochromic thin films, as well as biological studies[14] for templating cells and incorporating proteins. These organic LBL films, which are often referred to as polyelectrolyte multilayer (PEM) films, can be formed by sequentially immersing substrates into solutions of oppositely charged polyions. The ease of use of the LBL methodology in the assembly of charged polymers offers one the ability to tailor important parameters such as film thickness at the nanometer-scale and the chemical functionality of the top most layer of the PEM films. In addition, LBL organic films have been widely studied using various lithographic techniques. Hammond and co-workers have mainly focused on the LBL organic film assembly of various polyions on patterned monolayers by means of microcontact printing.[15] Indeed, micro-scale techniques for fabricating LBL structures using photolithography or micro-contact printing are well-established.[13,14] Developing such capabilities for DPN not only would allow one to significantly reduce feature size but also allow one to build chemically distinct LBL features on the nanometer length scale. Recently, Ivanisevic and co-workers have taken a step in this direction by demonstrating the deposition of charged polymers onto SiO_2 and polymer-coated SiO_2 films using DPN. Herein, we report an approach to integrating LBL with DPN in the fabrication of nanometer size patterns of multilayered polyelectrolyte structures. Furthermore, through the use of multiple pen arrays, we demonstrate, for the first time, the parallel writing capabilities of DPN in the context of this LBL patterning experiment.

In a typical experiment, dot and line arrays of a monolayer of mercaptohexa-decanoic acid (MHA) are generated using a single or multiple cantilever probes. The AFM probes were dipped into a 10 mM MHA acetonitrile solution for 10 seconds, dried with flowing N_2, loaded in an AFM or Nscriptor™, and then brought into contact with an Au substrate for a set period of time. Various passivating molecules were tested to minimize the nonspecific adsorption of polyelectrolyte onto the surrounding unpatterned gold areas, including octadecanethiol (ODT), 11-mercapto-1-hexadecanol (MHO), and 11-mercaptoundecyl -tri(ethylene glycol) (PEG). Nano sized PEM organic films were prepared by alternately immersing the patterned substrates into an aqueous solution of poly(sodium-4-styrenesulfonate) (PSS) and

poly(diallyldimethylammonium chloride) (PDDA). Because both PSS and PDDA are highly charged polymers, pH adjustment was not necessary to ensure that the polyelectrolytes in solution were charged. Patterned substrates are first immersed into an aqueous solution of PDDA (40mM, 0.5 M sodium chloride (NaCl)) for 10 min, rinsed with Milli-Q water, and dried with a stream of nitrogen. The substrates were then dipped into an aqueous solution of PSS (40 mM, 0.5 M NaCl) for 10 min, rinsed, and dried. After depositing each layer of PDDA and PSS, the substrates were cleaned in an ultrasonic bath for 10 sec to remove loosely adsorbed polyelectrolyte and to obtain uniform PEM organic films. These substrates were then alternately incubated in aqueous solutions of PSS and PDDA until the desired number of layers was achieved. In order to modify the top layer of PEM organic films with fluorescent material, the substrates were then soaked subsequently in aqueous solutions of poly(allylamine amine) (40 mM, PAA, 0.5 M NaCl) and fluorescence sodium salt (10mM). The generated PEM organic films on the DPN-generated patterns were characterized by tapping mode AFM and with an optical/fluorescence microscope.
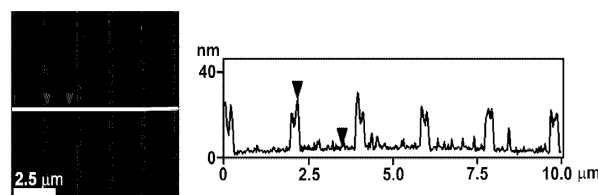

Figure 1. AFM image of line patterns of PE $_{PDDA/PSS}$ = 3 and its corresponding height profile.

Line arrays of MHA were also fabricated using DPN. The widths and heights of the lines of the MHA are 200 and 2 nm, respectively. The average heights determined from TMAFM show a linear increase, with values comparable to the average heights of the PEM dot arrays. The surfaces of the PEM line arrays bear a negative charge resulting from the adsorption of the final polyelectrolyte layer (PSS). These substrates were soaked in a 40 mM aqueous PAH solution with 0.5 M NaCl in order to investigate the deposition of the weak polycation onto the nanostructured strong polyanion surface. The adsorption of the weak polycation onto the PEM line array was determined by tapping mode AFM. As shown in Figure 1, the PAH was selectively deposited onto the patterned area with sharp boundary features. Furthermore, it shows that PAH was not adsorbed onto the PEG back-filled areas. The heights of the line arrays were determined to be approximately 19 nm. The height increase of the PAH layer is comparable to the thickness of each PSS and PDDA layer.

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