Selective Vapor-Phase Deposition of Conductive Poly(3,4-ethylenedioxythiophene) Thin Films on Patterned FeCl₃ Formed by Microcontact Printing

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We demonstrate a selective vapor-phase deposition of conductive poly(3,4-ethylenedioxythiophene) (PEDOT) thin films on patterned FeCl₃. The PEDOT thin films were grown on various substrates by using the vapor-phase polymerization of ethylenedioxythiophene (EDOT) with FeCl₃ catalytic layers at 325 K. The selective deposition of the PEDOT thin films using vapor-phase polymerization was accomplished with patterned FeCl₃ layers as templates. Microcontact printing was done to prepare patterned FeCl₃ on polyethyleneterephthalate (PET) substrates. The selective vapor-phase deposition is based on the fact that the PEDOT thin films are selectively deposited only on the regions exposing FeCl₃ of the PET substrates, because the EDOT monomer can be polymerized only in the presence of oxidants, such as FeCl₃, Fe(ClO₄), and iron(II) salts of organic acids/inorganic acids containing organic radicals.

Key Words : Vapor-phase polymerization, Micro-contact printing, Poly(3,4-ethylenedioxythiophene), Selective deposition

Introduction

π-Conjugated organic polymers having heterocyclic structures have good electrical conductivity, excellent transmittance in the visible frequency, and high chemical stability. Typical applications include optoelectronic devices, batteries, smart windows, sensors, and electronic circuit elements.[1-4] Among the several conducting polymers, polypyrrole and polythiophene have received much attention in recent years. They may be a good candidate for optoelectronic devices because of their high conductivity, good transparency, excellent stability, and film-forming properties.[5-8] The thin films of the conducting polymers have been shown to be useful as flexible organic and electronic devices. In general, they can be synthesized by either an oxidative chemical or electrochemical polymerization of monomer in liquid phase. In practice, however, it is not possible to use the wet methods to prepare the conducting polymers for the construction of flexible electronic circuitry because of their poor solubility and difficulties in retaining their electronic or optical properties. Recently, several groups have developed vapor-phase polymerization methods for generating their thin films with desired properties and functionalities.[9-12] We developed a new growth method of thin films of poly(3,4-ethylenedioxythiophene) (PEDOT), as the polythiophene derivatives, by using vapor-phase polymerization.[13,14] The PEDOT thin films were grown on various substrates by using the vapor-phase polymerization of ethylenedioxythiophene (EDOT) with FeCl₃ catalytic layers. They have high conductivity of 10 S/cm and excellent light transmittance of 95% at 25 nm in thickness.

Simple and reliable methods for the patterning of the conducting polymers are required, since there have been significant demands in the construction of flexible organic and electronic devices with micrometer sizes. A number of patterning techniques with the conducting polymers have devised, including photolithography,[15] template assisted synthesis,[16] scanning electrochemical microlithography,[17,18] electrochemical dip-pen lithography,[19] and soft lithography.[20-23] Among existing patterning methods, soft lithography is the most efficient method to fabricate new types of structures and devices on planar, curved or flexible substrates at low cost.[24] Soft lithography includes a number of non-photolithographic techniques that use a patterned elastomer (primarily polydimethylsiloxane, PDMS), as a stamp, mold, or mask, to transfer the pattern to substrates.[25] Microcontact printing, in particular, is the most versatile and cost-effective method that can routinely form patterned self-assembled monolayers (SAMs).[26-28] The SAMs (2-3 nm thick) are thin organic films which form spontaneously on solid surfaces. They can be used either as resists in selective etching or as templates in selective deposition to form patterned thin films.[29,30] Microcontact printing is low in capital cost and can generate patterns on nonplanar surfaces with a wide variety of materials. This method seems to be a general method for forming patterns of a variety of materials, such as colloids, acids, metal, polymers, and biological molecules, on surfaces of solid substrates through contact pattern transfer.[31,32] There has been a growing interest in forming a patterned thin film by site-selective deposition on a patterned template made by microcontact printing, as a simple low-cost fabrication process.[33,34] Since the EDOT monomers can be polymerized in vapor phase only on the FeCl₃ catalytic layer of the substrates, it offers an ideal method for selective deposition of the conducting polymer on patterned FeCl₃.

Here we report a patterning method of PEDOT thin films using microcontact printing of FeCl₃, followed by selective vapor-phase polymerization of EDOT. Our approach consists
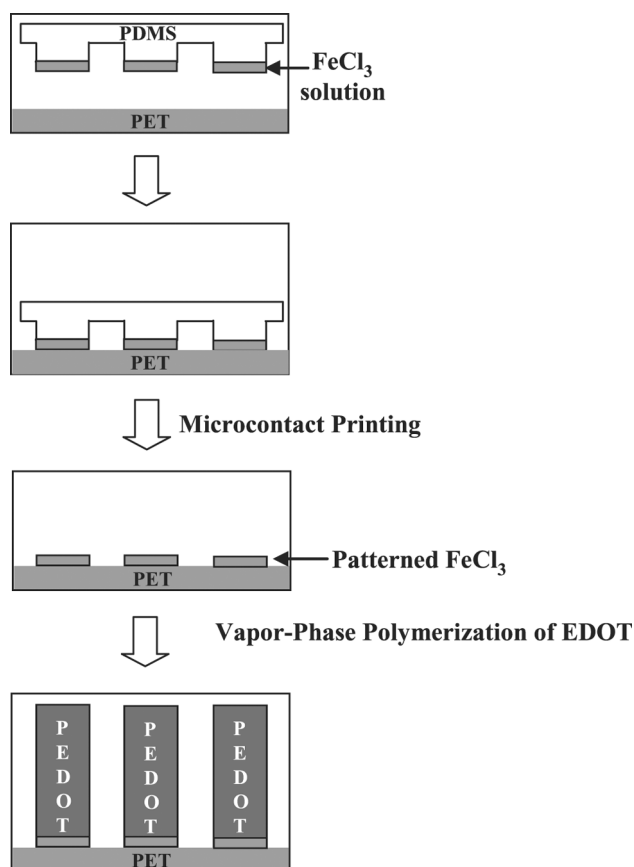
Figure 1. Schematic outline of the procedure to fabricate patterned PEDOT thin films by using microcontact printing and selective vapor-phase polymerization.

of two key steps, as shown in Figure 1. First, the patterned $FeCl_3$ catalytic layer was formed on polyethyleneterephthalate (PET) substrate by using microcontact printing. Second, the PEDOT thin films were selectively deposited onto the $FeCl_3$-patterned PET by vapor-phase polymerization.

Experimental Section

Materials. Ethylenedioxythiophene (Bytron M of Bayer AG), $FeCl_3 \cdot 6H_2O$ (Aldrich, 98%), methanol (Aldrich, 98%), and hexane (Aldrich; anhydrous, 99%) were used as received. Polydimethylsiloxane (Sylgard 184) was ordered from Dow Corning. Deionized water was purified with a Millipore Milli Q plus system, distilled over $KMnO_4$, and then passed through the Millipore Simplicity system. Polyethyleneterephthalate (PET) substrate (Mylar, 5 mil) were rinsed with water and methanol, extracted in refluxing hexane for 2 h, and then dried at reduced pressure.

Preparation of Patterned $FeCl_3$. Patterned $FeCl_3$ films on the PET substrates were made by using microcontact printing. Masters were fabricated by using conventional photolithography to pattern resists on silicon wafers. The masters have parallel lines and spaces with dimensions of 3 mm. Polydimethylsiloxane (PDMS) stamps were produced according to a previously reported procedure.[27,28] The PDMS stamps were inked with a methanol solution of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in the range of 1-10 wt %. The stamp was placed in contact on clean PET substrate at 288 K for 10-100 s. The stamp was carefully peeled off and the substrate was dried at 320 K for 3 min. Relative humidity was kept fixed at 40% in these experiments.

Preparation of PEDOT Thin Films. The $FeCl_3$-patterned PET substrates were exposed to an EDOT vapor for 20 min in a reaction chamber at 325 K under 1 atm. Following the polymerization, the grown PEDOT films were washed with methanol several times to remove unreacted oxidant, EDOT monomer, and by products (*e.g.* $FeCl_2$), and dried in air at 343 K for 3 min.

Analysis Techniques. Atomic force microscopy (AFM) images of the samples were obtained on a PSIA XE-100 operating in tapping mode. Tapping Si-Cantilevers (XE-CAT-NCS1, PSIA, Korea) with resonance frequencies in the order of 300-400 kHz and spring constants between 20 and 40 N/m were used for the experiments. The X-ray photoelectron spectroscopy (XPS) measurements were conducted using the ESCALAB MKII.[35,36] The conductivity of the PEDOT thin films was measured by standard four-point probe technique (Mitsubishi Chemical, Loresta-GP). The optical properties of the PEDOT thin films were measured by UV-Visible spectrometer (Perkin-Elmer, Lambda 25). Conducting-AFM was performed by Si cantilevers with a spring constant of 11.5 N/m, coated with Pt. (NSG10, NT-MDT, Russia). In C-AFM measurement, bias of 3 volts and contact force of 5.6nN was applied. Simultaneously, both topographic and current images were obtained in air. Measurements of local current-voltage characteristics were also carried out.

Results and Discussion

Iron(III) salts can be conveniently used as dopant ions for π-conjugated organic polymers having heterocyclic structures such as PEDOT. The EDOT monomer can be polymerized in the presence of oxidants such as $FeCl_3$. Patterned $FeCl_3$ films on the PET substrate were made by using microcontact printing. The masters we used for fabrication of stamps were silicon wafers with line patterned resists. The stamps were fabricated by casting polydimethylsiloxane (PDMS) on the masters. After curing, the PDMS stamps were peeled away from the masters. The PDMS stamps were inked with a 5 wt % $FeCl_3$ solution and were placed in contact on the PET substrate for 30 s. When the stamps were made using these masters, the raised lines of the master corresponded to the recessed spaces of the stamps. Figure 2 shows AFM topographic image and line profile in cross section of patterned $FeCl_3$ fabricated using the masters having 2.3 μm parallel lines with 3.6 μm spaces. Faint $FeCl_3$ patterns with a mean height of about 7 Å were visible on the PET substrate.

The PEDOT thin films were selectively deposited onto the $FeCl_3$-patterned PET substrate by vapor-phase polymerization using EDOT monomer. The selective vapor-phase polymerization of EDOT was done at 325 K for 20 min.
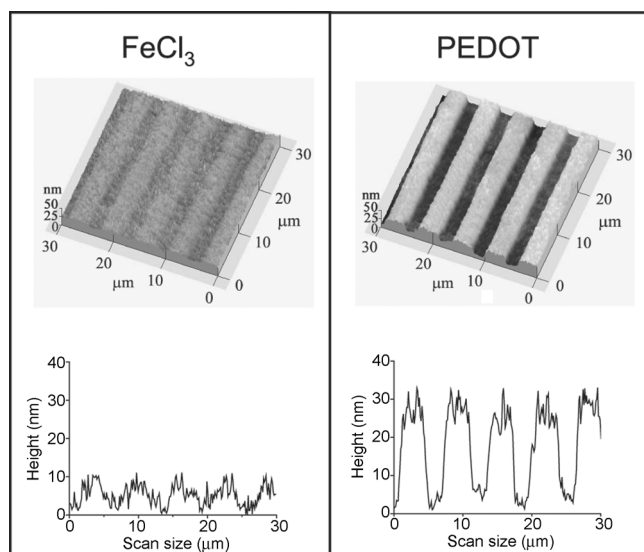
Figure 2. AFM images and line profiles in cross sections of the patterned $FeCl_3$ film by using microcontact printing on PET substrate and the patterned PEDOT thin films by using vapor-phase polymerization on the $FeCl_3$- patterned PET substrate.

Figure 2 illustrates AFM image and line profile in cross section of micropatterned PEDOT thin films, which were selectively deposited onto the $FeCl_3$-patterned PET substrate. The patterns of the PEDOT thin films were defined and directed by the patterned $FeCl_3$ generated with microcontact printing. The PEDOT thin films were selectively deposited only on the regions covered with $FeCl_3$ films of the PET substrate because the regions exposing PET did not have any oxidant to polymerize EDOT monomers. It is clearly showed that the patterned PEDOT thin films retaine the dimensions of the master patterns without noticeable line spreading. Additionally, the thickness of the patterned PEDOT thin film is about 25 nm.

XP survey and high-resolution spectra for the PET substrate following microcontact printing of $FeCl_3$ are shown in Figures 3(b) and 4. The presence of the patterned $FeCl_3$ film is indicated by a large increase in the iron and chlorin peak intensities, and a decrease in the carbon and oxygen peak intensities. The high-resolution spectrum of the Fe(2p) region shows characteristic shake-up peaks and a Fe($2p_{3/2}$) peak at 711.1 eV, which is assigned to Fe(III).[37] As shown in Figure 4, the Cl(2p) peaks are the same as those of the $FeCl_3$.[38] The peak area ratio for the iron and chlorin, corrected by the elemental sensitivity factors, is 1 : 3. The XPS data show that patterned $FeCl_3$ films were made on the PET substrate by using microcontact printing.

The XP spectra for the $FeCl_3$-patterned PET substrate following vapor-phase polymerization of EDOT, shown in Figures 3(c) and 4, indicate a large increase in the carbon and oxygen peak intensities and a complete loss of the iron and chlorin peaks. The S(2p) peak at 164.3 eV is the same as that of the thiophene,[39] indicating that the surface species generated from the vapor-phase polymerization of EDOT on the $FeCl_3$-patterned PET is a polythiophene derivative.
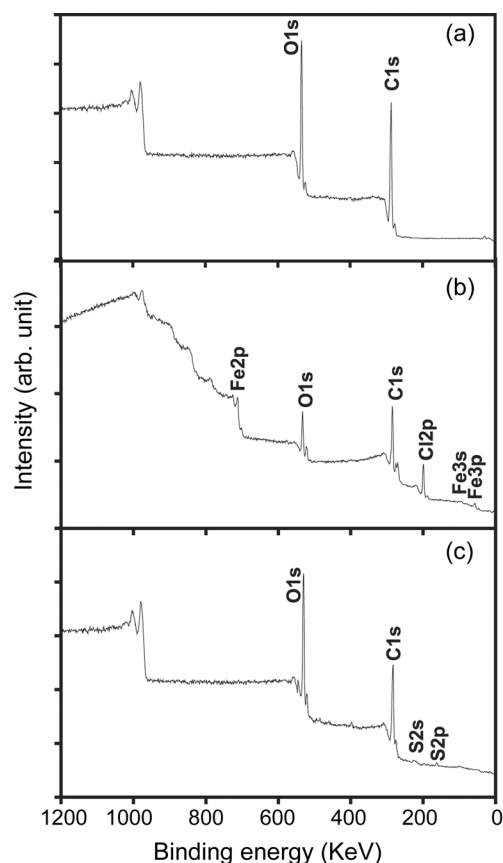

Figure 3. XP survey spectra of (a) the PET substrate, (b) the patterned $FeCl_3$ film, and (c) the patterned PEDOT thin film.
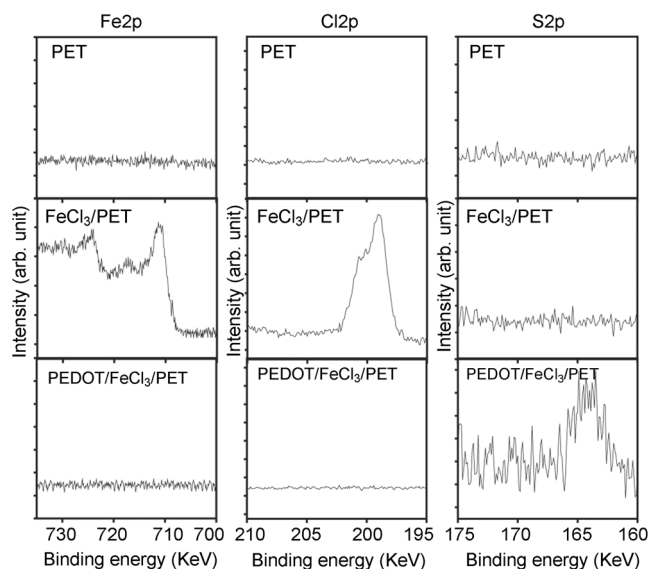

Figure 4. XR high-resolution spectra of the PET substrate, the patterned $FeCl_3$ film, and the patterned PEDOT thin film.

These observations suggest that the polythiophene thin film is formed on the $FeCl_3$-patterned PET substrate by using vapor-phase polymerization of EDOT.

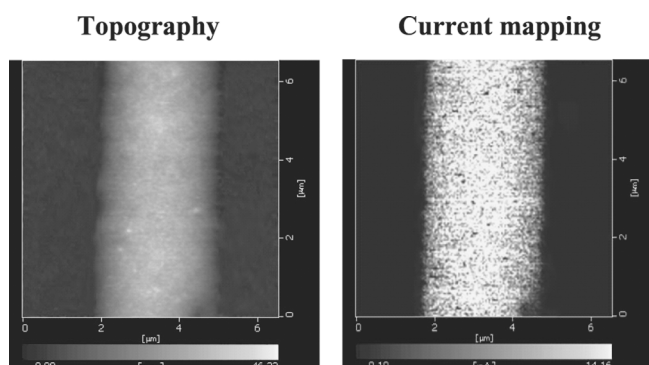Figures 5(a) and 5(b) show AFM topography with in-plane current map in the patterned PEDOT thin films on

Topography   **Current mapping**

Figure 5. AFM topographic and current images of the patterned PEDOT thin film on the FeCl₃-pattermed PET substrate.
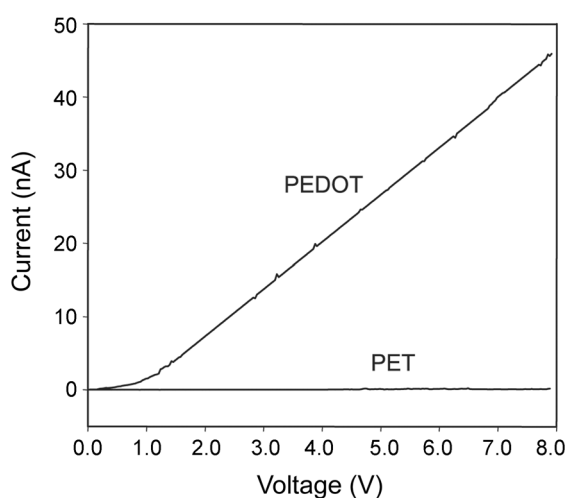

Figure 6. Current-voltage curves of both PET and PEDOT patterns.

PET. In-plane current map was obtained at applied bias of 3 V. Clearly, the regions, where selectively deposited with the PEDOT thin films showed significant current flow. No current flow could be observed in the rest of the PET substrate. At present, quantitative analysis of the current flow could not be done. It is required to know contact resistance or area between the metallic tip and "soft" PEDOT thin film for the estimate of the current flowing through quantitatively. The Local I-V characteristics of both PET and PEDOT patterns were shown respectively in Figure 6. While the curve for the PET substrate was essentially horizontal, indicating almost perfect insulation, the PEDOT patterns showed ohmic behaviors at the high electric field applied. In other words, the current was almost linear for the PEDOT thin films as we expected for a metallic phase. Therefore, the PEDOT patterns can be used as conductive wires for interconnections. The PEDOT thin films were analyzed by standard four-point probe technique and had high conductivity of 10 S/cm at 25 nm in thickness.

Conclusion

We describe a selective vapor-phase deposition of PEDOT thin films on FeCl₃-patterned PET substrates formed by microcontact printing. The PEDOT thin film is selectively deposited only on the regions exposing the FeCl₃ of the PET substrates because the EDOT monomer can be polymerized in the presence of FeCl₃. The vapor-phase polymerization offers an ideal method for selective deposition of conducting polymers on patterned catalytic films because it is very sensitive to surface conditions of the substrates.

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