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Research Article

Schottky Diodes and Thin Films Based on Copolymer: Poly(aniline-co-toluidine)

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Poly(aniline-co-o-toluidine) (PANI-co-POT) thin films were deposited on indium tin oxide- (ITO-) coated glass substrates by electrochemical polymerization under cyclic voltammetric conditions from aniline-co-o-toluidine monomer in an aqueous solution of HCl as a supporting electrolyte. These measurements showed that the optical band gap of the copolymer films is on the order of 2.65 eV. On the other hand, ITO/PANI-co-POT/Al devices were fabricated by thermal evaporation of Aluminum circular electrodes on the as-deposited PANI-co-POT films. The Current-Voltage characteristics of these devices are nonlinear. The diode parameters were calculated from I-V characteristics using the modified Shockley equation. The C-F characteristics were also measured.

1. Introduction

In recent years, considerable attention was given to the fabrication and characterization of thin films and Schottky diodes using conducting polymers as active materials. Intrinsically conducting polymers consisting of a π-conjugated backbone are attractive because of their unique electronic properties. As one of the most important conducting polymers, polyaniline and its derivatives have been extensively studied in different fields of science [1] because of the demand for high-performance materials in advanced technologies including microelectronic materials [2], rechargeable batteries [3], energy storage [4], sensors [5], photovoltaic cells [6], and actuators [7].

However, the common uses of polyaniline are restricted, due to its poor processability and low solubility. Various techniques, such as the modification of the monomer structure, the utilization of soluble precursor, and the preparation of copolymers and composites, have been introduced to enhance the processability and solubility. Indeed, the copolymerization has the advantage as the material obtained is homogenous and also the preparation methods are easy.

With regards to PANI-type copolymers, a pioneering work has been done by Wei et al. [8, 9]. They have shown that aniline copolymerized with o-toluidine yields a homogenous copolymer film with controlled conductivity.

On the other hand, several authors [10–13] used various metal/polymer junctions with polyaniline and its derivatives to make and study Schottky barrier-type diodes. They estimated the electronic parameters such ideality factor, barrier height, and so forth. However, no studies have been performed on metal/(PANI-co-POT) junction.

In our series of papers [14–17], we have studied the electrical properties of Schottky diodes based on polyaniline, as well as polythiophene and its derivatives. In the present study, we report on the electrochemical and optical properties of PANI-co-POT films on one hand, and on the other hand, on the electrical properties of ITO/PANI-co-POT/Al junctions.

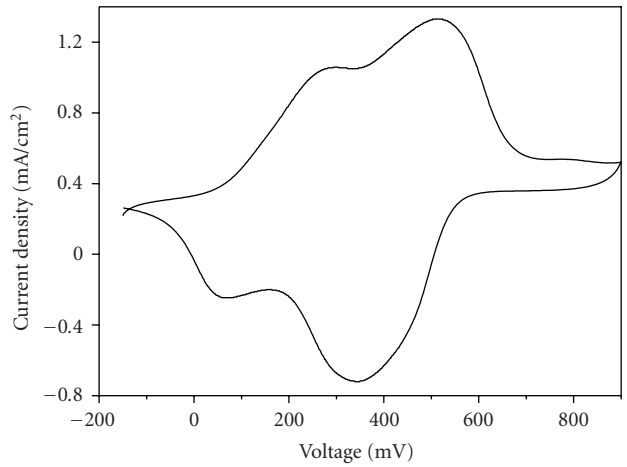

Figure 1: Cyclic voltammograms recorded during the synthesis of PANI-co-POT films.

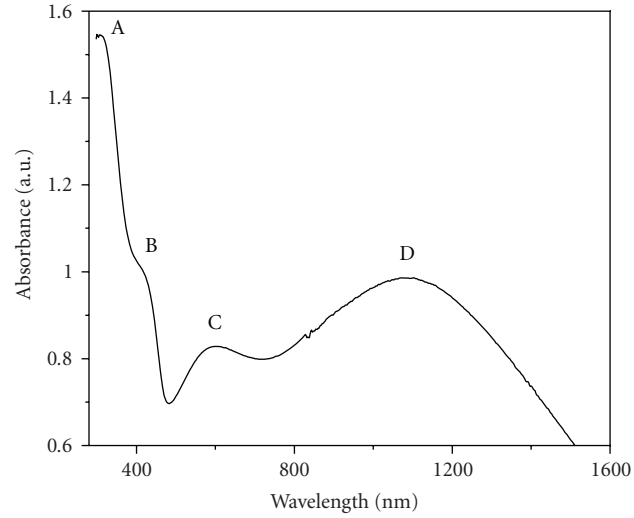

Figure 2: Optical absorption spectra of PANI-co-POT thin films.

2. Experimental Procedure

Poly(aniline-co-o-toluidine) (PANI-co-POT) films were electrochemically synthesized under cyclic voltammetric conditions [18]. Cyclic voltammetric studies were performed with a computer-controlled EG&G Model 273A potensiostat-galvanostat. A three-electrode cell assembly was used during the electrochemical polymerization with an ITO-coated glass substrate as a working electrode, a Platinum foil as a counter electrode, and a Saturated Calomel Electrode (SCE) as a reference electrode. All the potentials are referenced with respect to the SCE. The ITO-coated glass substrates were ultrasound-cleaned in acetone and distilled water several times and subsequently air-dried.

PANI-co-POT films were synthesized in aqueous solution of distilled o-toluidine and aniline (0.1 M) in HCl (0.5 M) solutions. To initiate the polymerization reaction, a fixed potential of 0.85 V/SCE was first applied for three minutes. Subsequently, 40 cycles were performed for this sample by scanning the potential between −0.15 and 0.9 V/SCE with a scan rate of 50 mV/s. At the end of the fortieth cycle, the thin film is washed with the corresponding fresh electrolyte solution in order to remove the low molecular soluble products and then dried in ambient air.

The optical transmission of the as-electrodeposited PANI-co-POT films was measured using a Shimadzu-3101-UVPC double-beam spectrophotometer in the wavelength range 400–900 nm.

Schottky-barrier-type devices were fabricated by depositing 2 mm diameter circular aluminum electrodes on electropolymerized PANI-co-POT thin films. The aluminum was deposited in a separate vacuum chamber by thermal evaporation of 99.99% purity Aluminum shots for three minutes at base pressure of 1.5×10^{-5} mbar.

The electrical measurements were performed on this ITO/PANI-co-POT/Al device at room temperature. The current voltage characteristics were measured using a Keithly 410 programmable picoamperemeter and a 610C programmable microvoltmeter. The capacitance measurements were carried out using a Keithley LCZ3300 impedance meter. All the instruments are controlled by a computer via a GPIB card.

3. Results and Discussion

3.1. Electrochemical Characteristics of PANI-Co-POT. The 40th cyclic voltammograms recorded during the electrodeposition of the PANI-co-POT films on ITO-coated glass is presented in Figure 1. The voltammogram present two anodic peaks at 0.29 and 0.52 V/SCE. These peaks are usually assigned to the oxidization of PANI-co-POT films deposited on the working electrode, most likely the conversion of amine units to radical cations [19]. They correspond to the formation of radical cations (polaron formation in emeraldine form) from the leucoemeraldine form, and their oxidation to dications (bipolaron formation in pernigraniline form), respectively.

While taking account of the results reported in our work [14], the current density of oxidization peaks of (PANI-co-POT) is greater to those of the POT-homopolymer. This is in good agreement with literature [18]. Therefore, the thin films based on PANI-co-POT will be thicker than those based on POT alone.

Indeed, the introduction of polyaniline units permits to decrease the steric effects of the $-CH_3$ groups and, therefore, to increase the conjugation and conductivity of the copolymer.

3.2. UV-Visible Absorption of the Electrodeposited PANI-Co-POT Films. Figure 2 shows typical UV-Visible absorption spectra of the PANI-co-POT. The spectra reveal the presence of several bands.

(1) Sharp peak (A) centered at 308 nm which is attributed to the π-π^* electronic transitions on the basis of the studies performed on polyanilines and theoretical band structure calculations [20]. This peak showed a shift relative to the corresponding transition in POT [14], thus revealing an increase in the conjugation length in PANI-co-POT as a result of copolymerization with PANI.

(2) Shoulder (B) at 426 nm can be assigned to the polaron generation, which suggests the protonation of the copolymer backbone (bipolaronic transition) occured.

(3) Hump (C) around 610 nm which represents the n-π^* transition between the HOMO and the LUMO orbital [21].

(4) Broad peak (D) centered at 1080 nm which can be assigned to the polaronic transitions, suggesting the presence of the free carriers.

The optical band gap energy (E_g) is obtained using the fundamental law [22]:

$$\alpha(h\upsilon) = A\left(E_g - h\upsilon\right)^n, \tag{1}$$

where α is the absorption coefficient, $h\upsilon$ is the photon energy, A is a proportionality constant, and $n = 1/2$ for direct transitions. A similar value of $n = 1/2$ was used by Huang et al. to calculate the band gap energy for substituted polyaniline [13]. E_g can then be obtained by plotting $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ (Figure 3) and extrapolating the linear fit to zero.

The allowed direct optical gap of the PANI-co-POT films is found to be on the order of 2.65 eV. This value is lower than that found in our previous work [14] for POT thin films. This is can be due to the effect of copolymerization with polyaniline which can permit to increase the degree of conjugation.

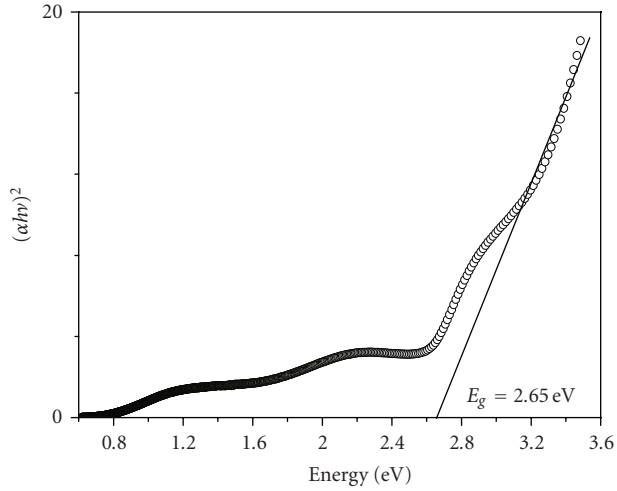

Figure 3: Plot of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$.

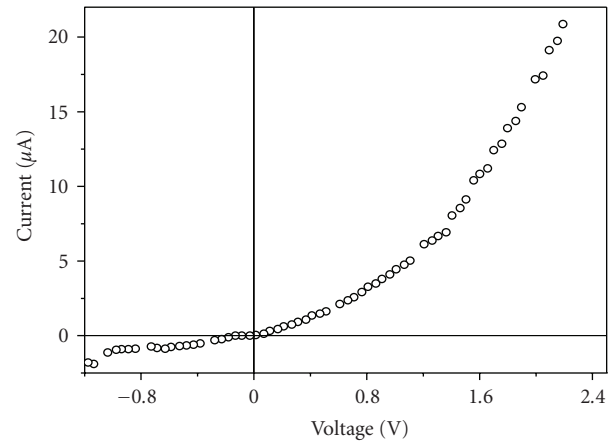

Figure 4: Current-voltage characteristics of ITO/PANI-co-POT/Al devices.

3.3. Electrical Properties of ITO/PANI-Co-POT/Al Device

3.3.1. Current-Voltage Characteristics. The I-V characteristics of the prepared ITO/POT-co-PANI/Al device are shown in Figure 4. This characteristic is nonlinear, asymmetric, and shows a rectifying behavior. This is further supported by the difference between the work function of PANI (4.1 eV) and aluminum (3.7 eV) [23].

The current transport across the polymer/metal junction is usually accounted for on the basis of thermoionic emission, Space-Charge Limited Current (SCLC), or Poole-Frenkel emission [24, 25]. The last two mechanisms are found not to be applicable for our diode in the exploited voltage range, as revealed by fitting their respective laws to experimental data. For the thermionic emission model, the I-V relationship is expressed by the modified Shockley equation [26]:

$$I = I_0\left[\exp\left(\frac{q(V - R_sI)}{\eta kT}\right) - 1\right], \tag{2}$$

where I_0 is the saturation current, q is the elementary charge (e), V is the applied voltage, k is the Boltzman constant, η is the diode ideality factor, R_s is the series resistance, and T is the absolute temperature.

The saturation current is given by [27]

$$I_0 = A^*T^2\exp\left(-\frac{q\Phi_B}{kT}\right), \tag{3}$$

where A^* is the effective Richardson constant which depends on the effective mass of the carriers (120 A cm^{-2} K^{-2} for free carriers) and Φ_B is the barrier height.

As shown in Figure 5, this model accounts well for the experimental data over the explored voltage range in the forward bias region. The fit ((2) and (3)) yielded the following diode parameters: $\eta = 22.1$, saturation current density $I_0 = 3.17 \times 10^{-5}$ (A/cm^2), $\Phi_B = 0.68$ eV, and $R_s = 2 \times 10^4\ \Omega$. These values are lower than those of ITO/POT/Al junction [14].

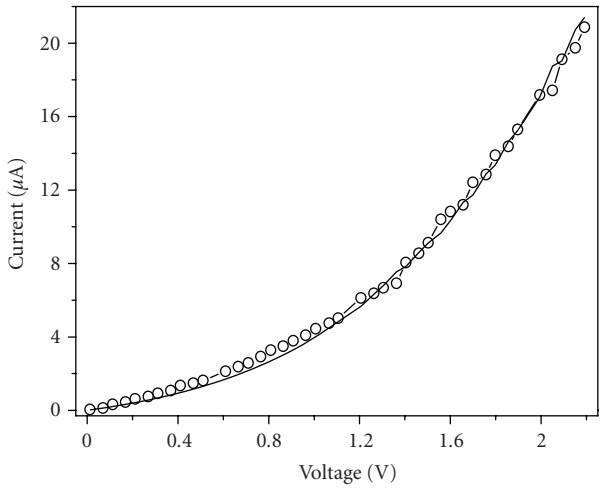

Figure 5: Experimental I-V characteristics of ITO/PANI-co-POT/Al device (∘) and fit (line) using (2) and (3).

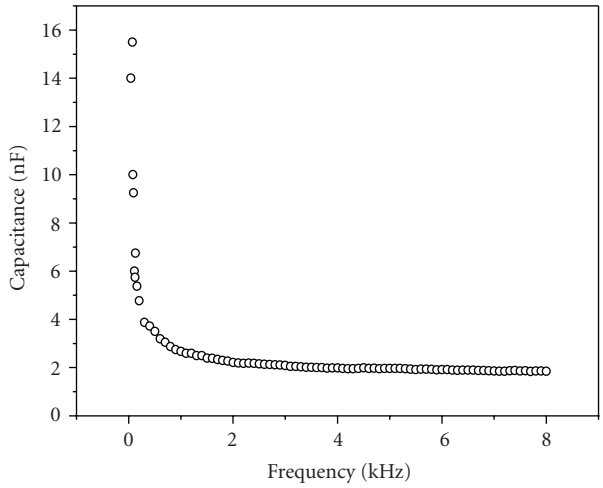

Figure 6: Capacitance-Frequency characteristics of ITO/PANI-co-POT/Al devices.

On the other hand, the value of the ideality factor of ITO/PANI-co-POT/Al Schottky device is greater than 1, but lower than that found by Saxena and Santhanam for the Schottky diodes based on a copolymer using poly(thiophene) [25]. This deviation of ideality factor from unity is generally attributed to the recombination of electrons and holes in the depletion region and/or the presence of barrier inhomogeneities, the reactive nature of the Al contact and trap assisted tunneling [28].

3.3.2. Capacitance-Frequency Characteristics. The zero-bias capacitance-frequency (C-F) characteristics of the ITO/PANI-co-POT/Al diode are presented in Figure 6. The capacitance decreases as the measuring frequency is increased and then stabilizes. Such a frequency dispersion of the capacitance suggests the presence of a distribution of localized states in the band gap of the amorphous polymer [29].

In addition, the capacitance of the ITO/PANI-co-POT/Al diode is lower than that of the ITO/POT/Al diode presented in our previous work [14]. This reflects an increase in the film thickness by the copolymerization of the POT with PANI, which is in good agreement with UV-Vis spectroscopy and cyclic voltametry results.

4. Conclusion

We have successfully deposited PANI-co-POT thin films on ITO-coated glass by cyclic voltammetry methods. ITO/PANI-co-POT/Al sandwich devices were also fabricated based on these films. The optical gaps of the obtained PANI-co-POT films are lower than those for POT thin films. The cyclic voltammetric investigation indicated that the current density of oxidization peaks of (PANI-co-POT) are greater to those of the POT- homopolymer.

On the other hand, the I-V characteristics of ITO/PANI-co-POT/Al diodes showed a rectifying behavior. The electronic parameters of the diodes are determined using the modified Shockely equation. The C-F measurements suggest a distribution of localized states in the band gap of the polymer.

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