

Surface Grafting of Polypyrrole onto Silicon Wafers

Daewon Sohn,^{*1,5} Hyoseung Moon,⁵ Michael J. Fasolka,¹ Naomi Eidelman,² Sang-Mo Koo,^{3,4}
Curt A. Richter,³ SeungEun Park,³ J. J. Kopanski,³ and Eric Amis¹

¹Polymer Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.

²American Dental Association Foundation, Paffenbarger Research Center,
National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.

³Semiconductor Electronics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899, U.S.A.

⁴Department of Electronic Materials Engineering, Kwangwoon University, Seoul 139-701, Korea

⁵Department of Chemistry, Hanyang University, Seoul 133-791, Korea

(Received July 24, 2007; CL-070789; E-mail: dsohn@hanyang.ac.kr)

A micromolding technique in capillaries was adapted to make uniform patterns of polypyrrole (Ppy), and the conductivities of the patterns were measured by direct contact IV curves and conductance AFM methods. Noncovalently bound Ppy patterns have high conductivity (low resistivity) before doping and brittle characteristics. However, the covalently grafted Ppy pattern shows relatively low conductivity and sticky viscoelastic properties.

The patterning of conjugated organic polymers on a solid surface is appealing because it can be used as a circuit for flexible displays¹ or as an organic semiconducting material.² The fabrication of micro- to nanoscale patterns of conducting polymer is crucial for making microelectronic devices on a solid substrate.³ Photolithography, microcontact printing, and inkjet-printing methods have been introduced for the formation of micropatterns. During these processes, the selective and strongly bound patterning is essential for the fabrication techniques. In general, the micropatterns are prepared by physical binding methods, which always have the problem of low affinity for the solid substrate.⁴ Here, we adapt a solution polymerization method inside capillaries to graft a conducting polymer onto the solid substrate. Polypyrrole (Ppy) is an inherently conductive polymer because of the interchain hopping of electrons.⁵ It is easy to prepare by standard electrochemical or chemical techniques; the surface charge can easily be modified by changing the dopant anion (X^-). Initiator and pyrrole monomers can easily produce a conducting polymer under ambient conditions. The micromolding in capillaries (MIMIC) technique has been used to fabricate microstructures of organic polymers.⁶ So far, prepared microstructures of Ppy have been limited by their weak affinity for the silicon surface. To increase surface affinity, a trimethoxysilyl group was grafted onto the surface, and then the pyrrole monomer was introduced to polymerize on the substrate.⁷

Single crystal undoped Si(110) wafers that were polished on one side were purchased from Wafer World Inc. and sliced into pieces of about 1.0×3.0 cm in size. A glass slide was also used for the direct conductivity measurement which requires an insulating substrate. Poly(dimethylsiloxane) (PDMS, Sylgard 184), which was used as an elastomer stamp, was purchased from Dow Corning. *N*-[3-(trimethoxysilyl)propyl]pyrrole (NTSPP) that can be covalently anchored to the surface OH group was purchased from Aldrich. Pyrrole monomer and iron(III) chloride were purchased from Aldrich. The silicone wafer was cleaned in an ozone cleaner (Jelight UVO-342) for 20 min and rinsed with

EtOH. The procedure for micromolding in capillaries (MIMIC), in which a PDMS (poly(dimethylsiloxane)) stamp is placed on a substrate to form microchannels, was introduced by Kim et al.⁸ Figure 1 shows a schematic picture of the MIMIC process. We prepared a line pattern of 3–10 μm in width by casting PDMS with a master that was prepared by photolithography. The ends of the channels in the mold were cut open to allow the solution to penetrate easily. A drop of 3% $\text{FeCl}_3/\text{EtOH}$ initiator solution filled these channels by capillary force. Ppy polymerization proceeded just after introducing the pyrrole monomer on the one end. Then, it was annealed at 75 $^\circ\text{C}$ for 1 h. When we removed the PDMS stamp, there were regular yellow line patterns on the Si wafer.

NTSPP was mixed with 95% EtOH and adjusted to pH 5 with acetic acid. The NTSPP solution was introduced to the MIMIC before the Ppy polymerization procedure. Anchored NTSPPs were alternatively connected by the pyrrole monomers, and these generated the Ppy patterns on the silicone wafer spontaneously within 5 min.⁹ Figure 2 shows the chemical structures of Ppy and Ppy-NTSPP.

IR spectra were measured between 4000 and 400 cm^{-1} at a resolution of 2 cm^{-1} with 256 coadded scans using a Nicolet Nexus 670 FTIR spectrometer (Madison, WI) continuously purged with dried air.

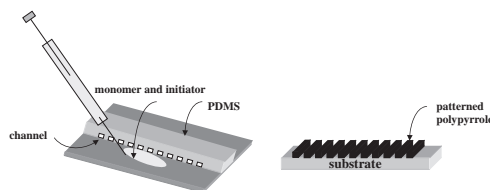


Figure 1. Schematic of the procedure for micromolding in capillaries.

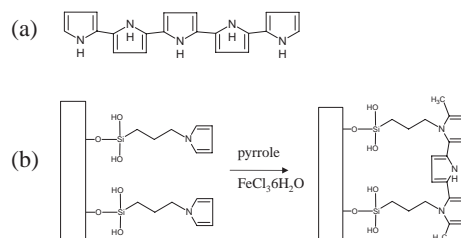


Figure 2. (a) Ppy structure and (b) the Ppy-NTSPP formation process.

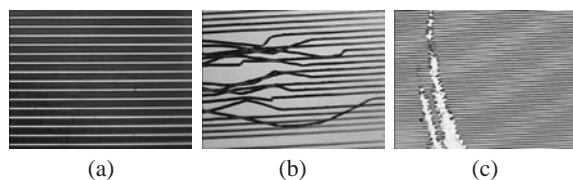


Figure 3. (a) Ppy patterns on a Si wafer, (b) scratched Ppy patterns, (c) scratched Ppy-NTSPP patterns. ($200 \times 150 \mu\text{m}$). a, b, c have been made by the different width stamps, 10, 3, and $5 \mu\text{m}$, respectively.

The current across the polymer channels of Ppy and Ppy-NTSPP was monitored by a source meter and plotted against the voltage applied to the line patterns. Scanning capacitance microscope (SCM) images of the samples were obtained by a commercial AFM using additional off-the-shelf and custom electronics for processing the capacitance signal.¹⁰

Figure 3 shows the polymerized Ppy patterns inside the capillaries. After drying the FeCl_3 solution, which filled the channels, the substrate changed to a yellowish color on the patterned side.

After the pyrrole monomer was introduced inside the channel, the patterns changed their color to black. Figure 3a shows the patterns after removing the PDMS stamp from the substrate and washing with two solvents, EtOH and toluene. The prepared Ppy has a 60° contact angle. When the initiator was mixed with the pyrrole monomer before insertion into the capillaries, the result was the same as the separated introduction. In both cases the affinity of the Ppy polymer for the Si substrate was relatively low. Figure 3b shows the prepared Ppy patterns on the silicon wafer after it was scratched by a needle. The patterns were not strongly attached on the surface, and we could separate each pattern from the substrate. This behavior is common in conducting polymers, which have low surface energy so that they can be used in antistatic applications.¹¹ When we introduce the NTSPP into the capillary, the silane group anchored to the substrate. In the second step, the pyrrole monomer was introduced with an iron chloride initiator. Polymerization in the presence of the grafted pyrrole proceeded inside the capillaries. Figure 3c shows the Ppy grafted onto the NTSPP (Ppy-NTSPP) patterns after removing the PDMS mold and washing with solvents. The patterns look like the physically bound Ppy patterns, but when we scratched the patterns with a needle they could not be peeled off the substrate. Strongly grafted Ppy-NTSPP has higher surface energy than that of Ppy, and it has a contact angle $<40^\circ$.

Figure 4 shows the IR spectra of the Ppy and Ppy-NTSPP patterns on the Si wafer. The characteristic peaks of Ppy are 1570 and 1480 cm^{-1} corresponding to the C–C and C–N stretching vibrations in the pyrrole ring, respectively.¹² When the trimethoxysilane group adsorbed on the substrate, a broad absorp-

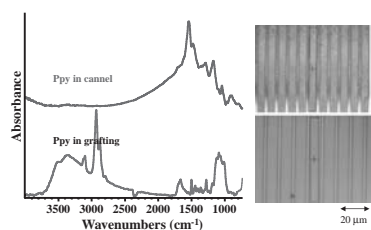


Figure 4. IR spectra of Ppy and Ppy-NTSPP patterns.

tion band at the $3600\text{--}3200 \text{ cm}^{-1}$ region and new bands of C–H stretching at $3000\text{--}2800 \text{ cm}^{-1}$ and the $1500\text{--}1300 \text{ cm}^{-1}$ region appeared. Hydrolysis of Si-O-CH_3 could produce a broad absorption at 3400 cm^{-1} . Two sharp maxima at 2953 and 2849 cm^{-1} are also evidence of bands from CH stretching, which is a dominant peak of NTSPP.¹³

In order to confirm the conductance of each Ppy and Ppy-NTSPP pattern, current–voltage (I – V) measurements have been made on each structure in a cascade probe station using an HP 4156A semiconductor parameter analyzer.¹⁴ A clear linear dependence of the current on the applied bias from -2.5 to $+2.5 \text{ V}$ demonstrates ohmic conduction. The current ratios with respect to the glass substrate are up to ca. 2.0×10^7 and ca. 2.0×10^2 for Ppy and Ppy-NTSPP, respectively. Ppy patterns show about 5 orders of magnitude higher levels of conduction than those of Ppy-NTSPP. We have tried more than 5 different patterns, and these values are the median value of the measurements. The resistivity of Ppy-NTSPP (ca. $2.4 \times 10^2 \Omega \text{ cm}$) is expected to be about 5 orders of magnitude higher than that of Ppy (ca. $2.0 \times 10^7 \Omega \text{ cm}$), assuming that contacts are ideal. Note that the actual resistivity of the polypyrrole can be lower because of the contact resistance between the probe and the pattern on the glass substrate, which has a resistivity of ca. $4.0 \times 10^8 \Omega \text{ cm}$.^{15,16}

In this study, we have demonstrated conducting patterns grafted onto a silicon substrate that have a relatively lower conductance than that of physically bound Ppy patterns. However, these patterns are strongly bound onto the substrate and have a more homogeneous electrical density profiles (EDP).

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- 16 I – V curves and AFM/SCM images are in Supporting Information which is available electronically on the CSJ-Journal Web site., <http://www.csj.jp/journals/chem-lett/index.html>.