

Conductive Polymer Patterning on a Photoswitching Polymer Layer

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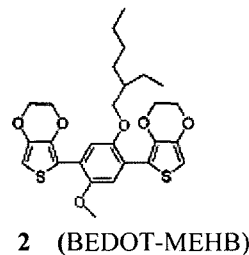
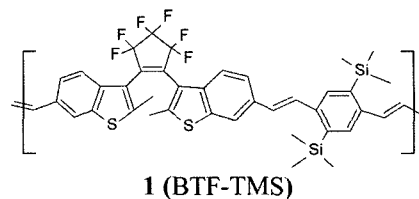
Received October 9, 2006; Revised November 20, 2006

Introduction

Patterning of conductive organic thin films in a nanometer level is crucial for the application of many functional organic materials in electronic devices.¹⁻³ The conventional photoresist processing used in inorganic device patterning requires etching, which often degrades many functional organic materials during the process and prevents correction or erasure of the formed image.⁴ Several other patterning methods have been demonstrated, including laser ablation,⁵ direct laser patterning by two-photon polymerization,⁶ ink-jet printing,⁷ photolithographic undercut formation,⁸ dry-film lift-off,⁹ electron-beam lithography,¹⁰ and conformal masking using elastomeric membranes.¹¹ Compared with the current method, conductive pattern formation through photoisomerization should be especially interesting because the pattern formed by photoisomerization is erasable and eventually controls the growth of the conductive polymer in the electropolymerization process. Photochromic materials that exhibit reversible electrical switching properties via photo-isomerization reactions¹² can bring about a new method of electrode patterning by selectively irradiating the desired area through a mask. Although much progress has been seen in photochromic materials and their switching properties due to extensive study on them,^{2,3} hardly any study has been performed on micropatterning and the controllability of conducting layer growth utilizing photo-induced conductivity change.

This study presents the growth of a conducting polymer film on a photochromic thin film which controls thickness of conductive polymer layer. Direct patterning of an organic conductive polymer could be formed through the photoisomerization of a diarylethene polymer (**1**), followed by the electropolymerization of an electroactive monomer such as 1,4-bis(2-[3',4'-ethylenedioxy]thienyl)-2-methoxy-5-2''-ethylhexyloxybenzene (BEDOT-MEHB) (**2**). The advantages of this method are its capabilities for generating device patterns scale using a simple, rapid and non-destructive process. Also

demonstrated herein are the growth and fabrication of conductive polymer arrays with thicknesses ranging from 2 to 400 nm.



Results and Discussion

A solution of polymer **1** in chloroform was spin-coated on an ITO glass. The thickness of the photochromic film ranged from 4-10 μm depending on the weight concentration of **1** (0.6-9 wt%).¹³ First, a photochromic pattern of **1** can be formed by irradiating the film with UV light (power: 62 mW) through a mask for 1-5 min. Upon irradiation, the area exposed to UV light became dark due to the isomerization of the 2,3-bis(2-methylbenzo[b]thiophene-3-yl)hexafluorocyclopentene (BTF) unit in **1**, to a closed form, whereas the shaded area remained transparent (open-form isomer).

The color pattern was stable for several hours under room light but disappeared with a visible light, erasing the pattern and forming a new pattern upon irradiation with UV light. This indicates that electrode patterning with light is rewritable.

The closed isomer of diarylethene is more conductive than the open isomer, due to the extension of pi-electron delocalization to PPV units and through the mainchain in the closed form, as proposed previously for diarylethene polymers.^{14,15} The conductivity of the area exposed to UV light was increased to lead to the electrochemical deposition of the conductive polymer on it and to ultimately result in the conductive polymer pattern. Thus, the photo-patterned polymer layer of **1** (Figure 1(b), top) was dipped into an electrochemical cell that contained an acetonitrile solution of **2** (0.01 M) with electrolyte salt (0.1 M LiClO₄). The compound **2** was polymerized and deposited in the area exposed to UV light through potential scanning between -1.0 and 1.0 V vs. Ag/AgCl, resulting in a conductive pattern (Figure 1(c)). The cyclic voltammogram of the P(BEDOT-MEHB) growth on the film of **1** (Supplementary Information, Figure S-1) showed

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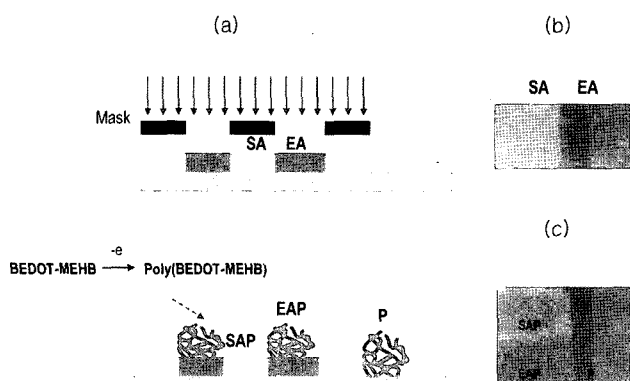


Figure 1. (a) Schematic illustration of the photo/electro-patterning process of the conductive polymer layer. (b) Digital photograph of the photo pattern generated through UV exposure. SA and EA represent the UV-shaded and UV-exposed areas, respectively. (c) Digital photograph of the conductive polymer pattern generated through the electrochemical polymerization of **2** on the photochromic polymer film of (b), with a d_B of 59 nm. SAP and EAP represent the electropolymerized area in the UV-shaded and UV-exposed areas, respectively.

a rapid growth of the anodic current density starting at around 0.7 V vs Ag/AgCl, which corresponds to the beginning of the monomer **2** oxidation.¹⁶ During the successive potential scans, the P(BEDOT-MEHB) film was deposited on the electrode surface. Thus, from the 2nd potential cycle, a new peak characteristic of the redox reaction for P(BEDOT-MEHB),¹⁶ was observed accompanied with film deposition.

The increase in the anodic and cathodic peak currents implies that the amount of the polymer on the electrode surface increased as the cycle continued, increasing the film thickness.

The deposition of P(BEDOT-MEHB) was evident from the increase in the film thickness, as determined by an alpha step, shown in Figure 2. The difference in film thickness of P(BEDOT-MEHB) between the UV exposed ($d_{EAP} = 40$ nm) and dark area ($d_{SAP} = 23.8$ nm) was 16.2 nm when the film thickness of **1** (d_B) was 59 nm. Notably, the thickness of the P(BEDOT-MEHB) growth in the area exposed to UV light was higher than that in the shaded area (SAP), indicating that the electropolymerization preferentially occurred in the UV-irradiated area. The thickness of the P(BEDOT-MEHB) growth on the bare ITO ($d_{P(BEDOT-MEHB)}$) under the same solution was 50 nm. The difference between d_{EAP} and $d_{P(BEDOT-MEHB)}$ arose from the difference in the conductivity of the ITO glass (10 S/cm) and that of **1** ($\sim 2.5 \times 10^{-8}$ S/cm).¹⁷ Since the conductivity of **1** was much lower than that of the ITO glass, the P(BEDOT-MEHB) growth on the polymer film of **1** was highly affected by the film thickness of **1** ($d_B = d_{EAP}$), as shown in Figure 3. The thickness of the P(BEDOT-MEHB) growth in the UV-irradiated area (d_{EAP}) was linearly correlated to d_B

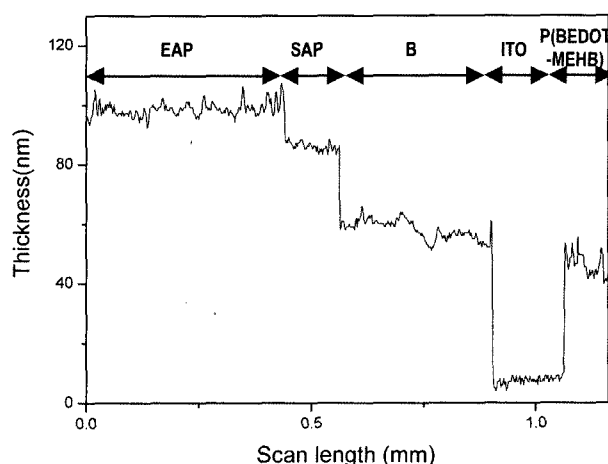


Figure 2. Surface profile of the P(BEDOT-MEHB) growth in the UV-exposed area of **1** (EAP), the UV-shaded area of **1** (SAP), and the bare ITO. B is the film of **1** untouched from the electropolymerization ($d_{P(BEDOT-MEHB)} = 40$ nm, $d_B = 59$ nm).

($d_{EAP} = 49 - 263 \times d_B$, correlation factor $R = 0.9798$).

Thus, in the very thin film ($d_B \sim 0$), the P(BEDOT-MEHB) film thickness (d_{EAP}) became similar to that of d_P (in this work, $d_P = 50$ nm). Although it was smaller than that in the area exposed to UV light, P(BEDOT-MEHB) was also grown in the shaded area. The difference between d_{EAP} and d_{SAP} arose mainly from the difference in the conductivity of the area exposed to UV light and that of the shaded area (3×10^{-9} S/cm),^{14,17} which is ultimately related to the difference between the closed and open forms of the BTF and the quantum yield of ring cyclization. We are currently investigating the method to minimize the conductive polymer growth in the shaded area.

An examination of the conductive polymer growth through AFM over the entire substrate provides further evidence that

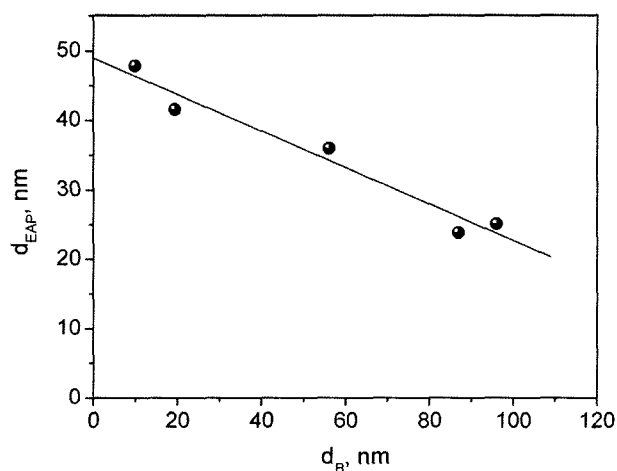


Figure 3. A plot of the P(BEDOT-MEHB) growth on the polymer film of **1** against d_B .

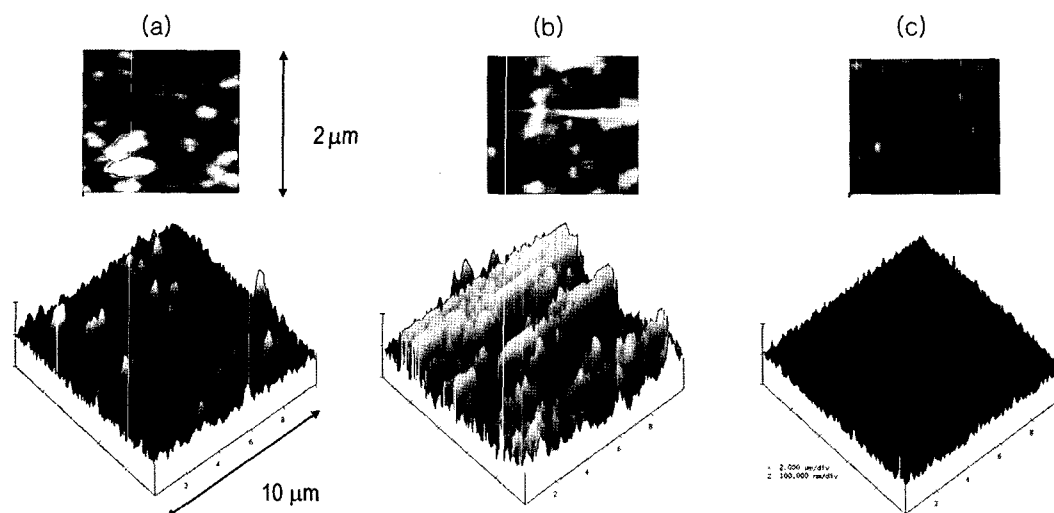


Figure 4. Topography of the P(BEDOT-MEHB) film in the UV-exposed area of **1** (EAP) (a), on the bare ITO (P) (b), and in the UV-shaded area of **1** (SAP) (c) as obtained through tapping-mode AFM.

P(BEDOT-MEHB) growth preferentially occurred in the area of **1** that was exposed to UV light. Figure 4 shows tapping-mode AFM images of the P(BEDOT-MEHB) grown on the different spots. Clearly, there is a large difference in the morphology of the P(BEDOT-MEHB) grown in the area of **1** that was exposed to UV light (a) and that of the P(BEDOT-MEHB) grown on the bare ITO electrode (b) or the area of **1** that was shaded (c). The AFM image of the P(BEDOT-MEHB) grown in the area exposed to UV light (a) shows an irregular surface composed of small particles with an average roughness (*rms*) of 17.1 nm. The average roughness of P(BEDOT-MEHB) grown in the area shaded to UV light (c) was 7.6 nm. On the other hands, the image of the P(BEDOT-MEHB) grown on the bare ITO showed markedly larger particles with an average roughness of 37.8 nm. Such a large difference in morphology as well as roughness of P(BEDOT-MEHB) layer could be due to the difference in current density during electropolymerization, as the photochromic layers have lower conductivity than that of the bare ITO.¹⁷

The P(BEDOT-MEHB) grown on **1** showed electrochromic properties, as shown in Figure 5. Its color was red at < -0.5 V and blue at ≥ 0.6 V, which are well-matched with the colors of the P(BEDOT-MEHB) grown on the bare ITO glass.¹⁶ The characteristic of visible absorbance of the reduced state of the P(BEDOT-MEHB) was observed at ~ 500 nm. The reduction appeared to begin at -0.5 V and continued essentially towards completion at -0.8 V. Coloration in the electrochromic window of the P(BEDOT-MEHB)/ITO is described in the inset of Figure 5, which shows digital images of films at different potentials. The electrochromic window switched from a sky-blue color when oxidized, to a deeply absorptive red color when in a reduced state, which are in good agreement with previous reports.¹⁶ When the thickness

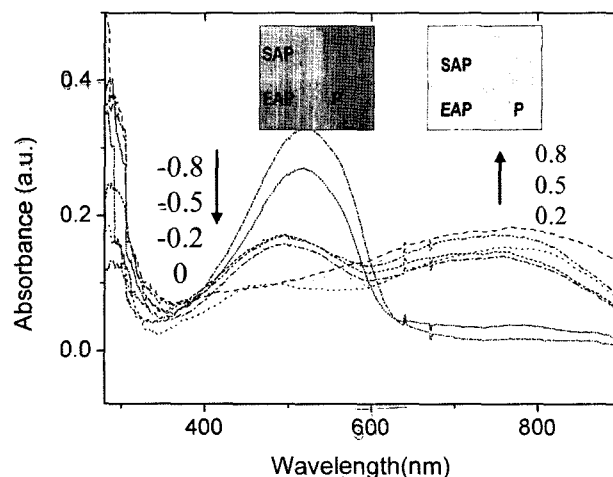


Figure 5. Spectroelectrochemistry of the P(BEDOT-MEHB)/ITO window ($d_{\text{P(BEDOT-MEHB)}} = 40$ nm, $d_{\text{ITO}} = 59$ nm). The spectra were taken from 0.8 to -0.8 V, as indicated in the graphs. The electrolyte was 0.1 M LiClO₄; its reference was Ag/AgCl. Inset shows digital photographs of the coloration of the UV-Vis spectral change charged to -0.8 (left) and 0.8 V (right). The P(BEDOT-MEHB)/ITO window (0.5×0.5 cm²) shown is immersed in acetonitrile containing 0.1 M LiClO₄ within an electrochemical cell.

of the P(BEDOT-MEHB) was increased, a darker color appeared. The color of the electrochromic window was much more intense in the P(BEDOT-MEHB) film grown on the UV exposed area (EAP) than the shaded area (SAP), as expected from the differences in of the P(BEDOT-MEHB) growth in the two area.

To demonstrate a practical device with a pre-patterned substrate, a comblike electrode with a 50 μm gap was fabricated. First, the solution of **1** (0.7 wt%) was coated with a d_B

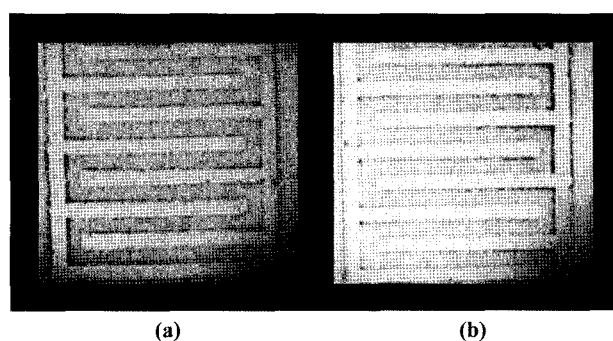


Figure 6. Digital photograph of an electrode pattern covered with P(BEDOT-MEHB) on top of the polymer **1** layer for (a) reduced and (b) oxidized state. The gap between the electrodes is $50\ \mu\text{m}$ ($d_{\text{P(BEDOT-MEHB)}}=40\ \text{nm}$, $d_{\text{B}}=59\ \text{nm}$).

of 10 nm, after which the comblike mask was placed on the surface of the PC film and UV light irradiation was performed for 3 min. The electrode with a photogenerated pattern was dipped in a solution of BEDOT-MEHB (same as above) and then applied in three consecutive cycles in the potential range of -1 to 1 V. A digital photograph of the final image through an optical microscope is shown in Figure 6 (a) and (b) for reduced and oxidized, respectively, in which the gap corresponds to $50\ \mu\text{m}$.

In conclusion, this paper describes the growth of conductive polymers on a photochromic polymer layer and the micro-patterning of polymer layers for organic electronic devices. The two-step patterning process was initiated by photoisomerization of **1**, followed by selective electropolymerization of **2** on a photo patterned layer of **1**. The method was used to produce a patterned electrochromic electrode. Since the patterning of organic conducting polymers such as P(BEDOT-MEHB) is crucial for organic photovoltaic cells, electrochromic displays and organic circuits, this technique is potentially useful for many organic electronic devices.

Acknowledgements. This work was financially supported by the Ministry of Science and Technology (MOST) of Korea and Seoul City (Seoul R&BD).

Supplementary Information. Experimental details and Figure showing the cyclic voltammogram during the electropolymerization of BEDOT-MEHB are available.

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