Electrochemically Nanopatterned Conducting Coronas of a Conjugated Polymer Precursor: SPM Parameters and Polymer Composition

Subhiah Jegadesan,†,‡ Prasad Taranekar,§ Swaminathan Sindhu,‡
Rigoberto C. Advincula,*§ and Suresh Valiyaveettil†,‡

Department of Chemistry and NUS – Nanoscience & Nanotechnology Initiative, National University of Singapore, 3 Science Drive 3, Singapore 117543, and Department of Chemistry, University of Houston, Houston, Texas 77204-5003

Received October 19, 2005. In Final Form: February 2, 2006

Here we describe the formation of precisely controlled corona-type nanopatterns on electroactive polymer precursor films using scanning probe microscopy (SPM) methods. The binary composition of electroactive groups in the polymer triggers the formation of corona-type nanopatterns at particular voltages and tip writing speeds through the electrooxidation of the polymer precursor film. Various parameters such as tip speed and applied bias were explored in the nanopatterning process, and the formation of a conductive nanopattern was investigated using conducting atomic force microscopy (C-AFM). The formation of the nanopattern was attributed to the flow of electrons from the AFM tip to the polymer film in a controlled electric field distribution. We also report a new method to distinguish the polymer composition and distribution of a polymer blend film by characterizing biasing differences in the patterning of a polymer film.

Introduction

In the past decade, electrochemical lithography techniques have allowed the formation of nanostructures through the selective deposition of metallic nanoparticles such as silver,1,2 copper,3,4 and platinum5 on conducting substrates.6 Electrochemical surface modifications via the oxidation of organic and inorganic semiconductor/conducting substrates have also been demonstrated.7,8 In recent years, scanning probe microscope (SPM)-based electrochemical nanolithography has attracted attention for the fabrication of nanostructures with a size range from sub-100 nm to micrometer-sized features using suitable films on conducting or semiconducting substrates.9 Unlike other techniques such as dip-pen nanolithography10 (DPN) and electrochemical nanolithography,5-7 electric field forces are used to direct the deposition of conducting organic materials such as polystyrene sulfonate and poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) films onto conducting or semiconducting substrates connected to a counter electrode. In addition to the use of organic materials, however, conductive metal nanoparticles such as Ni, Fe, Co, and Cu can be used.11,12 Surface modification of conducting polymer films using the dip-pen nanolitography technique has been reported.13,14

In this study, interesting electrochemical nanopatterning features, corona formation, and electric field distribution in precursor polymer films are reported. The use of these precursor polymers has been reported as an important route toward cross-linked conjugated polymer films.17 Because electroactive groups on the polymer backbone play a significant role in the electropolymerization process leading to a conductive pattern, several polymers based on a polystyrene backbone were investigated that contain carbazole and thiophene side groups.16 They were then investigated systematically to understand how DPN,5 where the pattern is formed by the deposition of “ink” molecules, in electrochemical nanolithography, the nanofeature can be derived from polymer films coated on a substrate. Such polymer nanopatterning procedures not only have high potential in nanodevice fabrication but also provide a platform to explore the fundamental mechanism of pattern formation and semiconductor properties of a polymer film.11 In addition to the formation of patterns from the polymer film, the fabrication of “raised” conducting nanopatterns is interesting with respect to technological applications in molecular electronics. Thus, the design and synthesis of suitable electroactive polymers and patterning to make conducting polymer circuits has been identified as an important area in the fabrication of organic nanodevices and nanoelectronics.12,13 Recently, the formation of conducting nanopatterns from an electroactive precursor polymer on conducting and semiconducting surfaces has been demonstrated by this group.14,15

10.1021/la052812k CCC: $33.50 © 2006 American Chemical Society
Published on Web 03/09/2006
electroactive groups on the side chain affect the electropolymerizability as well as the nanopatterning process of a precursor polymer film. In this work, interesting corona-type conductive nanopatterns were formed primarily with polystyrene functionalized with carbazole and thiophene groups (polymer A). The optimization of patterning parameters, the investigation of semiconducting properties, and the determination of the corona pattern formation mechanism were further explored. A new method for distinguishing the polymer distribution in polymer blend films is also reported on the basis of their patterning ability at different voltages.

To begin with, the molecular structure of the polymer that is used for the electrochemical nanopatterning studies is shown in Figure 1. The possible cross-linking structure due to electro-oxidation is also shown. The mechanism and electropolymerization phenomena of this type of polymer under ambient film conditions have been recently described. Detailed information on the synthesis of the polymer is given elsewhere. These polymers were observed to exhibit very good electropolymerizability based on the incorporation of thiophene and carbazole units. The mechanism involves a “trigger” effect for the thiophenes based on the initial oxidation of the carbazole units in a radical cation-to-neutral monomer reaction pathway.

Experimental Section

Thin films of polymer A were prepared by spin coating from their solution in toluene onto Si(100) substrates followed by drying under N₂ atmosphere. The thickness of the film was measured as 46 nm using both atomic force microscopy (AFM) and a profilometer (Alpha-Step 500 surface profiler, see the Supporting Information for details). The resistivity of the Si(100) substrate with native SiO₂ (Virginia Semiconductor Inc., Sb-doped,) was around 0.02 Ω·cm⁻¹. The experiment was performed under ambient conditions (relative humidity 50–75%, 21–23 °C) using a commercial Nanoman AFM (Nanoscope IV, Digital Instruments) and a gold-coated Si₃N₄ AFM tip with a force constant of 0.12 N/m in contact mode for patterning. Conductivity studies were performed on the polymer pattern using a conducting- AFM (C-AFM) setup in which a current sensor with a sensitivity range of microamps to femtoamps was used.

Results and Discussion

Figure 2a shows the formation of different-sized coronas on a spin-coated polymer film (polymer A) with diameters of 658, 2778, and 5320 nm based on tip-to-substrate biased voltages of −7, −9, and −11 V, respectively. This was done by holding the AFM tip for 2 s on the polymer film. Similarly, Figure 2b shows the lines drawn on the polymer film at different voltages of −7, −9, and −11 V using a tip speed of 1 μm/s. In these experiments, the dimensions of the patterned areas were observed to increase with increasing applied bias (negative). The size of the dot pattern is larger at higher voltages (−9 and −11 V). The same effect can be seen on the lines drawn at higher voltages such as −11 V. This observation indicates that with increased voltage the patterning rate of the polymer film was increased, which led to corona-type patterns. In this case, the only difference in the patterning condition between the dot and line pattern is the tip speed (i.e., the time at which the tip stays at a certain location on the polymer). In the dot pattern, the tip was positioned on the film for 2 s, whereas in the line pattern, the tip was moved over the film at a speed of 1 μm/s. This clearly indicates the importance of the electric field distribution in electrochemical nanopatterning procedures, which has not been observed in DPN-type nanopatterning.

To confirm whether the increase in pattern size is due to only applied voltage or AFM tip contact time, a polymer film was also patterned at a fixed low voltage of −7 V with different contact times between 1 and 8 s. Figure 2c shows the corona pattern at −7 V with different contact time of 1, 2, 4, and 8 s with corresponding pattern diameters of 190, 642, 980, and 1990 nm, respectively. The increase in pattern size shows that the patterning rate is increased with the contact time of the AFM tip. In other words, when the applied voltage time is increased, an increase in pattern width was also observed. The increase in pattern width with tip speed is also shown in Figure 2d, in which hexagons were drawn at −7 V with different tip speeds. Comparing the three hexagons, the hexagon drawn at 0.5 μm/s is a regular pattern, but when the speed was decreased to 0.2 μm/s, the pattern was seen along the line of the hexagon when increasing the diameter of the polymerized region. This effect can be further enhanced when the tip is moved at 0.1 μm/s, in which the whole polymer film close to the AFM tip end is patterned. These observations indicate that increases in both the voltage and the tip contact time increase the pattern size.

To understand the relationship of the height (relief structure) and corona from these patterns, the features were formed at −7 V by immobilizing the AFM tip for 6 s as shown in Figure 3a. It appears that the pattern height at the center is higher than other areas, indicating that the polymer under the tip is more exposed to the applied voltage, which causes more protruded areas at the center rather than in other areas. Recently, the distribution of the electric field in a C-AFM experiment for patterning polymer films has been modeled. Also, the formation of corona patterns on a dielectric film at high voltage has been reported using a Pin-plane corona model. The high charge concentration under the AFM tip due to the strong electric field leads to the central protruding pattern formation, and the localized discharge of electric fields form the corona pattern through the electropolymerization process. It has been reported that the formation of a corona-type oxide pattern on a Si substrate at high voltage (−45 V) occurs because of electronic conduction rather than ionic conduction. However, in this case we coat the Si substrate with an electroactive polymer and observe the formation of a corona-type pattern at a lower voltage (<12 V). The rapid patterning of this polymer is quite different from that of other previously investigated homopolymers such as PVK (poly-(vinylcarbazole)) and polythiophene, where such corona-type patterns were not observed. The maximum line width obtained by patterning the polymer PVK under an applied bias of −11 V with a tip speed of 1 μm/s was 182 nm. Upon comparing the patterning of other electroactive polymers such as PVK or polythiophene, an important difference is the presence of binary electroactive species (i.e., carbazole and thiophene on the polymer side chain). On the basis of previous studies of the electropolymerization mechanism of this copolymer, it is believed that in the absence of a monomer with a high electron affinity, the charge distribution is different, leading to a different polymer pattern formation.
binary electroactive groups (different oxidation potentials) on the polymer chain result in a higher-gradient electropolymerization pathway leading to the formation of the corona-type pattern at slow tip speeds. This unusual behavior can be correlated to the differences in the electrochemical behavior of the thiophene and carbazole homopolymer and copolymers. The electrochemical behavior of the thiophene and carbazole homopolymer and copolymers.

Figure 2. (a) Corona pattern of the polymer A film at various biases of −7, −9, and −11 V with a tip contact time of 2 s. The corresponding diameters are 658, 2778, and 5320 nm. (b) Line pattern of polymer A at a constant tip speed of 1 μm/s with different applied voltages of −7, −9, and −11 V. (c) Corona patterns drawn on a polymer film with a constant bias of −7 V at various tip contact times of 1, 2, 4, and 8 s and corresponding pattern widths of 190, 642, 980, and 1990 nm. (d) Height image of a hexagonal polymer pattern at −7 V with tip speeds of 0.5, 0.2, and 0.1 μm/s.

Figure 3. (a) Three-dimensional nanostructure of polymer corona pattern and the corresponding height profile formed at −7 V with a tip contact of 6 s and (b) the patterning of character PTC drawn at −7 V with a tip speed of 0.5 μm/s.
chemical properties based on the so-called “trigger effect” result from a radical cation to neutral monomer electropolymerization reaction pathway as described in another paper and in the Supporting Information.\textsuperscript{16,17} To demonstrate writing, the letters “PTC” were written with a line thickness of 150 nm at \(-7\) V with a tip speed of 0.5 \(\mu\text{m/s}\) (Figure 3b) using electrochemical nanolithography. Also, an array (5 \(\times\) 5) of dot patterns was fabricated at \(-7\) V with a tip contact time of 1 s (Supporting Information, Figure 2). These observations definitely show that by controlling the applied bias and tip speed one is able to create site specificity and size controllability of the patterns on the semiconducting substrate.

In addition to the formation of raised nanopatterns, electropolymerization results in the formation of electrically conducting nanopatterns based on the \(\pi\)-conjugation connectivity of the electroactive monomers. To confirm this, a 1 \(\mu\text{m}^2\) patterned area on the film was formed with an applied bias of \(-7\) V and a tip speed of 1 Hz (2 \(\mu\text{m/s}\)). The height image (topology AFM) and the current mapping image (C-AFM) of the square pattern are shown in Figure 4a and b, respectively. The current mapping image was obtained by scanning the image with a tip voltage of \(+4\) V, and the bright region on the film implies the conducting property as shown by the C-AFM image. This C-AFM image showed that the patterned region is more conductive than the unpatterned area with a current of 100 pA. Previous experiments on PVK have allowed direct measurements of \(I-V\) curves on this type of pattern.\textsuperscript{14,15}

The mechanism for the formation of a conductive nanopattern via electrochemical polymerization (cross linking) of carbazole and thiophene units should be initiated by the flow of electrons from the AFM tip to the film. The fact that these experiments were done under ambient conditions emphasizes the role of humidity (water vapor meniscus) between the tip and substrate in creating an electrochemical bridge.\textsuperscript{14} It also highlights the generality of the technique for electrochemical nanopatterning. If one intentionally incorporates electron scavengers into the polymer matrix, then it is expected that the electron scavenger will restrict the electron flow that should stop the formation of the corona-type pattern. To test this hypothesis as well as determine the mechanism of corona pattern formation, an equal volume of polymer A (0.3 wt %) solution in toluene was mixed with perfluoroundecyl methacrylate (40 mM), which is a known electron scavenger.\textsuperscript{20} After coating this mixture on the Si (100) substrate, nanopattern formation was attempted by holding the tip at a location with an applied bias of \(-12\) V for 12 s. As expected, no corona-type pattern was observed, but instead a dot pattern of 278 nm diameter (Figure 5a) was formed. This feature is much smaller than the corona pattern formed at \(-11\) V with a feature size of 5320 nm. This observation suggests that the electron scavenger in the film restricted the smooth flow of electrons to form the corona pattern. It is also possible that the formation of a dot pattern of 278 nm may be simply due to the effect of joule heating of the polymer as observed in other polymer films.\textsuperscript{11} In addition, we also mixed polymer A with pyridine in various proportions and studied the electrical distribution through the patterning of the polymer mixture film. Pyridine is a base that also affects the electropolymerization kinetics by scavenging the protons generated through the radical cation polymerization process. To study the effect of pyridine in polymer A, we prepared two polymer films with polymer A and pyridine mixed in volume ratios of 1:3 and 1:5 and did the patterning at various voltages by holding the tip for 12 s. The experimental results show that the polymer A and pyridine mixture (1:3) stops the formation of corona-type patterns and instead forms a dot pattern at \(-9\) and \(-11\) V. However, no feature was observed at \(-7\) V (Figure 5b), but for the film prepared using the 1:5 ratio, the pattern formed only at \(-11\) V, which suggests that corona-type patterning is dependent on pyridine concentration (Figure 5c). Moreover, the formation of a dot pattern at \(-11\) V for the 1:5 ratio may be largely due to a joule heating effect on the polymer.

To further investigate the behavior with other polymer blends, polymer A and polystyrene were mixed and coated onto a Si (100) substrate, and patterning was attempted. Because polymer A can be patterned at \(-7\) V (Figure 2a) but polystyrene cannot be patterned at this voltage (Figure 5d), a higher voltage was used.\textsuperscript{11} Taking advantage of this biasing difference in the patterning of different polymers, one can therefore use this property to distinguish the polymer distribution in a blend film. At \(-9\) V, polymer A showed a raised pattern, but polystyrene did not form patterns. A square pattern of 5 \(\mu\text{m}^2\) on the polymer film was formed with a tip voltage of \(-9\) V and speed of 10 \(\mu\text{m/s}\). Figure 5e shows the morphology of the polymer blend film on the Si(100) substrate before patterning, and Figure 5f

Figure 4. (a) Square patterning (1 \(\mu\text{m}^2\)) of the polymer A film at a scanning speed 1 Hz (2 \(\mu\text{m/s}\)) with a tip bias of \(-7\) V and (b) the corresponding current-mapping image of the pattern with a conducting current of 100 pA.
shows the morphology after the square patterning. The patterned region showed a randomly distributed ridge pattern over an area of 5 $\mu m^2$ characteristic of a morphology in which polymer A is reactive and polystyrene is not. The distribution of the raised feature is uniform within the boundary of the square region but not nearly homogeneous as in the case of pure polymer A alone (Figure 3a). This indicated that polymer A (with a polystyrene backbone) indeed formed a very good blend with polystyrene. In principle, this experiment can be utilized to identify the miscibility of polymer-blend films as well as control the morphology of patterning based on composition ratios. Interestingly, this approach for analyzing miscibility in polymer blend films does not require cumbersome TEM analysis methods. Last, we have found the patterns to be thermally stable even after annealing above the glass-transition temperature of polystyrene. This was the case as in our previous studies with the nanopatterning of PVK and is attributed to the cross-linked nature of the polymers after the electropolymerization process.

**Conclusions**

Electrochemical nanolithography using a precursor copolymer with binary electroactive species showed interesting corona patterning effects with controlled applied voltage and tip speed. This multielectroactive group facilitates a patterning based on relief height formation as well as corona size distribution by increasing the patterning rate and residence time of the tip from one position to another. This method also leads to the formation of conductive nanopatterns, which is confirmed by C-AFM imaging. Thus, pattern formation is based on an electropolymerization process and is not only due to joule heating. Also, the flow of electrons during the patterning can be regulated by the use of polymer blends with electron scavengers. A new method is proposed that can be utilized to distinguish the polymer distribution in blends on the basis of their patterning ability and film morphology. Optimization to control the rapid patterning of precursor polymers and their possible application to polymer and molecular electronics is underway in our laboratory.

**Acknowledgment.** We thank the Agency for Science and Technology Research (A*STAR) and the National University of Singapore (NUS) for funding support (S.V.), NUS-NNI for a research scholarship (S.J.) and a research fellowship (S.S.), and the Department of Chemistry for technical support. We also thank the National Science Foundation for partial funding under NSF-DMR (05-04435) and NSF-CTS (0330127).

**Supporting Information Available:** Experimental details showing the thickness measurements, dot array patterning of polymers, polymer synthesis details, electrochemical cyclic voltammetry data, and others. This material is available free of charge via the Internet at http://pubs.acs.org.

LA052812K