Electrical and Optical Properties of Polypyrrole Films Studied by Current Sensing Atomic Force Microscopy and Spectroelectrochemical Techniques

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Recently, we have demonstrated that current-sensing atomic force microscopy (CS-AFM) can be successfully applied to the characterization of conducting polymer films of various doping states.¹ The technique is very useful in studying doping distributions by obtaining two-dimensional current images and nanoscale electrical characteristics by measuring current-voltage curves. We have also shown that the optical properties can be measured at various doping stages together with electrical properties using a reflective absorption mode setup termed the near normal incidence reflectance spectroscopy (NNIRS)²; both the microscopic electrical properties and their averaged optical properties are correlated well with each other.³

Figures 1 and 2 show typical topography (a) and current (b) images obtained simultaneously for the surface of a polypyrrole (PPy) film galvanostatically grown for 10 s at a current density of 3.92 mA/cm² in acetonitrile (ACN with 1% water) and water, respectively. Well defined grains were observed in both topography images although current images are significanly different. The current image displayed in Fig. 1b shows that the currents higher than 1 μ A flow at a bias voltage of 50 mV over the whole surface area except for a few dark spots. The grain boundaries are more conducting than the top globular regions when the bias voltage was reduced to 3 mV, which is also clearly seen from the PPy film prepared in H_2O (Fig. 2b). From the very early growing stage (0.3 s deposition time), the PPy film obtained in ACN is very conducting as shown in Fig. 1b, while that prepared in H₂O shows slow increases of currents as shown in Fig. 2b.

The current-voltage (I-V) characteristics measured at randomly selected spots from the surfaces (Fig. 1b and Fig. 2b) show that the conductivity of the PPy film from ACN is much higher than that from H_2O and the former is more homogeneous. We also see the I-V curves having metallic properties only after 1 s deposition time in the case of the film made in ACN, which was attained only after 8 s in H_2O . The absorption spectrum of the surfaces such as shown in Fig. 1d indicates that the film is in a highly homogeneous conducting state, while that obtained from the PPy film prepared in water (Fig. 2d) show a broad ranges of doping states. The absorption spectra recorded at each growing stage of the films were analyzed along with their electrical characteristics.

We have also obtained the electrical and optical properties of chemically synthesized regioregular poly(3hexylthiophene) (P3HT) and electrodeposited P3HT films. The doping states of P3HT films were controlled by chemical or electrochemical oxidation, and their corresponding 2-dimensional current images, currentvoltage characteristics, and absorption spectra were obtained. These films show significantly different properties from each other, which were attributed to different chemical structures and morphologies.

REFERENCE

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Figure 1. Topographic (a) and current (b) images obtained from a PPy film galvanostatically grown for 10 s in ACN (with 1% water). The typical I-V curve (c) and absorption spectrum (d) measured on the surface (b).



Figure 2. Topographic (a) and current (b) images obtained from a PPy film galvanostatically grown for 10 s in water. The typical I-V curve (c) and absorption spectrum (d) measured on the surface (b).