MICROPATTERNING OF A CONDUCTING POLYMER COVALENTLY BOUND TO SILICON

Bruno Fabre and Danial D. M. Wayner

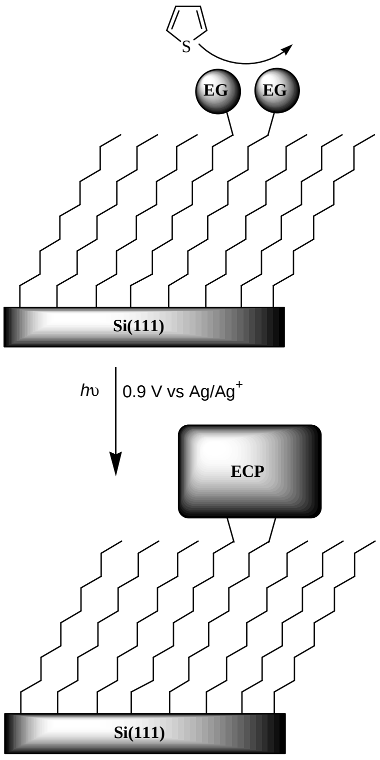
Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

The functionalization of semiconductor surfaces by electronically conducting organic materials such as π–conjugated polymers constitutes a convenient strategy for the fabrication of novel hybrid devices useful in molecular electronics. However, the electrical characteristics of such junctions are highly dependent on the nature of the interactions between the two components. The preparation of stable and high quality junctions requires that the conducting polymer is chemically bound to the semiconductor.[1,2] Moreover, the integration of such hybrid junctions in the electronic circuitry, e.g., in Schottky diodes, field-effect transistors and photovoltaic devices, requires the development of novel strategies for depositing locally the conducting polymer in order to fabricate micro- or nanometer-sized features.[3]

We describe here for the first time the patterning of a π-conjugated polymer covalently bound to a semiconductor surface, using a “reagentless” [4] photolithographic process. The method is based on the selective electrodeposition of polythiophene on Si(111) surfaces patterned with thiophene-terminated and chemically inert alkyl (e.g., *n*-decyl) monolayers (Scheme 1).[5] As a matter of fact, the photoelectrochemical oxidation of the patterned surface at ca. 0.9 V vs Ag/Ag$^+$ 10^{-2} M (~1.2 V vs SCE) in the presence of thiophene yields the deposition of ClO_4^- -doped polythiophene only on the parts containing the attached thienyl units. Indeed, the electropolymerization process is activated by the presence of these terminal groups in so far as much higher potentials are required to promote it on the alkyl regions. Figure 1 shows typical optical and AFM images of polymer structures formed using different patterned Si(111) surfaces. Polythiophene squares (Figure 1a) and disks possessing lateral dimensions in the range 10-100 μm for heights of some tens of nanometers can be generated. For thicker films, pillar-shaped structures can be obtained (Figure 1b).

In this first example where the conducting polymer is covalently bound to the semiconductor, each feature should behave independently like a high quality conducting organic material/semiconductor junction. So, through a fine-tuning of the electrochemically switchable conductivity of the polythiophene patterns, the polymer thickness and the length of the electronically insulating alkyl chain, it seems possible to control the electrical properties of these junctions.

(1) Fabre, B.; Lopinski, G. P.; Wayner, D. D. M. *Chem. Commun.*, in press.
(2) Kim, N. Y.; Laibinis, P. E. *J. Am. Chem. Soc.* **1999**, *121*, 7162.
(3) Holdcroft, S. *Adv. Mater.* **2001**, *13*, 1753.
(4) Wojtyk, J. T. C.; Tomietto, M.; Boukherroub, R.; Wayner, D. D. M. *J. Am. Chem. Soc.* **2001**, *123*, 1535.
(5) Fabre, B.; D. D. M. Wayner, submitted to *J. Am. Chem. Soc.*



Scheme 1. Strategy used for the patterning of polythiophene chemically bound to silicon. EG = di(2-thienyl)carbinol electropolymerizable group.

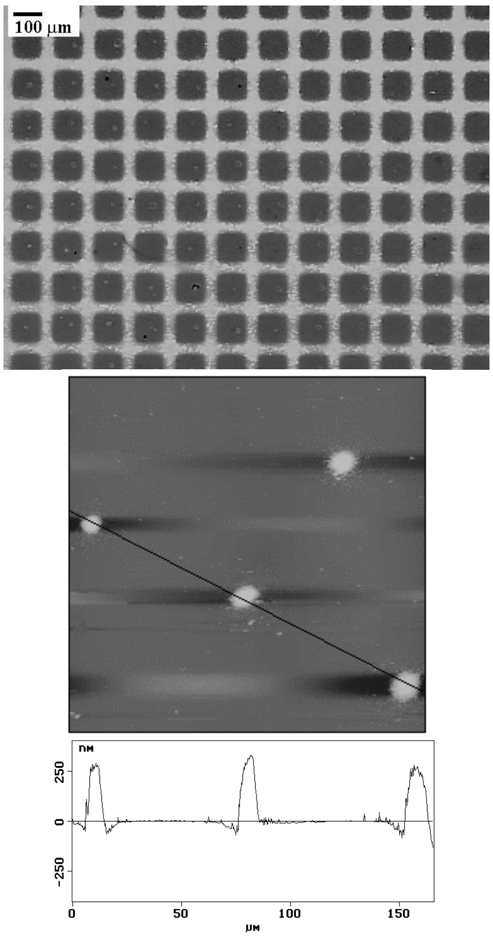


Figure 1. (a) CCD optical image of 40 nm thick ClO_4^- -doped polythiophene squares deposited onto a surface patterned with 100 μm squares of -$C_{10}H_{20}C$(2-thienyl)$_2$OH and 50 μm spacings of -$C_{10}H_{21}$, (b) AFM (150 x 150 μm^2) tapping mode image of ca. 300 nm high ClO_4^- -doped polythiophene pillars (ca. 10 μm diameter).