

Research Article

Spectroscopic Characterization of Electrodeposited Poly(o-toluidine) Thin Films and Electrical Properties of ITO/Poly(o-toluidine)/Aluminum Schottky Diodes

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Received 29 July 2007; Accepted 8 October 2007

Recommended by Yalin Lu

Poly(o-toluidine) (POT) thin films were synthesized by electrochemical polymerization under cyclic voltammetric conditions from o-toluidine monomer in an aqueous solution of HCl as a supporting electrolyte. The electrosynthesized films were characterized by UV-Visible, FT-Raman, and FTIR spectroscopies. The optical transmissions of the as-deposited films were measured in the 400–900 nm wavelength range. These measurements showed that the optical band gap of the polymer films is in the order of 2.52 eV. The FT-Raman and FTIR measurements showed that the POT film is composed of imine and amine units. ITO/POT/Al devices were fabricated by thermal evaporation of aluminum circular contacts on films deposited on ITO-coated glass. The nonlinear current-voltage characteristics of these devices indicate a rectifying behavior. The diode parameters were calculated from I-V characteristics using the modified Shockley equation. The measured C-V and C-F characteristics are presented.

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1. INTRODUCTION

π -conjugated polymers have received a great deal of attention due to their potential technological applications. These materials have been considered as active electrode materials in energy storage [1], optoelectronic devices [2], and display devices [3]. These polymers include polypyrrole [4], polyaniline [5], polythiophene [6], and other conjugated polymers [7].

In particular, polyaniline (PANI) has attracted attention due to its interesting electrochemical and optical properties, moderate conductivity, as well as environmental stability. This polymer may be obtained by electrochemical and chemical oxidative polymerization of aniline in aqueous solutions.

Poly(o-toluidine) (POT) is a PANI derivative which contains the $-\text{CH}_3$ group in the ortho position of the aromatic ring of the aniline monomer. Among the ring-substituted PANI derivatives, POT has been probably the most widely studied one. Indeed, Ram and Borole [8, 9] as well as other

authors [10] have studied the electropolymerization of o-toluidine using various electrolytes with different concentrations. These works revealed that POTs have interesting electro-optical properties and can be used as electrochromic and electronic devices.

On the other hand, a metal/polymer junction with electrochemically or chemically synthesized polyaniline has been used to make Schottky barrier-type diodes. R. A. Nafdey and other authors [11–14] studied Schottky barrier-type devices of doped PANI with various dopants (HCl, I_2 , FeCl_3 , formic acid, etc.). They estimated various electronic parameters such as the ideality factor, the barrier height, the work function, the Richardson constant, and the saturation current density from current-voltage (I-V) and capacitance-voltage (C-V) measurements that were carried out on metal/polyaniline junctions. However, only a few studies were performed on Schottky diodes using a substituted polyaniline derivative. Indeed, Huang et al. [15] and Carrara et al. [16] have reported I-V characteristics of Schottky diodes using a methoxy-substituted polyaniline

(*o*-anisidine and 2,5-dimethoxyaniline monomers). In this regard, no studies have been performed on metal/POT junctions.

The aim of this work is to fabricate POT thin films by cyclic voltammetry in aqueous electrolyte and Schottky diode based on these POT films. The junction properties of POT/Al devices were studied by following the I-V and C-V characteristics and were compared with those of other polymers such as polypyrrole, polythiophene, PANI, and some of its derivatives.

2. EXPERIMENTAL PROCEDURE

2.1. Electrochemical deposition of POT

POT films were synthesized electrochemically on indium tin oxide (ITO) coated glass electrode under cyclic voltammetric conditions in a simple one-compartment glass cell. Cyclic voltammetric studies were performed with computer-controlled potentiostat/galvanostat (EG&G model 273A).

A three-electrode cell assembly was used during the electrochemical polymerization employing ITO-coated glass substrate as working electrode, a platinum foil as a counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. All the potentials are referred to the SCE. The reference electrode was kept in close proximity of the working electrode ($d = 18$ mm) in order to minimize the electrolytic ohmic drop.

The ITO-coated glass substrates were ultrasound cleaned in acetone and distilled water several times and were air-dried. The *o*-toluidine monomer is distilled before use.

Poly(*o*-toluidine) films were synthesized in an aqueous solution containing 241.9 mL of HCl (2 M) and 8.1 mL of distilled *o*-toluidine (0.3 M). The potentials were scanned between -0.15 and 0.85 V/SCE with a scan rate of 20 mV/s. The 12th cycle is stopped at 0.45 V/SCE in the reverse scan. To initiate the reaction of polymerization, an alternative approach was also applied; namely, before the first cycle, a fixed potential of 0.8 V/SCE is applied during three minutes.

After the electropolymerization, the thin film is washed with the distilled water in order to remove the low-molecular soluble products and is dried in ambient air. The thickness of the obtained POT films is found to be 0.15 μm .

The microstructure of the obtained films was investigated by a scanning electron microscope (JEOL JSM 5500). A scanning electron micrograph of POT thin films is shown in Figure 1. The films were uniform and the examination of their surface morphology did not reveal any presence of pin-holes or porosity.

2.2. UV-visible spectroscopy

The optical transmission (absorption) of the electrodeposited POT films was recorded using Shimadzu-3101 PC double-beam spectrophotometer in the wavelength range of 400–900 nm. The transmission spectrum of the POT/ITO-coated glass sample was normalized with that of the ITO glass.

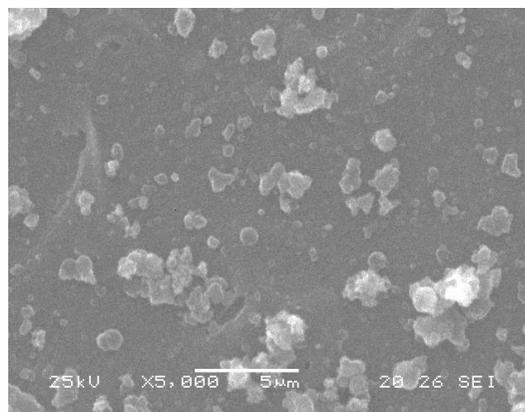


FIGURE 1: SEM micrograph of an electrodeposited POT thin film on ITO-coated glass.

2.3. FT-Raman and FTIR spectroscopies

The FT-Raman spectra were recorded using a Bruker RFS 100 FT-Raman instrument in the spectral range of 300–1800 cm^{-1} . The IR-excitation (1064 nm) line of 100 mW Nd-Yag laser was used.

FTIR measurements of POT film were obtained using an FTIR Bruker VERTEX70 instrument in the attenuated total reflection mode and in the spectral range of 500–2000 cm^{-1} . The resolution of the IR measurements was equal to 4 cm^{-1} .

2.4. Junction fabrication and electrical measurements

Schottky barrier-type devices were fabricated using the POT films deposited on ITO-coated glass substrates which provided the back contact. The front contact was made by 2 mm diameter circular aluminum dots. The aluminum was deposited by thermal evaporation of 99.99% purity aluminum shots for two minutes at base pressure of 1.5×10^{-5} mbar.

The electrical measurements were performed on ITO/POT/Al devices at room temperature. The impedance measurements (capacitance-voltage, capacitance-frequency) were carried out using a Keithley 3330 LCZ impedance meter. The current-voltage characteristics, on other hand, were measured using a Keithley 410 programmable picoammperemeter, a 610 C programmable microvoltmeter. All the instruments are controlled by computer via a GPIB card.

3. RESULTS AND DISCUSSION

3.1. Electrochemical characteristics of poly(*o*-toluidine)

Figure 2 shows the cyclic voltammograms (CVs) recorded during the electrodeposition of POT film on ITO-coated glass electrodes. These cycles clearly reveal the formation of electroactive conducting polymer films.

The regular increase of the current from one cycle to another indicates that the monomer dissolved in the solution is oxidized at the surface of the electrode and the conductivity

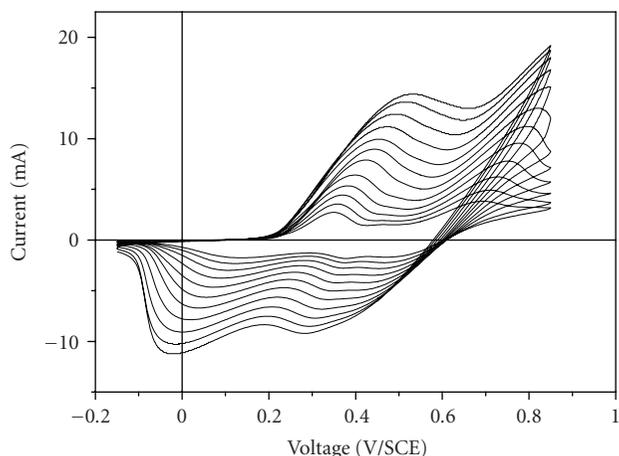


FIGURE 2: Cyclic voltammogram recorded during the synthesis of POT films in an aqueous solution of HCl.

of deposits is sufficient to assure the propagation of the polymerization process.

The cyclic voltammograms of the POT electrode present a first anodic (oxidation) peak at 0.42 V/SCE and a second oxidation peak at 0.79 V/SCE (for the 6th cycle). It should be noted that the oxidation potential of O-toluidine monomer depends on the size and nature of the anion present in the solution [17]. In the reverse scan, as the potential is decreased from 0.85 to -0.15 V versus SCE, the cathodic current is increased indicating that the POT film thickness is reduced. In addition, two reduction couples are present in the CVs at -0.02 and 0.28 V/SCE (for the 6th cycle).

The two peaks observed at 0.42 and 0.79 V/SCE are assigned to the oxidation of POT deposited on the working electrode, and most likely to the conversion of amine units to radical cations [18]. They, respectively, correspond to the formation of radical cations (polaron formation in emeraldine (E) form) from the leucoemeraldine form, and their oxidation to dications (bipolaron formation in pernigraniline form). Figure 3 represents the conversion of the fully reduced leucoemeraldine (LE) form of POT into its fully oxidized pernigraniline (PN) form [19].

While passing from one cycle to the other, the oxidation peaks shift towards higher potentials (from 0.35 to 0.53 V/SCE for the first peak and from 0.69 to 0.85 V/SCE for the second peak). This can be explained by the fact that the oxidation potential of the polymer increases with the length of the polymeric chain.

3.2. Optical properties of the electrodeposited POT films

A typical absorption spectrum of a POT film electrodeposited on IT-coated glass by cyclic voltammetry is presented in Figure 4. It shows two absorption bands centered at 436 nm and 580 nm. The first absorption band is usually attributed to $\pi - \pi^*$ electronic transitions of the benzene rings on the basis of studies performed on polyanilines and the-

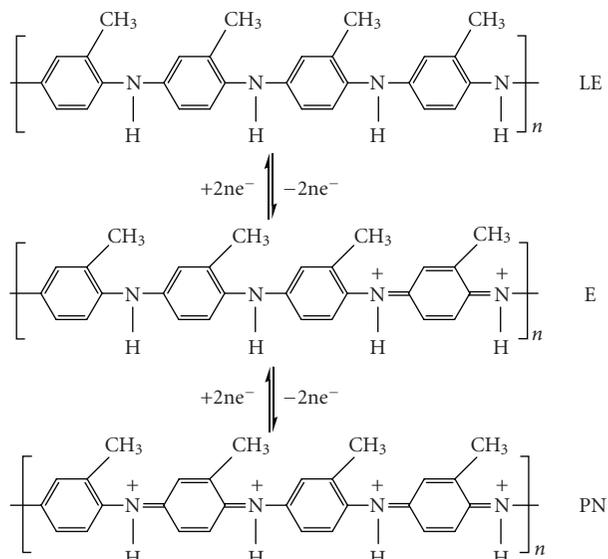


FIGURE 3: Reaction schemes for the electrochemical process of POT film in acidic solutions.

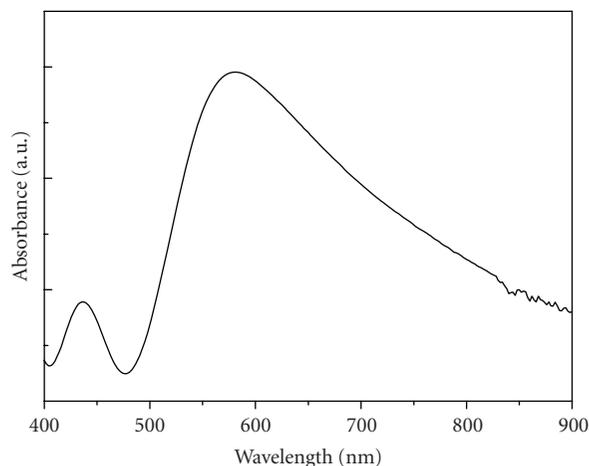


FIGURE 4: UV-Vis absorbance spectrum of an electrodeposited POT film.

oretical band structure calculations [10, 20]. The position of this peak is related to the degree of conjugation between the adjacent phenylene rings in the polymer chain [20]. This peak showed a hypsochromic shift relative to the corresponding transition in PANI, thus revealing a reduction in the conjugation length in POT as a result of the steric effects of the $-\text{CH}_3$ groups. The second absorption band at 580 nm is attributed to excitonic transitions between the HOMO orbital of the benzenoid ring and the LUMO orbital of the quinoid ring. It corresponds to the $n - \pi^*$ transition [20], which is attributed to the formation of pernigraniline base form of POT.

The optical band gap energy (E_g) is obtained using the fundamental law

$$\alpha = A(E_g - hv)^n, \quad (1)$$

TABLE 1: Assignments of FT Raman bands of electrodeposited POT films.

Wave number (cm^{-1})	Raman assignments
449	C-N stretching in SQ and Q rings
515	C-C stretching in SQ and Q rings
575	C-C stretching in B ring
727	C-C stretching in B ring
812	C-C stretching in B ring
1119	C-C in methyl-substituted SQ and Q rings
1157	C-H in SQ ring
1219	C-N in B ring
1260	C-N stretching in SQ and Q rings
1362	C-N stretching (protonation)
1499	C=N vibration in the polymer chain
1610	C=C stretching in B ring

where α is the absorption coefficient, $(h\nu)$ is the photon energy, A is a proportionality constant, and $n = 1/2$ for direct transitions and $n = 2$ for indirect allowed transitions. The value of n for our sample is estimated from the slope of the $\text{Log } \alpha$ versus $\text{log } h\nu$ plot by taking a linear fit. The value of n is approximatively equal to 0.5 suggesting a direct transition. A similar value was used by Huang et al. to calculate the band gap energy for substituted polyaniline [15].

In this case, the optical band gap energy (E_g) can be obtained by plotting $(\alpha h\nu)^2$ versus $(h\nu)$ and extrapolating the linear portion of $(\alpha h\nu)^2$ to zero. In our case, the allowed direct transition optical gap is found to be 2.52 eV for the POT films. This value is lower than that found by Ram et al. [8] for POT films deposited on ITO-coated glass by cyclic voltammetry, dip-coating, and Langmuir-Blodgett techniques. This may be due to differences in the conditions of synthesis such as the nature of the electrolyte, the range of the potential applied, the thickness of the layer, the degree of polymerization of the polymer, and so forth. In comparison with the band gap energy of PANI lying between 4.1 and 4.28 eV [21], this downshift is attributed to the presence of $-\text{CH}_3$ groups in POT and its doping state. In our case, the POT films are neutralized by rinsing them with distilled water.

3.3. FT-Raman and FT-IR spectra of electrodeposited POT films

The FT-Raman spectra of electrodeposited POT films by cyclic voltammetry on ITO-coated glass are presented in Figure 5. The assignments of the Raman bands are grouped in Table 1.

The intense bands in the Raman spectra are situated at 1362 and 1610 cm^{-1} . The first band is a characteristic of the C-N stretching mode. On the basis of the studies performed on PANI [22], this band is a characteristic of the doped form of PANI; it can be due to the doping action of the distilled water and the atmosphere gases on the POT film. The second band at 1610 cm^{-1} is assigned to the C-C stretching mode in the benzenoid (B) rings.

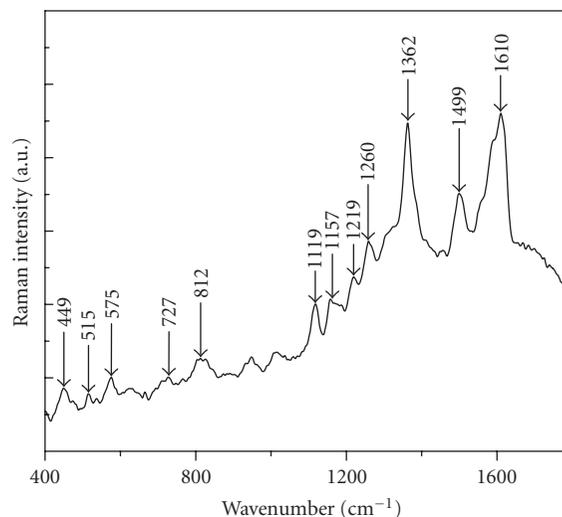


FIGURE 5: FT-Raman spectrum of an electrodeposited POT film (1064 nm excitation).

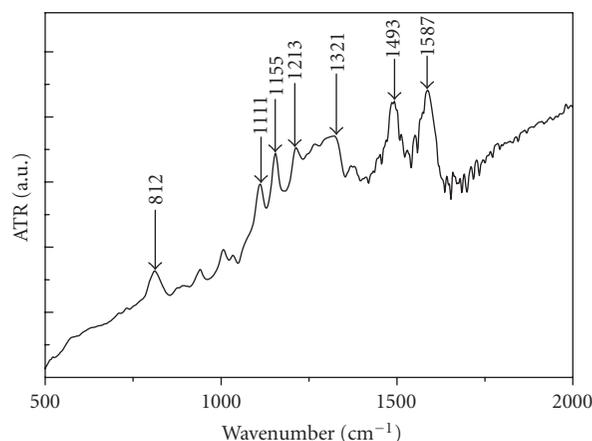


FIGURE 6: FTIR spectrum of an electrodeposited POT film.

Contrary to PANI [23], a new band appeared at 1119 cm^{-1} in the POT spectrum. This band is attributed to the C-C vibration in the methyl-group substituted semiquinoid (SQ) and quinoid (Q) rings.

The presence of the characteristic bands of quinoid (Q) and benzenoid (SQ) rings shows that the electrodeposited POT by cyclic voltammetry is composed of amine and imine units.

The FTIR spectra of the electrodeposited POT film by cyclic voltammetry on ITO-coated glass substrate are presented in Figure 6. This spectrum exhibits the following main spectral features [24–26].

- (i) The broadband at 1587 cm^{-1} can be assigned to the C-C stretching mode combined with C=N stretching vibrations of the quinoid rings.
- (ii) The band at 1493 cm^{-1} is attributed to the C-C stretching modes in the benzenoid units.

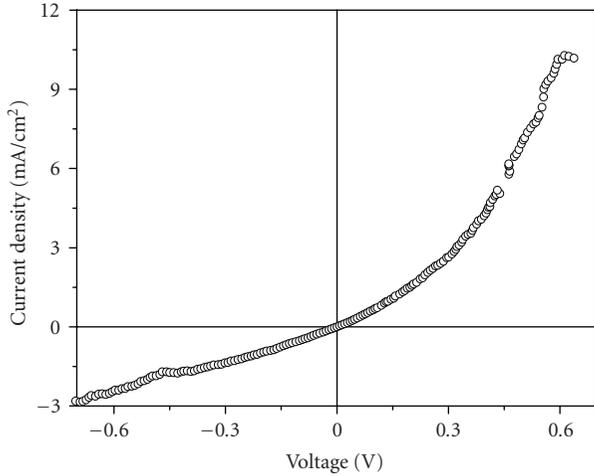


FIGURE 7: Current-voltage characteristic of ITO/POT/Al devices.

- (iii) The bands at 1321 cm^{-1} and 1213 cm^{-1} are assigned to the C-N stretching vibrations in the polymer chain.
- (iv) The band at 1155 cm^{-1} is related to the C=N stretching mode; this band is a characteristic of doped POT. It can be due to the doping of the POT films by the ambient gases.
- (v) The band at 1111 cm^{-1} can be attributed to charge delocalization on the polymer backbone.
- (vi) The band located at 812 cm^{-1} represents the paradisubstituted benzenoid rings in POT film.

In addition, the presence of quinoid and benzenoid bands (1587 and 1493 cm^{-1}) shows that the electrodeposited POT by cyclic voltammetry is composed of imine and amine units. Therefore, the FTIR spectroscopy results are in good agreement with the FT-Raman spectroscopy results.

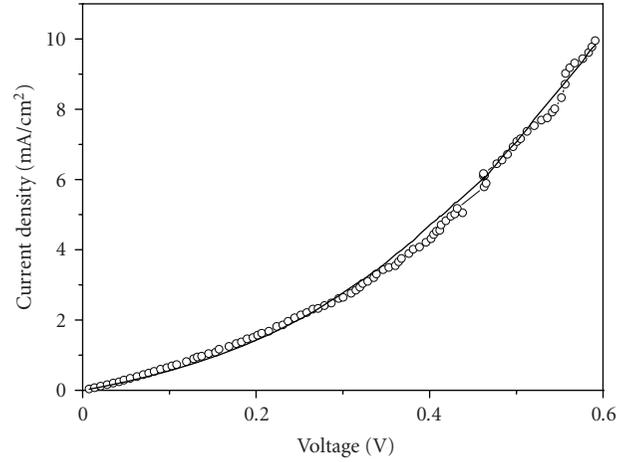
3.4. Electrical properties of ITO/POT/Al device

3.4.1. Current-voltage characteristics

Figure 7 shows a typical J-V characteristic of an ITO/POT/Al device at room temperature. The rectification ratio of these devices is about 4.12 at $\pm 0.6 \text{ V}$. This value is higher than that obtained for poly(o-methoxyaniline) electropolymerized on ITO-coated glass [15].

With polyaniline being well known as an intrinsic p-type semiconductor, the work function of this polymer is usually reported to lie between 4.1 and 4.28 eV [27, 28]. Contacts of PANI with lower work function materials such as aluminum ($\varphi_{\text{Al}} = 3.7$ to 4 eV), as in our case, are therefore expected to be rectifying contact. Metals with work functions higher than those of PANI, such as gold ($\varphi_{\text{Au}} = 5.1 \text{ eV}$) and ITO ($\varphi_{\text{ITO}} = 4.7 \text{ eV}$), are expected to be ohmic contacts.

The current transport across the polymer/metal junction is usually accounted for on the basis of thermionic emission, space charge-limited current (SCLC), or Poole-Frenkel emission [28–31]. The last two mechanisms are found not to be applicable to our diodes in the exploited voltage range, as revealed by fitting their respective laws to experimental data.

FIGURE 8: Experimental I-V characteristic of ITO/POT/Al devices (\circ) and fits (line) using (4) in the forward bias region.

For the thermionic emission model, the J-V relationship is expressed by

$$J = J_0 \left[\exp \left(\frac{qV}{\eta kT} \right) - 1 \right]. \quad (2)$$

J_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, and T is the absolute temperature.

The saturation current density is given by

$$J_0 = SA^* T^2 \exp \left(- \frac{q\Phi_B}{kT} \right), \quad (3)$$

where S is the surface area of the diode (top Al contact), A^* is the Richardson constant which depends on the effective mass of the carriers ($120 \text{ A cm}^{-2} \text{ K}^{-2}$ for free carriers), and Φ_B is the barrier height.

A better model, taking into account the series resistance (R_s) of the structure, was used. This model is described by the following modified Shockley equation:

$$J = J_0 \left[\exp \left(\frac{q(V - R_s J)}{\eta kT} \right) - 1 \right]. \quad (4)$$

As shown in Figure 8, this model accounts well for the experimental data over the explored voltage range in the forward bias region. The fit (4) yielded the following diode parameters: $\eta = 7.3$, saturation current density $J_0 = 8.9 \cdot 10^{-4} \text{ (A/cm}^2\text{)}$, and $R_s = 380 \Omega$.

The value of the ideality factor of ITO/POT/Al Schottky devices is higher than unity, but lower than that found for the polypyrrole/metal and polyhexylthiophene/metal Schottky diodes [30, 31]. The deviation of ideality factor from ideal value may be due to the following effects [13, 32, 33]:

- (i) recombination of electrons and holes in the depletion region,
- (ii) presence of barrier inhomogeneities as well as the reactive nature of Al contact,

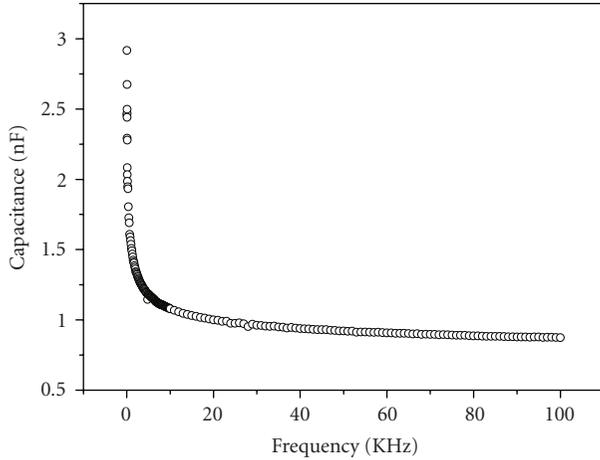


FIGURE 9: Capacitance-frequency characteristic of ITO/POT/Al structure.

(iii) possibility of presence of other conduction mechanisms such as bulk-limited currents in various voltage ranges and trap-assisted tunneling [6].

The barrier height Φ_B obtained from J_0 (see (3)) is equal to 0.59 eV. This value is in good agreement with those reported for a metal/polymer interface [31, 34, 35].

3.4.2. C-V and C-F characteristics

Figure 9 displays the frequency dependence of the zero-bias capacitance in the frequency range of 40–100 KHz. The capacitance decreased by a factor of two when the frequency was increased to 10 kHz. This dispersion in capacitance can be explained on the basis of a distribution of localized states in the band gaps of the amorphous polymer [36]. The influence of the barrier inhomogeneities and series resistance of the diode is not ruled out as in the case of poly(3-methylthiophene)-based diodes [37, 38].

Figure 10 shows the voltage dependence of the capacitance at 1 kHz for applied voltages between -0.5 V and $+0.5$ V. As expected, the capacitance increased slightly when the voltage was scanned from the reverse bias region to the forward bias region. This behavior further confirms the rectifying nature of the POT/Al contact. The plot (C^{-2}) versus (V) is not linear, which further suggests a distribution of deep states in the forbidden band.

4. CONCLUSION

We have successfully deposited poly(o-toluidine) thin films on ITO-coated glass substrates by cyclic voltammetry. Al/POT/ITO devices were also fabricated. The optical band gap of the obtained POT films is found to be 2.52 eV; it is lower than that of films deposited by dip-coating and Langmuir-Blodgett techniques. The FTIR and FT-Raman spectroscopies results are in good agreement with those of the UV-Vis spectroscopy. On the other hand, the Al/POT/ITO devices showed a rectifying behavior. The I-V

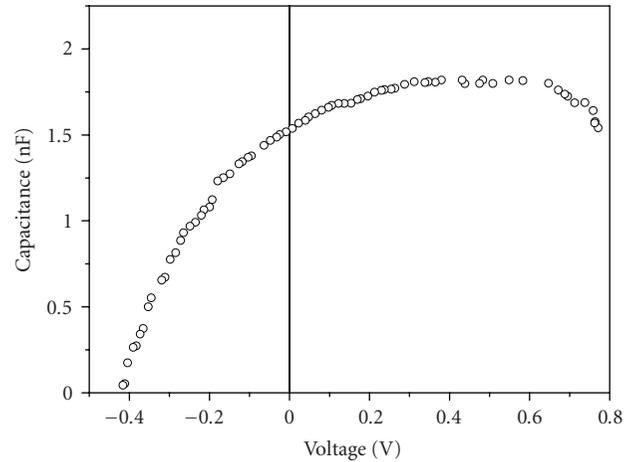


FIGURE 10: Capacitance-voltage characteristic of ITO/POT/Al structure.

characteristics of these devices are fitted with the modified Shockley diode equation. The large value of ideality factor suggests the presence of other transport mechanisms (bulk-limited current and/or trap assisted tunneling). This is further supported by both C-V and C-F measurements which suggest a distribution of localized states in the band gap of the polymer.

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