Electropolymerization of Electroinactive Polypyrrole Film for a Nonlinear MIM Switching Device

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Thin films of electroinactive polypyrrole (PPy) were electropolymerized in NaOH aqueous solutions on ITO (indium tin oxide) electrodes for the purpose of constructing nonlinear MIM (metal-insulator-metal) switching devices for large scale flat panel displays. Electroactivity and morphology of PPy films were greatly affected by the NaOH concentration. Highly anodic potential (1.5 V vs. Ag/AgCl) electrolysis in NaOH solution produced carbonyl groups in the PPy chain, so that electroinactive PPy was nonconducting in as-prepared conditions. The MIM structure of ITO/PPy/ITO was fabricated by ITO sputtering onto the PPy film. The device using the PPy film prepared from 0.01 mol dm⁻³ NaOH aqueous solution showed nonlinear and symmetric current-voltage (I-V) characteristics. In spite of using the nonconductive PPy, a dependence of I-V characteristics on polymerization time was observed, and a proper polymerization time was required to produce an MIM device.

1 INTRODUCTION

Electropolymerized films are insensitive to air. They are able to be prepared highly conducting, semiconducting and insulating materials when varying their polymerized conditions. Highly conducting or semiconducting polymers, formed by electropolymerization, have been extensively investigated from a practical point of view for electronic device application. Indeed, Schottky junction-type diodes¹⁾ and field-effect transistors (FETs)²⁾ have been demonstrated using, e.g., a copolymer of pyrrole and N-methylpyrrole units, and polythiophene respectively. An application of electroinactive or nonconducting polymers formed with a electropolymerization technique, however, has scarcely been tried in this field. We have fabricated an MIM (metal-insulator-metal) device using an electropolymerized nonconducting film as an insulator^{3,4)}.

The MIM device is a nonlinear, two terminal device, and its structure is simpler than that

of a TFT (thin film transistor). An application of it to the switching element for the multiplexed liquid crystal (LC) display is expected⁵⁾. The insulator of the MIM switching device is practically used with a Ta₂O₅ layer formed by anodizing a sputtered Ta film. Its fabricating process is still complex, and a simplified fabricating-process is required in order to realize a large area LC panel. On the basis of this requirement, some insulating organic films, such as polyimide formed using a Langmuir-Blodgett method⁶⁾, polyfuran using plasma polymerization⁷⁾, and polyethylene using an evaporated method⁸⁾ have been reported. We have already reported an MIM device using undoped poly-N-methylpyrrole (PMPy) film as an insulator³⁾. An electropolymerization method is highly suitable for larger area fabrication, but the undoped PMPy film reported in ref. 3 is very sensitive to its anion undoping process, so that the stability of electric characteristics of this element must be developed.

In this paper, we try to use directly formed nonconducting polypyrrole (PPy) as an insulator⁴⁾, instead of undoped polymers, and report and discuss the nonlinear properties of the MIM device using the electroinactive PPy insulator.

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2 EXPERIMENTAL

2.1 Chemicals and solutions

Reagent grade pyrrole (Tokyo Kasei Co., Ltd.), NaClO₄ (Kanto Chemical Co., Inc.) and NaOH (Kokusen Chemical Works Ltd.) were used without further purification. Photoresists OMR-83 and OFPR-800 (Tokyo Ohka Kogyo Co., Ltd.) were used for ITO (indium tin oxide) glass substrate preparation and for etching the upper ITO electrode respectively. Aqueous solutions containing 0.25 mol dm⁻³ pyrrole monomer and 0.05, 0.01, and 0.001 mol dm⁻³ NaOH electrolyte salts were used for the preparation of PPy films. They were deaerated by argon gas before use.

2.2 Film preparation and electrochemical measurements

For the electropolymerization and electrochemical measurements, the cell was assembled with an ITO working electrode, a Pt counter electrode, and an Ag/AgCl reference electrode. Cyclic voltammetry at 10 mV s⁻¹ was employed for surveying both electropolymerization behavior and the redox process. PPy films were formed by constant potential electrolysis at 1.5 V vs. Ag/AgCl with varying electrolysis time. Electroactive PPy for Fourier-transformed infrared (FT-IR) and visible (Vis) spectroscopic measurements were formed by constant potential electrolysis at 0.65 V vs. Ag/AgCl from an aqueous solution containing 0.2 mol dm⁻³ pyrrole monomer and 0.1 mol dm⁻³ NaClO₄ electrolyte salt.

2.3 Fabrication and current-voltage (I-V) characteristics measurement of an MIM device

Device fabrication was performed as previously reported^{3,4}. A schematic representation of the MIM device is shown in Fig. 1. The holes for deposited polypyrrole layer were prepared on the ITO (ca. 400 nm thick) glass substrate using a photolithographic technique. The hole sizes were 100, 300, 500, 700, 1000 μm in diameter. PPy films formed by constant potential electrolysis at 1.5 V vs. Ag/AgCl were used for fabrication of the device. After a

Fig. 1. Schematic representation of the MIM device structure.

rinse in water and drying by a stream of argon gas of the PPy coated electrode, the upper ITO electrodes (ca. 60 nm thick) were prepared by using sputtering and etching technique. I-V characteristics of the device were measured between ± 10 V by 0.5 V steps in the dark.

2.4 Apparatus

The microscopic FT-IR spectroscopic measurement was carried out by a JEOL JIR-5500. Vis spectra were recorded on a HITACHI U-3200 spectrophotometer. The morphology of PPy films was observed with a JEOL JSM-T20 scanning electron microscope (SEM). Film thickness was measured using a contact profile meter (Alpha-step 200 TENCOR INSTRUMENTS). For the film preparation, the Potentio/galvanostat HA-301 (Hokuto Denko Co., Ltd) was employed. I-V characteristics were measured using a YOKOGAWA HEWLETT-PACKARD 4140B pA meter / dc voltage source.

3 RESULTS and DISCUSSION

3.1 Selection of the polymerization solution

Electropolymerization of insulating PPy has already been reported briefly by Murthy et al.⁹, but details of the polymerization condition have scarcely been described. We prepared three polymerization solutions containing 0.001, 0.01, and 0.05 mol dm⁻³ NaOH, and surveyed electropolymerization behavior and the redox process of PPy films with cyclic voltammetry in polymerization solutions. Cyclic voltammograms over the range between -0.3 V and 1.8 V vs. Ag/AgCl for each solution are shown in Fig. 2. For the lower NaOH concentration (Fig. 2-(a)), anodic current for polymerization is shown at the first cycle and then the redox process is observed. This means that the PPy film obtained in 0.001 mol dm⁻³ NaOH solution is somewhat electroactive and its conductivity is not very low. The PPy film formed from this polymerization solution is considered to be unsuitable for use in an MIM device. On the other hand, anodic currents for polymerization are also observed in both Figs. 2-(b) and 2-(c), however, the redox process is not shown. This indicates that PPy films obtained from these solutions are electroinactive and the conductivities are very low. For polyaniline¹⁰ and polyphenol¹¹, it was reported that the electroinactive and low conducting films are obtained in high pH solutions. But Li et al. reported that, even in NaOH electrolyte solution, electroactive PPy film showed the redox process with a decrease in

Fig. 2. Cyclic voltammograms at 10 mV s^{-1} in various NaOH aqueous solutions containing 0.25 mol dm^{-3} pyrrole: (a) $0.001 \text{ mol dm}^{-3}$, (b) 0.01 mol dm^{-3} , and (c) 0.05 mol dm^{-3} NaOH. Figures indicate the cycle numbers.

conductivity when an adequate scan range was selected, and that it became electroinactive when the anodic scan went to a higher anodic potential¹²⁾. Judging from these reports, the electroinactivity of the PPy films obtained from 0.01 and 0.05 mol dm^{-3} NaOH solution is considered to be affected by highly anodic potential electrolysis rather than high pH value. Highly anodic potential ($1.5 \text{ V vs. Ag/AgCl}$) electrolysis was employed for film preparation.

Next, we tried to electropolymerize PPy films for MIM devices in 0.01 and 0.05 mol dm^{-3} NaOH polymerization solutions by constant potential electrolysis at $1.5 \text{ V vs. Ag/AgCl}$. The surface morphology, the film thickness and the adherence to the ITO electrode are considered to affect I-V characteristics of the device significantly. The surface morphology of electroinactive PPy films were observed and are shown in Fig. 3, indicating the SEM images of PPy films obtained from 0.01 and 0.05 mol dm^{-3}

(a) 0.01 mol dm^{-3} NaOH

(b) 0.05 mol dm^{-3} NaOH

Fig. 3. SEM images of PPy films electropolymerized at $1.5 \text{ V vs. Ag/AgCl}$ from polymerization solutions (a) 0.01 mol dm^{-3} and (b) 0.05 mol dm^{-3} NaOH. Each solution contains 0.25 mol dm^{-3} pyrrole.

Fig. 4. The relationship between film thickness and electrolysis time at $1.5 \text{ V vs. Ag/AgCl}$ from 0.01 mol dm^{-3} NaOH polymerization solution containing 0.25 mol dm^{-3} pyrrole.

NaOH polymerization solutions. In Fig. 3-(a), the PPy film obtained from 0.01 mol dm^{-3} NaOH solution is thin (ca. $0.2 \mu\text{m}$ thick) and very smooth, so it would be free of the pin-hole defects. On the other hand, in Fig. 3-(b), the PPy film from 0.05 mol dm^{-3} NaOH solution is thicker than that from 0.01 mol dm^{-3} NaOH. However, wrinkles are observed, so the adherence of this film to the ITO electrode is found to be very low. Therefore, we selected the PPy film obtained from 0.01 mol dm^{-3} NaOH polymerization solution for an MIM device because of its low conductivity and good adherence to the ITO electrode.

Figure 4 shows the dependence of the film thickness on polymerization time when the PPy films were electropolymerized at 1.5 V vs. Ag/AgCl. Electroinactive PPy has low conductivity in as-prepared conditions, so the film thickness shows a rapid rate of increase at the start of polymerization and the deposition rate of the film slows down with a proceeding of deposition. The thickness of the PPy film is found to be saturated at ca. $0.2 \mu\text{m}$.

3.2 Vis and IR spectra

The Vis spectra of electro-active and -inactive PPy films are shown in Fig. 5. Curve (a) in Fig. 5 shows the spectrum of the electroactive PPy film formed from polymerization solution containing NaClO_4 as an electrolyte at 0.65 V vs. Ag/AgCl. The spectrum contains broad absorption of more than 600 nm , originating from what is called the bipolaron absorption¹³. But such a bipolaron absorption is not observed in the electroinactive PPy film formed from 0.01 mol dm^{-3} NaOH polymerization solution at 1.5 V vs. Ag/AgCl for 60 min even in as-prepared conditions (curve (b)). Li et al. reported a similar spectrum in undoped and low conducting PPy by in situ spectrum measurement¹². These facts imply that the electroinactive PPy is not in a bipolaron state and also that it is very low conducting in as-prepared conditions.

Figure 6 shows the FT-IR spectra of electro-active and -inactive PPy film species. Both in electro-active (curve(a)) and -inactive (curve(b)) PPy films, the absorption peaks assigned to pyrrole rings (ca. 860 , 1017 , 1162 , 1524 , and 3218 cm^{-1}) are demonstrated. A strong absorption peak at 1697 cm^{-1} is clearly observed in curve (b), not so clear in curve (a). This peak can be attributed to the C=O stretching vibration, indicating that the carbonyl (C=O) groups exist in the electroinactive PPy chain. The carbonyl groups may be intro-

Fig. 5. Vis spectra of electro-active and -inactive PPy films: (a) electroactive PPy film formed at 0.65 V vs. Ag/AgCl from an aqueous solution containing 0.1 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} NaClO_4 , (b) electroinactive PPy film formed at 1.5 V vs. Ag/AgCl for 60 min from an aqueous solution containing 0.25 mol dm^{-3} pyrrole and 0.01 mol dm^{-3} NaOH.

Fig. 6. FT-IR reflection spectra of electro-active and -inactive PPy films: (a) electroactive PPy film formed at 0.65 V vs. Ag/AgCl from an aqueous solution containing 0.1 mol dm^{-3} pyrrole and 0.2 mol dm^{-3} NaClO_4 , (b) electroinactive PPy film formed at 1.5 V vs. Ag/AgCl for 60 min from an aqueous solution containing 0.25 mol dm^{-3} pyrrole and 0.01 mol dm^{-3} NaOH.

duced by highly anodic potential electrolysis (1.5 V vs. Ag/AgCl). The possibility of attacks of nucleophilic hydroxide anions from the NaOH electrolyte to α - or β - carbons is shown in scheme 1.

(a) Hydroxide ion attack at α -carbon

(b) Hydroxide ion attack at β -carbon

Scheme 1

The positive charged sites in PPy chain would exist in π -conjugated systems, so these two reactions shown in (a) and (b) are considered to occur simultaneously. Similar carbonyl group formation was reported as an irreversible overoxidation reaction which changed an electroactive polypyrrole¹⁴⁾ or polythiophene

¹⁵⁾ to an electroinactive and low conducting state. The nucleophilic reactions would occur at electrophilic sites of the positive charged bipolarons and lead to shortening of π -conjugated length of the PPy chain. Such reaction makes the PPy films electroinactive and low conducting in as-prepared conditions, and this film preparation method probably consists of both the polymerization and the irreversible overoxidation reaction.

3.3 I-V characteristics of the MIM device

Figure 7 shows I-V characteristics of the MIM device using the PPy film formed from 0.01 mol dm⁻³ NaOH polymerization solution at 1.5 V vs. Ag/AgCl for 60 min. The positive and negative directions in Fig. 7-(a) and (b) correspond to a positive and negative bias in the ITO glass substrate respectively. The symmetric and nonlinear I-V responses and increases in currents, ca. 5 orders of magnitude (Fig. 7-(a)), are reproducibly observed, and the switching behavior of threshold voltage at ca. ± 5 V is obtained as shown in Fig. 7-(b). A number of measurements also confirmed the stability of the electric properties of it. The hole size did not influence I-V characteristics. As for the reproducibility and no necessity of undoping process, this device is superior to that using the undoped PMPy film reported previously³⁾. Thus the electroinactive PPy films were found to be

Fig. 7. I-V characteristics of the MIM device using the electroinactive PPy film formed at 1.5 V vs. Ag/AgCl for 60 min from aqueous solution containing 0.25 mol dm⁻³ pyrrole and 0.01 mol dm⁻³ NaOH: (a) log I-V, (b) I-V.

suitable for an insulator of the MIM device from a practical point of view.

Next, we tried to fabricate the devices with varying polymerization time. When polymerization time is shorter than 30 min, high applied-voltage caused the breakdown of the I-V characteristics. On the other hand, polymerization for more than 30min confirmed the stability of them. Figure 8 shows the typical I-V characteristics of the devices using PPy film deposited for 30 and 60 min. The resistance and threshold voltages are found to increase with the passage of polymerization time. These phenomena can be explained as follows.

(1) An increase in the film thickness lowers the electric field of the PPy film, improving the resistance value.

(2) The structural change which improves the resistivity value proceeds during polymerization.

The former is easily confirmed by the results in Fig. 4. The latter is suggested by the relationship between PPy film conductivity and polymerization time. Figure 9 shows the relationship between polymerization time and the conductivity, $\sigma_{0.5}$, of PPy films measured at currents of +0.5 V. The $\sigma_{0.5}$ value is found to clearly decrease with polymerization time. This is probably caused by the structural change of

the PPy film. The Vis spectra of PPy films were measured with varying polymerization time. The Vis spectra of the PPy film of different polymerization time are shown in Fig. 10. With the passage of polymerization time, the bipolaron peak, which is slightly observed

Fig. 9. The dependence of the conductivity, $\sigma_{0.5}$, in electroinactive PPy films measured at 0.5 V on polymerization time.

Fig. 8. I-V characteristics of the MIM device using PPy films deposited for (a) 30 min and (b) 60 min.

Fig. 10. Vis spectra of the PPy films as a function of polymerization time: (a) 5 min, (b) 30 min, (c) 60 min.

at 760 nm, becomes smaller, and disappears completely at more than 45 min polymerization. This may be due to the attack of hydroxide anion to the positive site of the bipolaron leading to the destruction of it. Thus the improvement of the resistance value probably is due to both the increase of the film thickness and the proceeding overoxidation reaction.

4 CONCLUSION

The electroinactive and nonconducting PPy films were able to be electropolymerized from NaOH aqueous solution at highly anodic potential electrolysis. Their electroinactive and less conductivity were for the most part caused by the overoxidation reaction. The concentration of NaOH affected not only the electroactivity but the morphology of the PPy film. The ITO/PPy/ITO type MIM device using the electroinactive PPy showed stable nonlinear I-V responses, and the possibility of its practical use was demonstrated. The dependence of the I-V characteristics on polymerization time was explained by the increase in film thickness and structural changes of the PPy film.

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