

Creating Nanoscale Structures by Local Protonation of Thin Polymer Films by Dip Pen Nanolithography

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ABSTRACT

The local swelling of thin ultraviolet-crosslinked poly(4-vinylpyridine) films by protonation was studied using Dip Pen Nanolithography (DPN) under ambient conditions. A phosphate buffer solution of pH4 was used as "ink". A series of experimental results suggest that the obtained structures are due to the local increase in film thickness caused by the protonation of the film's pyridyl groups with the buffer solution molecules delivered by the tip. Line features with heights from 7 nm to 25 nm have been obtained.

Keywords: Protonation, DPN, Swelling, P4VP, Nanoscale

INTRODUCTION

Among the current lithography techniques the Dip Pen Nanolithography (DPN) proves to be particularly promising since it is the only sub-50 nm technique that can directly deposit molecules under ambient conditions [1]. It uses an Atomic Force Microscope (AFM) tip to deliver collections of molecules onto the target substrate [2]. Using DPN a huge variety of nanoscale patterns been successfully applied to create varieties of micron- and nanoscale-sized patterns composed of small molecules [2,3], conducting polymers [4], biological macromolecules [5,6], polymer single crystals [7], pH-sensitive block copolymers [8], and inorganic materials [9,10] on metals, semiconductors, and monolayer functionalized surfaces. Generally, in order to create stable nanostructures, the ink molecules must be able to anchor themselves to the substrate via chemisorption or electrostatic interactions. In this study we used a slightly different approach to fabricate nanostructures by DPN. Instead of anchoring molecules to a surface we delivered protons from a phosphate buffer solution with pH 4 into a polymer film poly (4-vinylpyridine) causing it to swell. To the best of our knowledge this is the first demonstration of stimulating the mechanical response of polymeric material substrates by protons in a nanoscale. The results reported here is a nanometer-scale version of the observed macroscale experiment swelling of UV-crosslinked P4VP films under external acidic stimulation, as reported recently [11]. In that experiment, a 20% increase in thickness was observed when crosslinked P4VP films were soaked in pH 4 buffer solution for 10 minutes. Figure 1 shows the

proposed mechanism of the swelling. The pyridine molecules protonate to form pyridinium ions and the charge repulsions between these ions make the film increase in thickness. Here we report evidence that the same mechanism of swelling of P4VP occurs by microscopic protonation, which establishes a complete new way to create nanostructures.

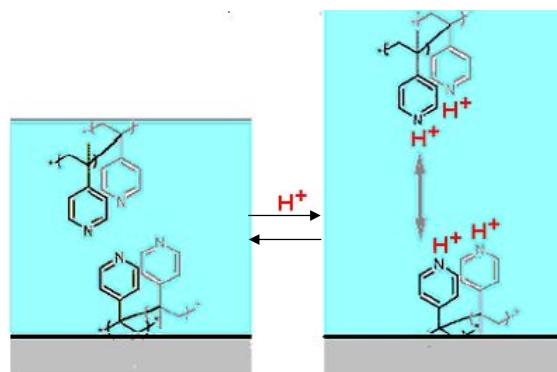


Figure 1: The swelling of UV-crosslinked P4VP films by protonation.

EXPERIMENTAL

Materials: poly(4-vinylpyridine) (P4VP) (molecular weight ca. 160,000, Aldrich), n-butanol (Fisher Scientific) were used as received. Sodium phosphate monobasic and sodium phosphate anhydrous dibasic were obtained from Mallinckrodt Chemical works.

Preparation of polymer thin films: A 10mg/mL solution of P4VP was prepared in n-butanol. Silicon wafers (1cmx1cm) were cleaned by sonicating in isopropyl alcohol for 15 minutes. The wafers were then dried using stream of nitrogen. P4VP solution was spin-coated onto the cleaned wafers at 2000 rpm for 60 seconds. The P4VP films were then irradiated using a 450W medium-pressure Mercury lamp for 5 minutes. The intensity of the lamp was measured to be 5.1 mW/cm², using a 254-nm sensor. The 5 minutes irradiation time included 2 minutes warm up time for the lamp to reach its maximal intensity. The irradiated films were then soaked in n-butanol for 24 hours to remove the unbound polymer. The film thickness was measured after each step at three different locations on the wafer and was

averaged. The thickness measured was 35 ± 1 nm. A Gaertner ellipsometer, model L116A with a 2 mW He/Ne laser at an incident angle of 70° , was used for the thickness measurements. Refractive indices used for the calculation were 1.465 for SiO_2 and 1.581 for P4VP.

Preparation of the AFM tip: Phosphate buffer solution (0.1M) of pH 4 was prepared using NaH_2PO_4 and Na_2HPO_4 . To coat the AFM tip (NSC 15, Mikromasch) with pH4 buffer solution, the tip was soaked in buffer solution for 1 minute. The tip was then dried in air for 10 minutes. This process is outlined in Figure 2. The tip was then mounted on the head of a MultiMode scanning probe Microscope (Nanoscope IIIa, Veeco). We used the same tip in all experiments but cleaned and coated it anew before each of the trials. As an initial check, all the samples were scanned with the buffer coated tip at a scan rate of 2Hz in Tapping Mode (TM) before nanostructures were created. This ensured us that the sample surface was smooth and that there were no structures similar to the ones which were created. These high rates did not transfer the buffer molecules to the surface.

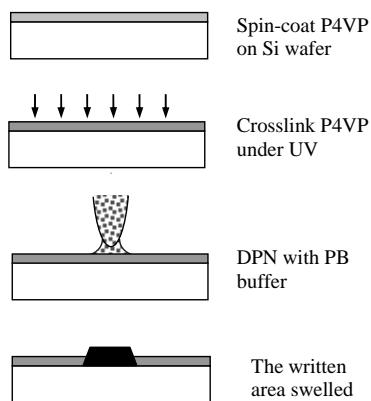


Figure 2: Procedure of creating nanostructures by local protonation.

I) Creating a pair of crossed lines on a P4VP film: The AFM was switched to Contact Mode (CM) for creating the pattern. The parameters were a scanning velocity v of 100 nm/sec, a deflection set point of 0.0 V, a scanning length l of 5 μm and a scan angle of 45° . The image of the line created was observed in TM. A second writing step was performed with the same parameters and same conditions, but at a scan angle of 135° and another image was taken.

II) Writing on a P4VP film using different contact forces: Three different deflection set points 0.0 V, 0.5 V and 1 V with a scanning velocity 40 nm/sec and scanning length 2 μm were used to create the lines.

III) Writing without pH4 buffer solution: An uncoated tip was used in a similar way as described for case II, for comparison purposes.

IV) Delivering protons to polystyrene films: We prepared a different thin polymer film (polystyrene), one that did not swell when tested with acidic buffer solutions at a macroscopic scale experiment. Then we scanned it with a coated tip in CM at a scanning velocity of 40 nm/sec. The scanning length was 2 μm and the deflection setpoints were 0.5 V and 1.0 V.

RESULTS AND DISCUSSION

I) Crossed perpendicular lines on a P4VP film: The scanning in CM produced a line that was 150 nm wide, 5 μm long and averaged 20 nm high. The height fluctuates between 16 nm and 24 nm. After the second scanning step another line perpendicular to the first one was created. Although it was produced under the same conditions it is not as high as the first one but only 5 nm (see Figures 3 and 4). We believe that the difference in height was caused by running out of the buffer molecules on the AFM tip, because further scanning without renewal of the coating did not lead to any structures.

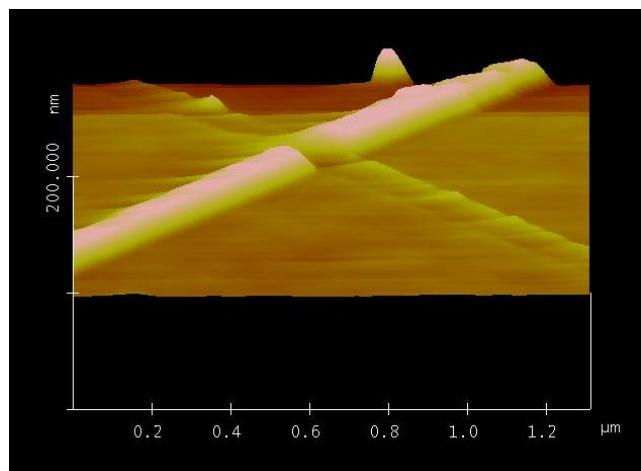
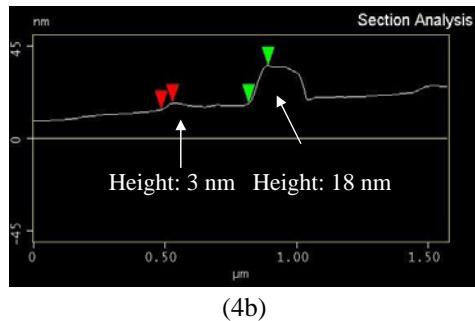


Figure 3: 3D-view of the crossed lines fabricated on a P4VP film.



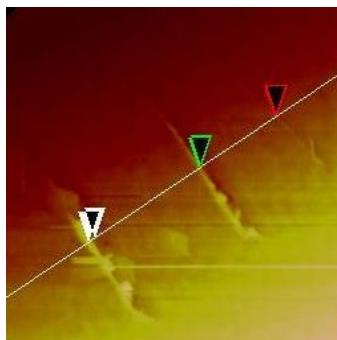
(4a)



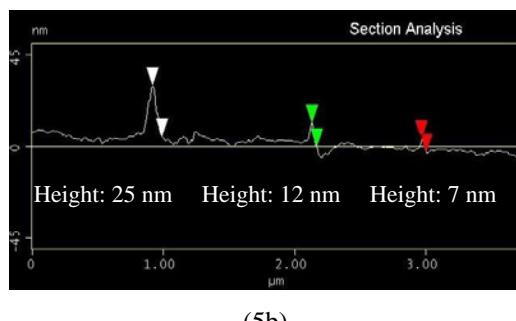
(4b)

Figure 4: Section Analysis of the crossed lines fabricated on a P4VP film.

II) Writing on a P4VP film using different contact forces: We produced lines of different height by applying different forces to the tip. It is observed that the height and width were thereby increased with increasing applied force. This is shown in Figure 5. The height of the line corresponding to the deflection setpoint 1 V was 25 nm, whereas the others were 12 nm and 7 nm respectively. The first produced line was the one with a deflection setpoint of 0.0 V (the one with the lowest height). We produced the lines in this order to make sure that we do not run out of the ink. The dependence of the height on the applied force shows that the number of delivered molecules increases with a greater force and, probably, a deeper penetration of the tip with respect to the polymer film. This result contrasts with what is found in more typical dip-pen nanolithography methods, where no dependence on the applied contact forces is found [12, 13].



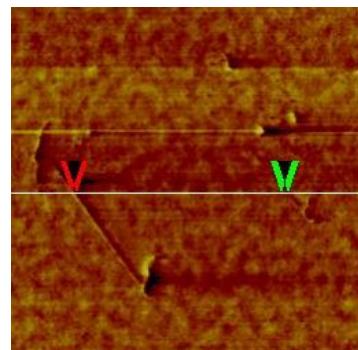
(5a)



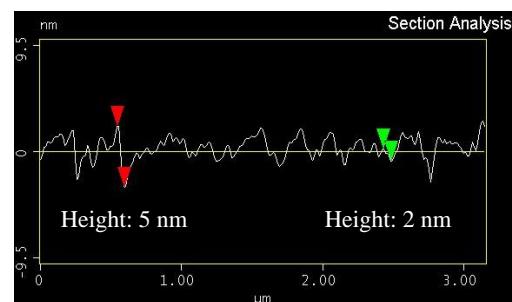
(5b)

Figure 5: Section Analysis of the lines fabricated using different contact forces on a P4VP film.

III) "Scratching": By scanning the polymer P4VP in CM with an uncoated tip at the same applied forces as in experiment II) we "scratched" the polymer film (Figure 6). The dent has a force dependent depth and is deeper when a higher force was applied to the tip. It is 5 nm deep and 200 nm wide at the highest applied force. We obtained no visible structure at the smallest applied force. The structure of the lines is obviously different from the ones created with a coated tip. This supports our claim that the buffer solution is the cause for the elevated lines in experiments I) and II).



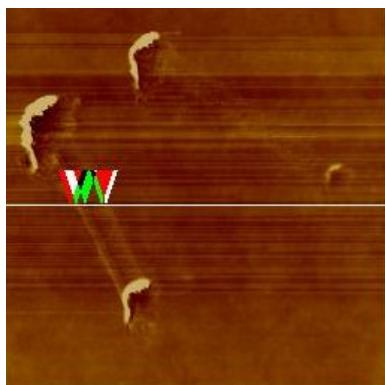
(6a)



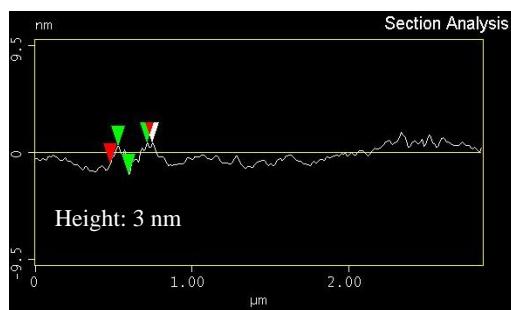
(6b)

Figure 6: Section analysis of the dents on a P4VP film created with a bared AFM tip without any buffer ink.

IV) Creating nanostructures on polystyrene: A control experiment was carried out using a photocrosslinked polystyrene thin film; it was tested at the same writing conditions. As shown in Figure 7 no elevated lines were obtained but only "scratches". Their depth is again dependent on the applied force and has a value of 4 nm at the higher and 2 nm at the lower force. This indicates that the elevated lines in experiment I) and II) are indeed produced by swelling of the poly(4-vinylpyridine) film. Note the elevated features at both ends of the dents. We believe that when the tip is first pressed into the surface it pushes some material away that collects in hillocks. When the tip is retracted it pulls some material off the surface that sticks to the tip through capillary forces but eventually pulls free and forms hillocks.



(7a)



(7b)

Figure 7: Section analysis of the dent on a polystyrene film created with a buffer-inked AFM tip.

These results show that we obtain raised features only by delivering protons to P4VP film. No features are obtained when delivering protons to polystyrene film, neither when scanning the P4VP in CM without delivering protons to the polymer. Hence we provide a strong indication of selective protonation of P4VP at microscopic scales. The height of the line increases with increasing force despite the scratching that we obtained with an uncoated tip. We suggest that by increasing the applied force there is a larger area from which protons can diffuse into the polymer and hence lead to more swelling. As in other DPN experiments, the uncertainty in pattern formation always constitutes a problem because of the complex processes of DPN, i.e. the formation of the water meniscus, the diffusion of the ink molecules onto the substrate [14], humidity, temperature, and morphology of both tip and substrate, all can influence the result of DPN.

CONCLUSION

We successfully demonstrated the creation of polymer nanostructures, and provide evidence that the driving mechanism is the local protonation of the UV-crosslinked P4VP films with molecules from a pH 4 buffer solution delivered by an AFM tip. The height of the structures can be controlled by changing the contact force, which is a distinct feature that differentiate our method from the more

common DPN technique. Finally, we would like to point out that this new capability to control the mechanical response of materials at the nanometer scale offers many technological applications. In the area of biotechnology, for example, it can be employed to construct valve gates in nanofluidic devices [15], or pillar arrays to sort out molecules by their sizes [16]. Because the swelling of P4VP is a reversible process, this technique may also find uses in erasable nano-storage devices. Additional studies about the dependence of the protonation on the scanning velocity and the reversible process are underway.

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