

Direct Electrochemical Nanopatterning of Polycarbazole Monomer and Precursor Polymer Films: Ambient Formation of Thermally Stable Conducting Nanopatterns

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The direct nanopatterning of polycarbazole on ultrathin films of a “precursor polymer” and monomer under ambient conditions is reported. In contrast to previous reports on electrochemical dip-pen nanolithography using monomer ink or electrolyte-saturated films in electrostatic nanolithography, these features were directly patterned on spin-cast films of carbazole monomer and poly(vinylcarbazole) (PVK) under room temperature and humidity conditions. Using a voltage-biased atomic force microscope (AFM) tip, electric-field-induced polymerization and cross-linking occurred with nanopatterning in these films. Different parameters, including writing speed and bias voltages, were studied to demonstrate line width and patterning geometry control. The conducting property (current–voltage (*I*–*V*) curves) of these nanopatterns was also investigated using a conducting-AFM (C-AFM) setup, and the thermal stability of the patterns was evaluated by annealing the polymer/monomer film above the glass transition (*T*_g) temperature of the precursor polymer. To the best of our knowledge, this is the first report in which *thermally stable* conducting nanopatterns were drawn directly on monomer or polymer film substrates using an electrochemical nanolithography technique under ambient conditions.

Introduction

Fabrication of nanopatterns from suitable polymers using surface probe microscopy (SPM) methods is currently of great interest for developing nanoelectronic devices.¹ Current trends in miniaturization of optoelectronic devices requires the patterning of conducting materials in nanoscale geometries and resolution because of its perceived applications in various fields such as molecular electronics, miniature displays, data storage, and sensor technologies.^{2,3} Various approaches have been developed using negatively biased conducting atomic force microscope (C-AFM) probes to generate nanopatterns, which includes metal or oxide patterns on metal^{4a}/semiconducting^{4b,4c}/ion conducting substrates⁵ and raised patterns on polymer surfaces.⁶ A few research groups have fabricated nanopatterns from conducting polymers using SPM techniques, which include dip-pen nanolithography (DPN), electrochemical DPN, electrostatic nanolithography, and e-beam lithography.^{7–12} Among these methods, DPN and electrochemical

DPN involves depositing materials from an AFM tip to the substrate, whereas, in other methods, patterns were drawn on thin polymer films on a solid substrate by exposure to an electric field or e-beam. Patterns have been formed on polymer films due to Joule heating of the polymer by an applied electric field without chemical change.^{6,12} In electrostatic nanolithography, the patterns are created without chemical changes on the polymer, whereas, in electrochemical nanolithography, chemical changes such as cross-linking or polymerization can occur due to the formation of an electrochemical bridge. Electrochemical nanopatterning of a conducting polymer on a solid-state precursor polythiophene film under a liquid electrolyte environment has been demonstrated.¹³ Also, the electrooxidation of terminal vinyl groups of an alkylsilane monolayer to form carboxylic acid groups has been described.¹⁴ In addition to nanopatterning, the electrochemical process has been used to image chemically modified insulators and their electrostatic interaction. This has been demonstrated by probing the electrode potential between a chemically modified tip and a substrate in redox probe microscopy (RPM), which includes both patterning and surface modification elements.¹⁸

In this work, a protocol is reported for the controlled nanopatterning of conducting polycarbazoles through the direct

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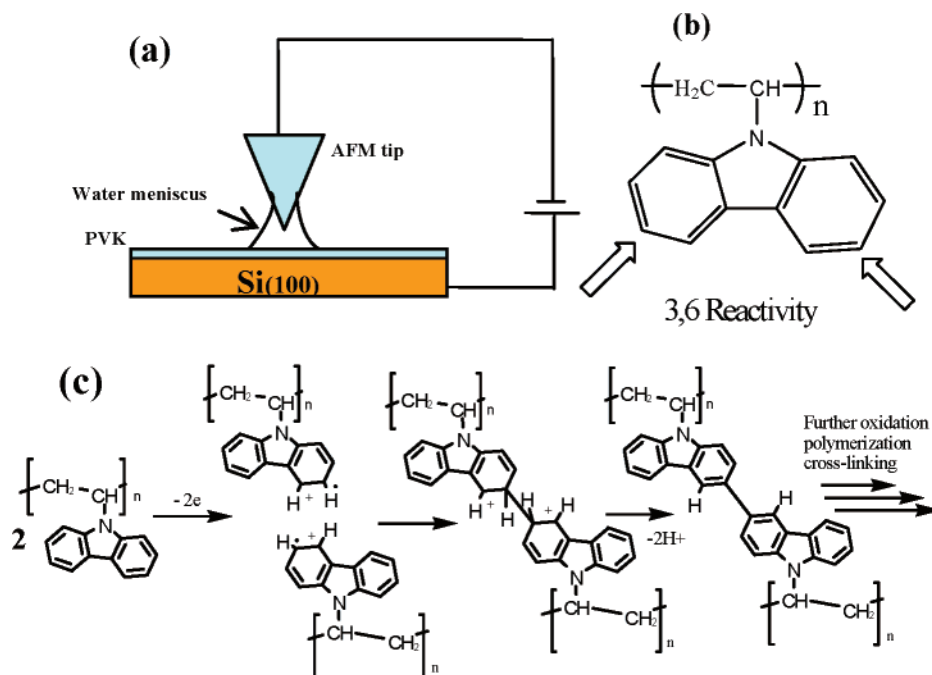


Figure 1. (a) Schematic diagram of electrochemical nanolithography. (b) Chemical structure and possible polymerization sites of PVK. (c) Mechanism for electropolymerization (cationic) and cross-linking of PVK.

electrochemical polymerization on thin films using a voltage-biased AFM tip. The properties of poly(vinylcarbazole) (PVK) materials as “precursor polycarbazoles” and their electrooptic applications as ultrathin films has been reported by our group.¹⁵ In the PVK film, the side chain carbazole units can be polymerized and cross-linked to form insoluble and electrically conducting moieties. Moreover, cross-linked PVK polymers (formation of oligocarbazoles) show interesting properties, particularly in photoconduction, electroxerography, and photovoltaic components, and provides a very efficient matrix for current carrier transport due to their reactive carbazole moieties.^{15,16} Recently, the electrochemical oxidation of PVK films on Au substrates was demonstrated by C-AFM, which lead to the formation of nanoscale lines.¹⁷ In this paper, the controlled patterning ability in thin films of both PVK polymer and carbazole monomer using direct electrochemical nanolithography is reported. In contrast to previous methods including DPN using monomer ink or electrolyte-saturated films in electrostatic nanolithography,^{7–13} these patterns were directly prepared electrochemically on spin-cast monomer and polymer films under ambient temperature and humidity conditions. Properties such as conductivity and thermal stability of the patterns were compared and found to be differentiated from the original films. Optimization of writing parameters such as writing speed, bias voltages, and pattern geometries was explored.

Experimental Section

The PVK (1 100 000 MW) and carbazole monomer were purchased from Aldrich and used without further purification. The Si substrate was previously cleaned in ethanol by sonication followed by washing with acetone and dried in N₂ gas. The PVK polymer and carbazole monomer films were prepared by spin-coating (6000 rpm) from 0.5 wt % solutions in toluene onto doped Si(100) substrates

followed by drying under N₂ atmosphere. Transparent films were obtained, and the thickness of the films was measured as ~46 nm on a Si substrate using a profilometer (Alpha-Step 500 surface profiler), or up to 64 nm on a Au/mica surface using these spin-coating conditions (Supporting Information, Figure 1SI). No optimization was made to correlate film thickness with spin-coating conditions, for example, concentration and rpm speed. The experiments were performed under ambient conditions (humidity 25–74%, 21–23 °C conditions) using a commercial AFM (Dimension 3100, Digital Instruments) with a Au-coated Si₃N₄ tip having a force constant of 0.12 N/m in contact mode for patterning. Conductivity studies such as current–voltage (I–V) measurement and current mapping of the patterned surface were performed using a C-AFM setup within a range of microamperes to femtoamperes. Other experimental setup details, including electrochemical cyclic voltammetry (Supporting Information, Figure 5SI), FT-IR (Supporting Information, Figure 6SI), and AFM profilometry are discussed in the Supporting Information.

Results and Discussion

There are many factors that can influence the electrochemical nanopatterning of a polymer film. This includes substrate topology and conductivity, tunneling current, bias voltage, electrochemical bridge, electric-field distribution, and ultrathin film qualities. To begin with, the Si(100) substrate was chosen because of its semiconductor properties, which allowed us to apply an effective bias voltage between the tip and the substrate through the monomer/polymer film. The resistivity of Si(100) substrate with native SiO₂ (Virginia Semiconductor Inc., Sb-doped,) was around 0.02 ohm cm. The polymer films were spin-cast, annealed, and evaluated for homogeneity and flatness prior to nanolithography. The thickness was also evaluated by profilometry. The effect of tip speed and applied bias on the polymer patterns were then investigated, followed by the investigation of conductivity and thermal stability of the patterns. Figure 1a,b represents the schematic diagram of the direct electrochemical nanolithography protocol and the chemical structure of PVK. As reported earlier, the carbazole units on the PVK backbone are capable of oxidative cross-linking primarily through a radical cation route in an electrochemical environment (Figure 1c).¹⁵

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The ambient conditions of the experiment allowed this anodic oxidation to proceed without the presence of added electrolytes.¹⁷ This is in contrast to previous work by other groups where solution dipping was used to introduce electrolytes prior to patterning.¹³ In this case, the relative humidity is sufficient to create an electrochemical bridge with the dielectric medium and the cathode (tip) and anode (Si substrate). Previous work by Mirkin et al. demonstrated the ubiquitous presence of this water meniscus on both hydrophobic and hydrophilic surfaces (except under ultrahigh vacuum conditions) where there is substantial capillary force between the cantilever tip and substrate.^{7b} Furthermore, this force/water layer does not have a significant effect on film morphology, as reported by De Yereo et al.²³ Overall, the choice of the Si substrate and the simplicity of doing the experiment under ambient conditions allowed the investigation of various patterning parameters involved in the direct electrochemical nanopatterning of the carbazole and PVK films.

Nanopatterning of Carbazole Monomer. Using the spin-coated carbazole monomer film, polymerized nanopatterns were generated on a silicon substrate with a negatively biased tip. Figure 2a shows the contact mode AFM image of the nanopatterned monomer film on a Si substrate. A clear image could be obtained when the patterned surface was scanned with an AFM tip at a relatively weak contact force of 2–5 nN. When the contact force is raised, the AFM image showed an increased number of scratches over the film surface. The polymerized lines are characterized by a height increase over the film owing to both Joule heating,¹² caused by the applied current, and the electropolymerization process. The electropolymerization in this case should result in the formation of linear polycarbazole polymers through the 3,6 position of the carbazole (Supporting Information, Figure 4SI). The formation of an electrochemical bridge between the negatively biased AFM tip (cathode) and the Si substrate (anode) is facilitated by the influence of humidity on the monomer dielectric film (Supporting Information) to form counterions.¹⁷ Polymer lines of varying line width of 187, 162, 140, 128, 87, and 78 nm, were drawn using various tip speeds of 1, 2, 4, 6, 8, and 10 $\mu\text{m/s}$, respectively, by moving a negatively biased tip over the monomer film (Figure 2). It also showed that the pattern size decreased with increasing tip speed, but the height remained relatively constant (~ 2 nm) during the patterning. The pattern width and height were found to increase with increasing tip voltage. The pattern height varied only when the voltage was changed and remained constant at a particular tip bias. In addition to the nanoline, other complex patterns such as that termed “NANO”, with a width of 86 nm, were drawn using a tip bias of -7 V (Figure 2b).

To study the conductivity of the nanopattern, a square area of the film was patterned by scanning the negatively biased AFM tip across a $1\ \mu\text{m}^2$ area with a scan speed of 1 Hz at -5 V. Figure 3a shows the protruding square pattern of an electropolymerized carbazole (forming conjugated polycarbazole) with a height of 5 nm. The corresponding C-AFM image (scanned at positive bias, $+5$ V) (Figure 3b) shows that the patterned area is more conductive with a current of 10 pA compared to the unpatterned area. This C-AFM experiment is somewhat similar to scanning

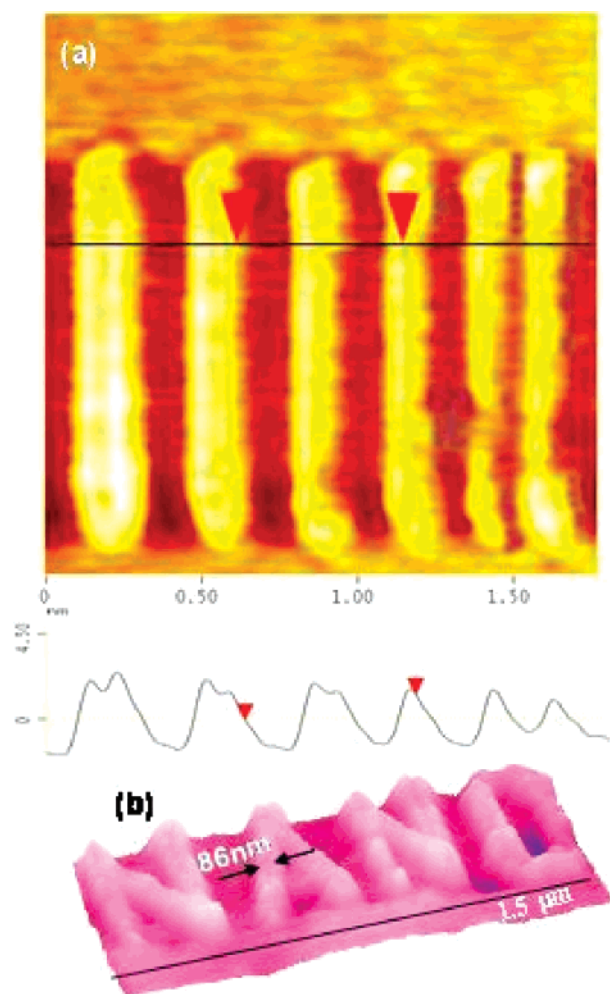


Figure 2. (a) Nanopatterns drawn on carbazole film at a constant bias of -7 V at various tip speeds of 1, 2, 4, 6, 8, and 10 $\mu\text{m/s}$, corresponding to a line width of 187, 162, 140, 128, 87, and 78 nm, respectively, and imaged by contact mode AFM (height). (b) Three-dimensional (3D) image of “NANO” on the carbazole monomer film patterned at -7 V with a pattern width of 86 nm. Height is at ~ 2 nm.

tunneling microscopy (STM), where the topographic image is formed because of a constant tunneling current. In the case of C-AFM, a current may tunnel from the AFM tip to the nonconducting polymer film during scanning (tip voltage: $+5$ V) such that the current mapped image shows the current is much lower for the unpatterned area than it is for the patterned area. This change can be clearly seen from the image where the patterned area is more conductive than the unpatterned area by C-AFM.

The thermal stability of the patterns was also investigated by heating the substrate for 3 h at different temperatures of 150 and 270 $^{\circ}\text{C}$. At both temperatures, the patterns were stable and the conductivity did not change after heating. The pattern shown in Figure 4 represents a feature annealed at 270 $^{\circ}\text{C}$ for 3 h and then cooled to room temperature. Even though the temperature is above the melting point (245 $^{\circ}\text{C}$) of carbazole, the thickness or aspect ratio of the patterns did not change after annealing at a high temperature. To our knowledge, this is the first report in which heat-stable features were created on a molecular monomer film. In this case, the formation of a high T_g and T_m linear polycarbazole prevented the thermal collapse of the nanopatterns, which would have been the case if no polymerization took place.

Nanopatterning of PVK Film. Similar to the patterning of the carbazole monomer film, nanopatterns on PVK polymer films

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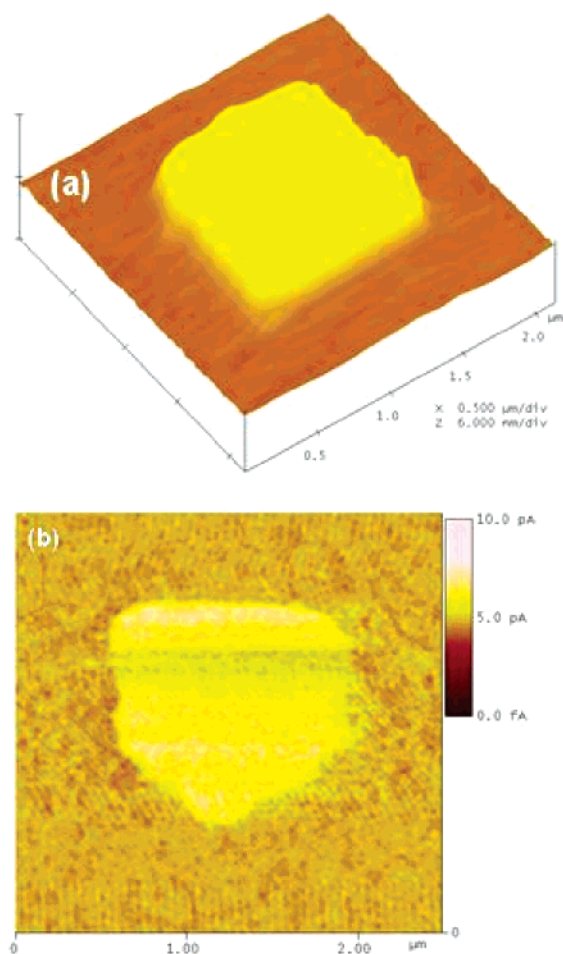


Figure 3. (a) Square patterning of $1 \mu\text{m}^2$ on carbazole film at a scanning speed of 1 Hz with a tip bias of -5 V imaged by contact mode AFM, and (b) the corresponding current mapping image (C-AFM) of conductive square pattern with a conducting current of 10.0 pA at an applied bias of $+5 \text{ V}$ for imaging.

deposited on Si substrate were formed under various tip speeds and biases. A square-shaped pattern with an area of $1 \mu\text{m}^2$ was created by scanning the PVK film with an AFM tip at -7 V at a tip speed of 1 Hz. Also, the conducting property of the pattern was investigated using the C-AFM imaging method. The thermal stability of the patterned feature was then studied by annealing the pattern at 150 and 270°C for 3 h.

Figure 5a shows that protruding nanopatterned lines were fabricated on the PVK film when the negatively biased AFM tip was moved on top of the polymer film. The nanolines were formed at voltages of -5 , -7 , -9 , and -11 V , with line widths of 83, 128, 162, and 231 nm and heights of 4, 5, 6, and 6 nm, respectively (Figure 6a,b). Similar to the carbazole film, PVK patterns also showed a similar relationship with the applied voltage. Previous work on a Au/mica substrate electrode/cathode under ambient conditions showed the same relationship between the bias voltage and the line widths of the patterns (Supporting Information, Figure 2SI). In contrast to the carbazole film patterning, the height increase is greater with increasing bias. Height (topological) images of pattern "PVK" written with a tip speed of $1 \mu\text{m/s}$ and an applied bias of -7 V are shown in Figure 5b, with a pattern width of 149 nm and average height of 2 nm.

Such speed–pattern dependence on nanopatterning was also observed on lines written on a PVK film spin-coated on a Au/mica substrate (Supporting Information, Figure 3SI), for example, from 0.5 to $3.0 \mu\text{m/s}$. The minimum voltage for patterning was

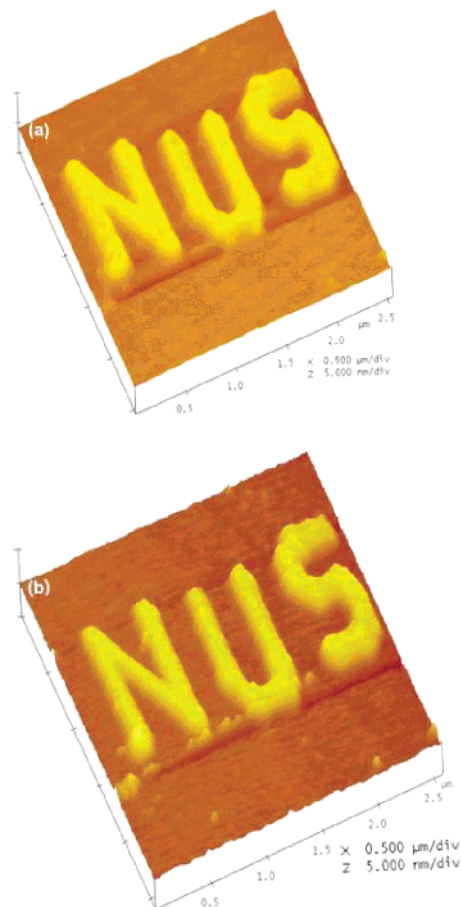


Figure 4. The AFM height image of the patterned character "NUS" before (a) and after (b) heating of the carbazole film at 270°C for 3 h.

lower at -3.0 V for those substrates because of the more conducting Au. Thus, these results show that patterns of specific sizes and shape could be drawn by controlling the applied voltage and tip speed on various conducting substrates. Figure 7a shows that different polygon patterns grown on a PVK film at various speeds with applied voltages of -5 and -7 V are possible.

In contrast to the carbazole monomer, the electropolymerization in the precursor PVK results in the formation of a cross-linked polycarbazole pattern in the precursor polymer film.^{15,17} This is due to the preference for both intra- and intermolecular reactions of the "tethered" carbazole units within a polymethylene backbone (Figure 1 and Supporting Information, Figure 4SI). Because of the electropolymerization of PVK by cross-linking between the carbazole moieties to form polycarbazole units, it is anticipated that the patterned area should also be more conductive. To check the conductivity of this cross-linked pattern, a $1 \mu\text{m}^2$ area was again patterned at a scanning speed of 1 Hz with an applied bias of -5 V (Figure 7c). This time, two approaches were followed to find the conductivity of the pattern. In the first approach, current mapping was done by scanning the patterned surface with a conductive AFM tip at a sample bias of $+5 \text{ V}$. In another approach, I–V measurements on the patterned area were done by immobilizing the AFM tip at a particular spot (maintaining position) and ramping the tip with a voltage range from 0 to 12 V. The current mapping image is shown in Figure 7b, in which the pattern exhibited a conductivity of 10 pA . In the I–V curve measurements, the current reaches a saturation conductivity of 142 nA at a bias of 8 V (Figure 7d). Again, no conductivity was observed from the unpatterned area. However, electro-cross-linking between the carbazole units on the polymer backbone to

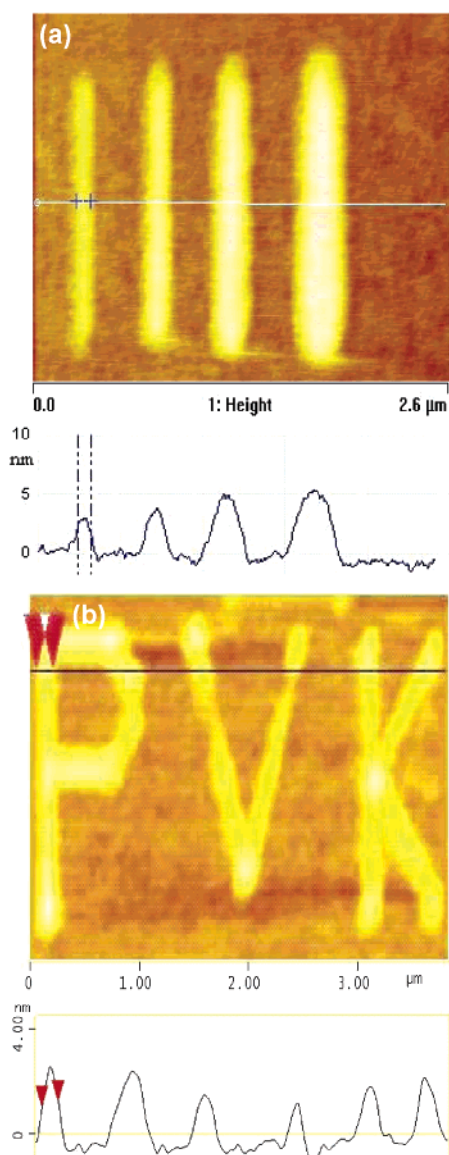


Figure 5. (a) Nanolines written on PVK film at a constant tip speed of $1 \mu\text{m/s}$ with the different biases of -5 , -7 , -9 , and -11 V with line widths of 83, 128, 162, and 231 nm, respectively. (b) AFM image with height profile of the pattern “PVK” drawn at -7 V at a tip speed of $1 \mu\text{m/s}$.

form conjugated units leads to higher conductivity of the pattern. It was previously reported that an electrochemical reaction on a conducting organic surface creates an insulating layer,¹⁹ whereas, in this case, a conductive nanopattern is formed from a nonconducting surface. During the I – V measurements, the electrical field reached a value of 10^7 – 10^8 V/cm. Typically for such high electrical fields, holes are injected and transported to a conjugated polymer in the form of polarons.²¹ Any observed hysteresis in the I – V behavior is probably related to polaron dissociation at this high field. In this case, no hysteresis was observed in the I – V curve up to the tip voltage of 8 V. This indicates that, at higher fields (above a critical e -field), the dissociation of polarons as well as electrical annealing occurs, which leads to a hysteresis in the I – V curve response. The same effect was recently reported for an MEH-PPV polymer, where the hysteresis in the I – V curve is observed only at high fields.²² Since the current conduction depends on the thickness and electrical properties of the polymer, it will be interesting to investigate the current mobility at various fields and thicknesses for these films.

The thermal stability of the patterns on the polymer film was studied at 150 and 270 °C. It was found that, when the sample is heated below T_g (200 °C for PVK) in a vacuum, no changes were basically observed on the pattern. But, by heating to 270 °C for 3 h, small changes on the polymer patterns were observed (Figure 8). This could be attributed to the “softening” of the polymethylene backbone of PVK and the connectivity within the polymer film, as seen in the fusing of the letters “U” and “S” of the pattern. This is in contrast to the non- T_g characteristics of the patterned monomer films. Nevertheless, the conductivity of the patterns was not affected by annealing.

Comparison of PVK and Carbazole Monomer Film Patterning. From the above experiments of nanopatterning both the precursor polymer and monomer films, the observed patterns showed some significant differences in the patterning process, which include the variation of pattern width and height with respect to the applied bias, tip speed, conductivity properties, and thermal stability.

The significant difference between the patterning of the carbazole monomer and the PVK polymer includes changes of the pattern width based on the tip bias without changing the pattern height. In the case of PVK, the changes occurred in both the width and the height of the patterns with an increase in applied bias. On the other hand, no variable height changes were observed for the monomer film. This may be due to the significantly higher degree of freedom and linear polymerization for the carbazole monomer compared to the precursor. This may also be due to the fact that, in a PVK film, the side group monomer is tethered to a polymer backbone and therefore governed by the viscoelastic nature of the polymer where the effect of local Joule heating has been shown to be dramatic under higher applied electric fields.¹²

In addition, the effect of relative humidity in the formation of a water meniscus, which acts as a two-electrode nanocell between the tip and substrate,²⁰ and the adsorption of moisture and gases on polymer films needs further investigation. When the tip voltage is more than the threshold voltage (greater than -4 V), the oxidation of the carbazole ring generates the cationic species. The presence of water with dissolved CO_2 in an ambient air environment is the source of carbonate and bicarbonate anion species, which are able to neutralize the generation of cation charges. Also, the effect of the catalytic electrolysis of H_2O is unknown.

During the patterning process, the carbazole film pattern was formed at -3 V, whereas the patterning of the precursor polymer required a slightly higher -4 V on a Si substrate. However in previous experiments, PVK polymers can be patterned on Au substrates at -3 V (see Supporting Information).¹⁷ The difference in the patterning voltage of PVK polymers is therefore attributed to the conducting nature of the substrate. Therefore, in the future, it is possible to use substrates with various conductivities to selectively address the electropolymerizability of monomers or polymers in a film. Figure 6c shows the variation of the pattern width based on the tip speed in which PVK showed larger differences compared to the carbazole film. The polymer and monomer showed a similar conducting property, which implies the common polymerization of carbazole moieties in both instances. The conductivity of the PVK pattern on Si(100) substrate was estimated using the following relation:

$$\sigma = d/A_t R^{24}$$

where d is the film thickness and A_t ($= \pi r^2$) is the area of the

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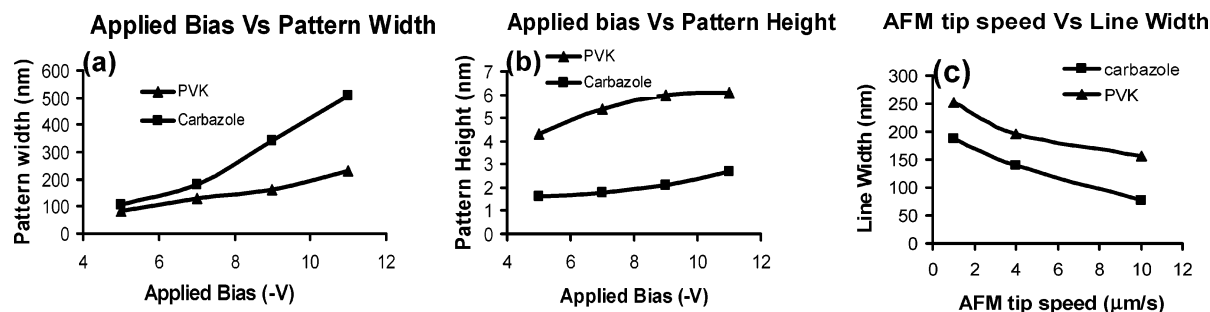


Figure 6. Variation of pattern width (a) and height (b) with applied bias for polymer and monomer. (c) Plot of line width vs AFM tip speed during PVK and carbazole patterning.

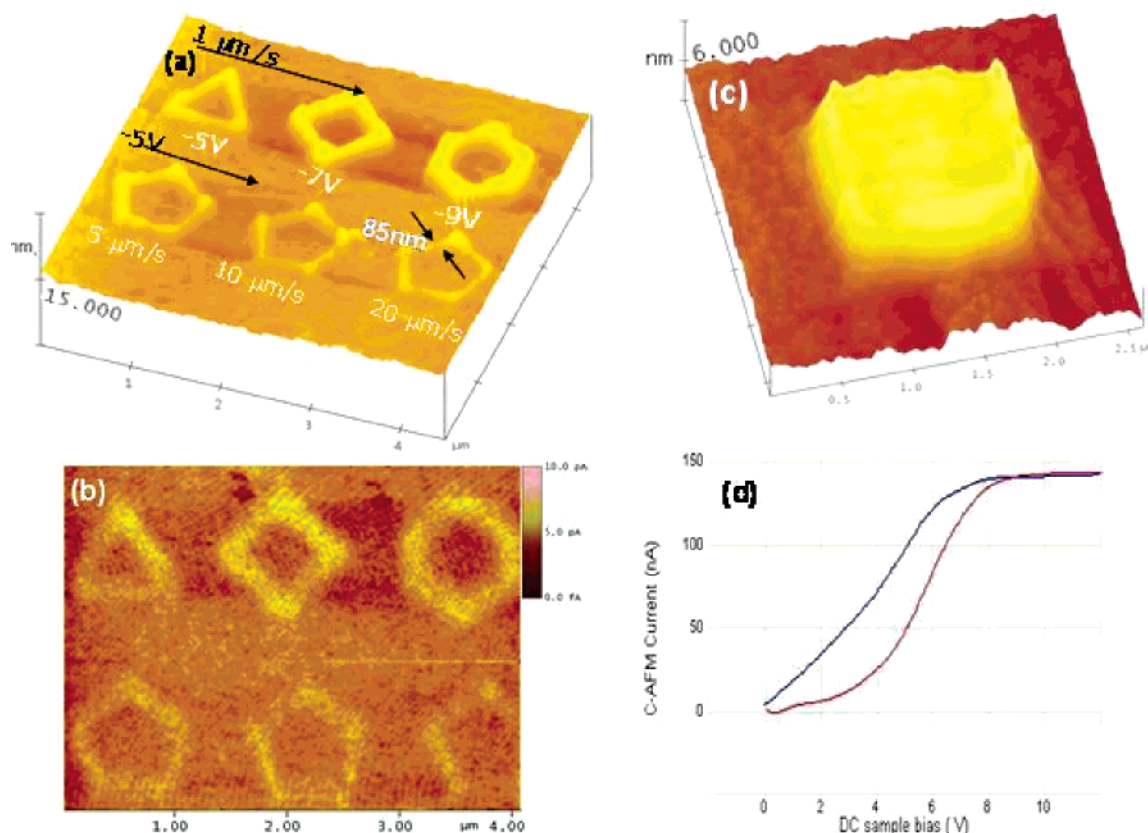


Figure 7. (a) AFM height images of the electrochemical patterned polygons at different tip voltages and speeds. (b) Corresponding C-AFM image of polygon patterning with a conductive current of 10 pA. (c) Square ($1 \mu\text{m}^2$) patterning of PVK film at tip scanning speed of 1 Hz with a tip bias of -5 V and imaged by contact mode AFM. (d) Corresponding I-V curve hysteresis measurements on the patterned square of the PVK film.

C-AFM probe in contact with the surface. Here the contact radius between the tip and substrate is 50 nm. R is the resistance of the pattern, estimated from the inverse slope of the I-V curve. If the I-V curve is not linear, the slope of the curve was estimated from the linear fit of the curve. Using this approach, the conductivity (σ) of the PVK pattern on Si substrate (where $d = 46 \times 10^{-9} \text{ m}$, and $R = 0.04 \times 10^9 \Omega$) was estimated as $1.5 \times 10^{-3} \text{ S/cm}$. The conductivity (σ) of the pattern is lower than the reported conductivity value ($10^{-3} - 10^{-4} \text{ S/cm}$) of polycarbazole that was prepared by the usual electropolymerization method.²⁵ However, the conductivity value together with the nonohmic behavior of I-V curve (Figure 7d) shows that the pattern is semiconductive. Since the understanding of the polymer-solid interface is very important for many technological applications, we also explored the conductivity for the polymer/Au(111) interface. The I-V curve of patterned PVK on a Au(111) surface

followed the ohmic behavior,¹⁷ and we estimated the conductivity from the I-V curve as 0.2 S/cm , which confirmed that our patterns are conductive.²⁶ These results show that the polymer-solid interface plays a significant role in the electronic properties of the polymer, and these studies are eventually important for nanoscale device fabrication.

Since the thermal annealing of polymers below their T_g enhances the device performance,²⁷ we aimed to carry out thermal studies below and above the T_g and then investigate how these patterns are affected due to thermal effects with AFM. The thermal studies showed that the carbazole monomer pattern was stable up to 270°C ; in contrast, the PVK pattern showed some instability when annealed at 270°C for 3 h (Figure 8). Both monomer and polymer patterns were stable when annealed below T_g (150°C). The rms value of surface roughness for the carbazole monomer

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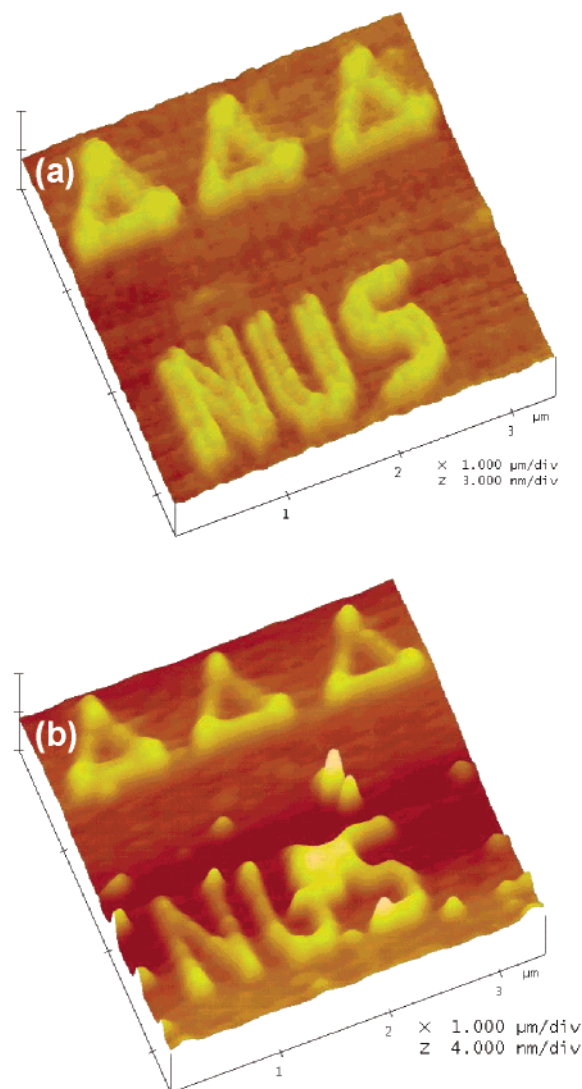


Figure 8. 3D height AFM images of the patterns (a) before and (b) after heating at a temperature of 270 °C for 3 h on PVK polymer film.

film before and after heating is 0.4 and 0.6 nm, respectively, and for the PVK polymer film, it is 0.5 and 0.9 nm, respectively. It was previously shown that polymer thermal stability will be increased with the presence of more aromatic rings in the backbone,²⁸ and that the glass transition temperature (T_g) is decreased (i.e., the stability decreased) with the increase of alkyl

chain content on the polymer backbone.²⁹ Since our polymerized carbazole films form linear aromatic polymer chains, this is more likely to be the reason for more stable patterns even after heating at 270 °C. But in the case of the precursor PVK polymers, though it cross-linked between the carbazole moieties, there is still a flexible alkyl chain content in the backbone of the polymer (or presence of un-cross-linked units) that may be the cause for greater thermal instability of the polymer patterning.

Conclusion

In summary, the formation of more conducting and thermally stable nanopatterns on PVK precursor polymer and carbazole monomer films using a biased AFM tip and C-AFM setup has been reported. The variation of polymer nanopatterning features with respect to the applied bias and tip speed were investigated. In terms of patterning and conductivity, both the monomer and polymer films have shown to be promising candidates for developing conductive nanopatterns on a substrate. The influence on height features and thermal stability differentiates the use of the two starting materials. The ability of these materials (different precursor polymers and monomers) to form more conductive patterns with nanometer precision using the electrochemical nanolithography method should lead the way to forming conductive nanowires/patterns on conducting/semiconducting substrates with potential advantages toward sensors and molecular electronics. Thus, this study will open up the investigation of other precursor polymer materials, electropolymerizable monomers, and ultrathin film assemblies with parameters of patterning relating to the T_g of the polymer, electropolymerizability, writing speed, and applied potential. A main advantage of this method is the use of ambient temperature and humidity conditions for these experiments.

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Supporting Information Available: Experimental details showing thickness-profilometry experiments, writing-speed pattern feature relationships, schematic diagram of monomer and PVK polymerization, electrochemical cyclic voltammetry, and FT-IR measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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