ANISOTROPIC ELECTRODEPOSITION OF POLYPYRROLE

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Abstract

Polypyrrole is challenging to process because of its insolubility. Electrodeposition techniques that are often used to synthesize high quality polypyrrole films rely on the presence of a conducting substrate for patterning. However, once the conducting substrate is present the anisotropy of deposition can be used to bridge insulating gaps. The bridging of gaps between electrodes is demonstrated on glass and paper subsrates, and it is shown that lateral deposition rates across the insulting surfaces can be at least ten times faster than the vertical deposition rate. It is also shown that scratches on the surface of working electrodes can be used to pattern electrodeposited polypyrrole. These techniques may prove useful in fabricating polymer electronic devices from electrodeposited conducting polymers.

Keywords: Polypyrrole, Electropolymerization, insulating substrate, lateral deposition, patterning, organic electronics, conducting polymer.

1. Introduction

Electrodeposition produces amongst the highest conductivity polypyrrole (>400S/cm) with excellent mechanical properties [1-3], but deposition is traditionally thought to be limited to the surfaces of conductive electrodes. Such localized deposition has been useful in creating polypyrrole micromechanical devices [4]. Electrodeposition would be more useful if it could also enable high quality polypyrrole coatings to be grown on insulating surfaces.

It has been shown that electrodeposited polymers will bridge micrometer scale gaps between working electrodes [5,6]. However this was thought to be a disadvantage in device fabrication because patterning was not restricted to the metal surface [6], but spread out beyond it. It is now found that if electrodes are located on an appropriate substrate, the rate of electrodeposition parallel to the substrate can be several times faster in the lateral direction than in the perpendicular direction. The speed ratio of deposition in parallel to perpendicular orientations has reached up to ten on a glass substrate.

Anisotropy in growth speed has been observed in copper and nickel electrodeposition [7,8]. However the preferred direction of growth in these metals is parallel to the applied field. In the case of polypyrrole, fast growth is being achieved perpendicular to the direction of the applied field.

Another finding is that patterning of polypyrrole can be achieved on a silicon substrate by scratching the wafer surface, leading to the creation of electrodeposited polypyrrole wires that can extend several centimeters. The deposition and patterning methods should help overcome barriers to conducting polymer device fabrication.

2. Experimental

To test the effect of substrate, electropolymerization was done using three different working electrodes. In all cases the counter electrode was a sheet of stainless steel located far from working electrode to ensure that electric field lines are perpendicular to the working electrode. The electropolymerizations were carried out under constant current using a propylene carbonate solution containing 98% pure pyrrole (0.1M) and tetraethylammonium hexafluorophosphate (0.1M). All experiments were done at room temperature and all chemical materials were bought from Aldrich Chemical Co.

2.1 Experiment No.1: Electrodeposition on Gold Electrodes with a Glass Substrate.

The working electrodes used are two squares of gold, 10 mm on a side and 80 nm thick, on a glass substrate, where the gold is thermally evaporated. The initial gap between gold electrodes is 100 µm and they are electrically connected together during the electrodeposition. A current density of 0.05 mA/cm^2 is applied for a 13 hours.

2.2 Experiment No.2: Electrodeposition on Graphite Electrodes with a Paper Substrate.

The working electrodes are two graphite squares drawn on paper using a pencil. Each side of the squares has length of 10 mm. The gap between two squares is 1 mm and the resistance between the two points (10 mm apart) on the each of the electrodes is 6.5 kΩ before the deposition. A current density of 0.25mA/cm^2 is applied a15 hour deposition.

2.3 Experiment No.3: Electrodeposition on P-type Silicon.

The working electrode is a square segment of highly doped p-type silicon cut from a wafer (purchased from University Wafer–USA) which was scratched to create a line pattern on the electrode. The width of scratches was about 100 µm. A current density of 2.5mA/cm^2 was applied for 50 seconds.

3. Results and Discussion

3.1. Experiment No.1. Gold on Glass.

Figure 1 shows the process of electrodeposition on the gold squares at different times. Initial bridging between the two gold electrodes is achieved 5.5 hours after beginning electrodeposition. At the end of the experiment (13hours) the thickness of polypyrrole film reaches 28µm and the gap of 100µm is completely filled. As electropolymerization of polypyrrole begins from the edges of the gold electrodes, the average lateral growth distance is 50µm when the gap is filled. Hence, the speed ratio of the electropolymerization in parallel to perpendicular to the substrate was at least 1.8 (50µm /28µm ≈ 1.8).

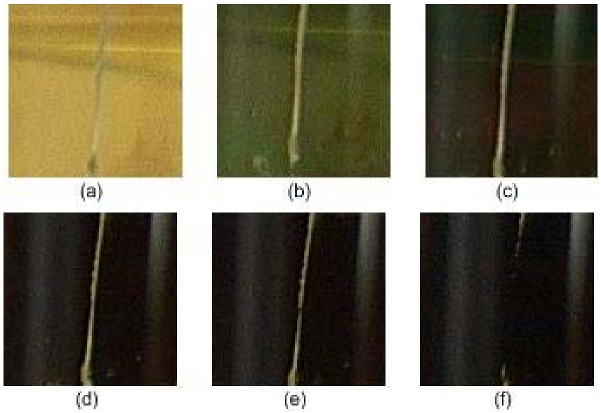

Fig. 1. Electrodeposition of polypyrrole on gold electrodes (gap=100µm) with glass substrate at (a)0h (b)0.1h (c)1h (d)3h (e)5.5h (f)13h after the beginning of process

At some points the ratio is significantly higher because the first bridge is observed after 5.5 hours at which time the thickness of deposited polypyrrole is less than 14 µm.

During the deposition, the polypyrrole does not adhere uniformly to the glass in the gap. Observation of the gap suggests that the regions where the polymer deposited directly on the glass where also the locations of the fastest lateral growth. This hypothesis was tested by using a strip of polypyrrole as working electrode of which a portion of the length was held next to a glass substrate using Kapton© tape. Electrodeposition of polypyrrole at a current density of 0.125mA/cm^2 over 21 hours showed that the lateral growth next to the tape, where the polypyrrole is in contact with the glass, extended by 3mm while the thickness of the polymer increased by only 310 µm. The lateral to vertical growth ratio in this case is almost 10.

3.2. Experiment No.2.

Experiment No.2 was done with a paper substrate to show that if substrate adhesion can be improved then the gap is filled more uniformly. Good adhesion of polypyrrole to the paper is expected because the paper is both porous and flexible.

Figure 2 shows the process of electropolymerizaton of polypyrrole on a paper substrate. After electropolymerization the surface of the deposited layer was very smooth and polypyrrole was deposited inside the paper as well as on the top of electrodes. The total thickness of paper and polypyrrole is 210 µm, while the thickness of paper before deposition was 112 µm. Polypyrrole grows both into and out of the paper, but it is assumed that all of the 98 µm gain in thickness is due to growth away from the surface. The average lateral growth along the surface of the paper is 500 µm, yielding a ratio of growth rates of 5.

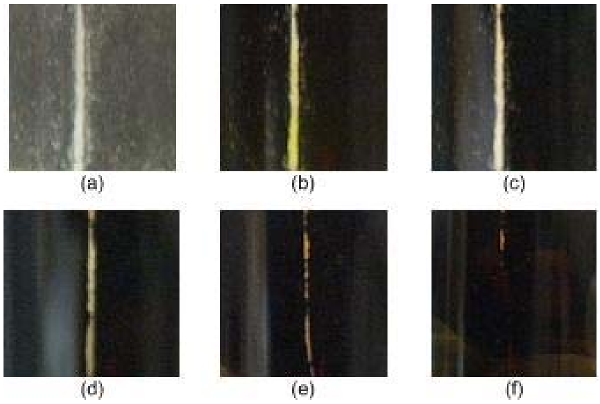

Fig. 2. Electrodeposition of polypyrrole on graphite electrodes (gap=1mm) with a paper substrate at (a)0h (b)1.5h (c)6h (d)9h (e)12h (f)15h after the beginning of process.

After deposition the resistance between two points (10 mm apart) on one electrode is 37 Ω, the same resistance is found between two points that are 10 mm apart, but separated by the region where the gap had been. The fact that the resistance is low across the gap suggests that deposition is uniform and relatively thick.

3.3. Experiment No.3.

Figures 3a and 3b show a portion of a silicon working electrode before and after electrodeposition. A 2 mm diameter circle and a line are scribed onto the substrate. Polypyrrole has grown in the scribed regions and not on the remainder of the substrate.

Similarly on another portion of the substrate lines are scribed into the silicon. Once again, deposition occurs preferentially along the marks.

Although the deposition begins in the scribe marks, after approximately ten minutes polypyrrole growth is observed to spread across the entire substrate.

One reason that the electropolymerization may be initiated in the scribe marks is that the native silicon oxide, which behaves as a high resistive layer, is removed by the scribe, revealing the underlying conducting substrate. Polymer first fills the indentations and then spreads across the substrate surface.

Another reason for initiation at the indentations is that the charge density is higher at the edges of an equipotential surface which increases the concentration of charges at the walls of scratches, and that the scribe mark provides a better nucleation site. These effects were tested by scribing a gold electrode in a similar experiment. Again it was observed that electropolymerization begins in the scratches, but in this case the polypyrrole very quickly covered the entire surface of the gold electrode.

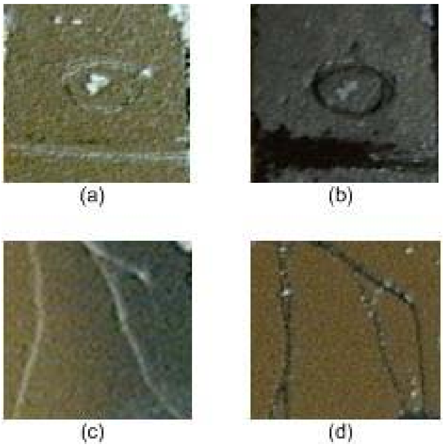

Fig. 3. (a,c) scratches on opposite sides of a p-type silicon wafer before electrodeposition. (b,d) electrodeposited polypyrrole inside the scribe marks. The diameter of circle in a and b is 2mm and the length of the lines in c and d is approximately 6 mm.

The scribing of the silicon's oxide covered surface enables patterning by preventing the immediate spread of growth across the entire electrode.

4. Conclusions

We have studied lateral electrodepolymerization of polypyrrole over insulating surfaces between working electrodes. Lateral deposition is up to ten times faster than deposition perpendicular to the electrode surface. This effect is demonstrated on glass and paper substrates. Rapid lateral growth only occurs were the polymer is in contact with the insulating substrate. The paper substrate proved to be effective in maintaining contact during deposition. The demonstration of polypyrrole/insulator structures that are electrodeposited promises to enable electrodeposition methods to be employed more widely as a technique for polymer electronic device fabrication.

In addition the effect of scribing on controlling the location of deposited polypyrrole was investigated on silicon and gold electrodes. Polypyrrole is preferentially deposited within these scribe marks. On silicon, the surface beyond the scribe marks resists coverage, likely due to the presence of the native silicon oxide. The scribing can be used to pattern polypyrrole on surfaces to produce a micron width sample that is several centimeters in length.

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References

[1] R.S. Kohlman, A.J. Epistein, Insulator-Metal transition and Inhomogeneous Metallic State in Conducting Polymers, in: T.A. Skotheim, R.L. Elsenbaumer, J.R. Reynolds (Ed.), Handbook of Conducting Polymers, Marcel Dekker, New York, 1998, (Chapter 3).
[2] K. Sato, M. Yamaura, T. Hagiwara, Study on the Electrical Conduction Mechanism of Polypyrrole Films, Synth. Met. 40 (1991) 35.
[3] J.D.W. Madden, P.G.A. Madden, I.W. Hunter, Characterization of polypyrrole actuators: modeling and performance, Proc. SPIE Vol.4329 (2001), 72-83.
[4] E.W.H Jager, E. Smela, O. Inganäs, Microfabricating Conjugated Polymer Actuators, Science 24 (2000), 1540-1545.
[5] H. Koezuka, A. tsumura, H. Fuchigami, K. Kuramoto, Polythiophene field-effect transistor with polypyrrole worked as source and drain electrodes, Appl. Phys. Lett. 62(15) (1993), 1794-1796.
[6] G. Horowitz, Organic Field-Effect Transistors, Adv. Mater 10, No.5, (1998) 365-377.
[7] V. Fleury, W.A. waters, L.Allam, T. Devers, Rapid Electroplating of Insulators, Nature, 416 (2002), 716-719.
[8] J.D.W. Madden, I.W. Hunter, Three-Dimensional Microfabrication, J. Microelectromechanical Sys. Vol.5 (1996), 24-32.