

# Direct Current Electrical Characterization of Plasma Polymerized Pyrrole-*N,N,3,5* Tetramethylaniline Bilayer Thin Films

M. M. Kamal,<sup>1</sup> A. H. Bhuiyan<sup>2</sup>

<sup>1</sup>*School of Engineering and Computer Science, Independent University, Bangladesh IUB), Baridhara, Dhaka 1212, Bangladesh*

<sup>2</sup>*Department of Physics, Bangladesh University of Engineering and Technology (BUET), Ramna, Dhaka 1000, Bangladesh*

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**ABSTRACT:** The direct current conduction mechanism in plasma polymerized pyrrole-*N,N,3,5* tetramethylaniline (PPPy-PPTMA) bilayer thin films has been discussed in this article. A parallel plate capacitively coupled glow discharge reactor was used to deposit PPPy, PPTMA, and PPPy-PPTMA thin films at room temperature onto glass substrates. The Fourier Transform Infrared analyses showed that the PPPy-PPTMA bilayer thin films contained the structural characteristics of both the PPPy and PPTMA. The current density-voltage characteristics of PPPy-PPTMA bilayer thin films of different deposition time-ratios indicated an increase in electrical conductivity as the proportion of PPTMA was increased in the bilayer films. It is also observed that the conductivity of the bilayer thin film is reduced compared with its component thin films. It is seen that in the low voltage region the current conduction obeys Ohm's law, while the charge transport phenomenon

appears to be the space charge limited conduction in the higher voltage region. The mobility of the charges, the free charge carrier density, and the permittivity of the PPPy, PPTMA and PPPy-PPTMA bilayer thin films have been calculated. The permittivity for PPPy, PPTMA and PPPy-PPTMA bilayer thin films were found to be  $1.07 \times 10^{-10}$ ,  $2.2 \times 10^{-11}$ , and  $1.26 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ , respectively; the free charge carrier density were  $(3.56 \pm 0.01) \times 10^{22}$ ,  $2 \times 10^{21}$  and  $(5.19 \pm 0.02) \times 10^{22} \text{ m}^{-3}$  respectively; and the mobility of the charges were found to be  $(4.4 \pm 0.01) \times 10^{-19}$ ,  $1.3 \times 10^{-13}$  and  $(2.1 \pm 0.01) \times 10^{-19} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$  respectively. PACS: 72.80.Le, 73.21.Ac, 73.40.Rw, 73.50.Gr, 73.61.Ph. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1033–1040, 2012

**Key words:** plasma polymerization; PPPy-PPTMA bilayer thin film; FTIR analysis; DC conduction; J-V characteristics; SCLC

## INTRODUCTION

Different types of conduction mechanism have been described for thin organic dielectric films. The complex conduction behavior in organic solids could be explained usually in terms of electron emission from cathode, i.e., Schottky-Richardson mechanism; or by electron liberation from the traps in the bulk of the material, i.e., Poole-Frenkel (PF) mechanism. The possibilities of tunneling or Fowler-Nordheim mechanism for very thin films and space charge limited conduction (SCLC) etc. have also been investigated in the literature.<sup>1</sup>

Many reports on the investigation of direct current (DC) electrical properties of plasma polymerized thin films have been appeared in the literature.

Akther and Bhuiyan<sup>2,3</sup> studied the current density-voltage (J-V) characteristics of plasma polymerized *N,N,3,5*-tetramethylaniline (PPTMA) thin films of different thicknesses at different temperatures with aluminum (Al) electrodes and reported that the films showed Ohmic behavior at the lower voltage region and SCLC dominated by exponential trap distribution at the higher voltage region. Kumar et al.<sup>4</sup> studied the optical and electrical properties of plasma polymerized polypyrrole (PPPy) and iodine-doped PPPy. They concluded that the conductivity of PPPy film was dependent upon the number of extrinsic carriers and the conduction mechanism in the undoped PPPy film was found to be a Schottky-type mechanism. Valaski et al.<sup>5,6</sup> investigated the influence of electrode material and film thickness on charge transport properties of electrodeposited polypyrrole (PPy) thin films. They observed that the selection of metals with high work function as the electrode resulted an increase in the mobility and the positive free carrier concentration and consequently in its electrical conductivity.<sup>5</sup> From the study on the influence of the film thickness on the

Correspondence to: M. M. Kamal (mkamal@secs.iub.edu.bd or amkamalbd@gmail.com).

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conductivity,<sup>6</sup> they concluded that when thickness of the PPy thin film was increased ( $d > 300$  nm) the charge transport was observed to be SCLC, but for the films of lower thickness ( $d \leq 300$  nm), the charge transport was limited by thermoionic emission. The charge mobility was also found to be increased for the lower thickness of PPy thin films. John et al.<sup>7</sup> reported from the electrical conductivity studies of PPPy thin films with Al-polymer-Al structure that the mechanism for carrier transport in PPPy was SCLC. Shukla and Gaur<sup>8</sup> investigated the electrical conduction in solution-grown polymethylmethacrylate (PMMA), polyvinylidene fluoride (PVDF) and PMMA-PVDF double-layered samples in the metal-polymer-metal sandwich configuration at different electric fields and temperatures with a thickness of about 50  $\mu\text{m}$ . From the current-voltage ( $I$ - $V$ ) characteristics they observed that the electrical conduction followed PF mechanism in PMMA and PVDF films, whereas, the nonlinear behavior of  $I$ - $V$  characteristics of PMMA-PVDF double-layered films was interpreted on the basis of SCLC mechanism. It was also reported that the conductivity of the polymer films was increased on the formation of their double-layer laminates. Morales et al.<sup>9</sup> studied the electronic conductivity of bilayer aniline-pyrrole thin films and observed that the plasma technique was capable of forming chemically bonded layered polymers with several possible combinations. They also found that, the bilayer aniline-pyrrole films had greater electrical conductivity at room temperature than that shown by the separate homopolymers.

The thin films produced by plasma polymerization are generally pinhole-free, homogeneous, and crosslinked and therefore are insoluble, thermally stable, chemically inert and mechanically tough. Furthermore such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass, and metal surfaces.<sup>10,11</sup> Because of these excellent properties they have been undertaken very actively in the last few decades for a variety of applications such as protective coatings, membranes, biomedical materials, electronic and optical devices, adhesion promoters, anticorrosive surfaces, humidity sensors, electrical resistors, scratch resistant coatings, optical filters, chemical barrier coatings, etc. The generation of multilayer/composite thin films also has a wide variety of applications, e.g., in biocompatible materials, in the modification of surfaces, in protective coverings of metals, in the design of complex materials, etc.<sup>9</sup> Because of their versatile applications, although the multi-layer thin films have drawn much attention to study their different properties, reports on the electrical properties on organic bilayer thin films are less abundant in the literature. In this context, a systematic study on the electrical properties of PPPy-

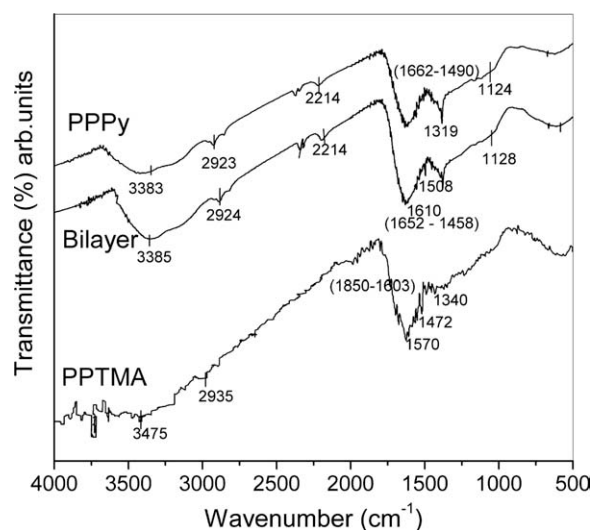
PPTMA bilayer thin films of different compositions prepared in different deposition time-ratios was undertaken. It is to be noted that derivatives of aniline and pyrrole are well known organic materials. Different properties of plasma polymerized thin films of these organic materials have been reported by many investigators.<sup>2,7</sup> These two materials are chosen to prepare and to characterize the bilayer thin film because it is usually observed that the bilayer and composite thin films give rise to different properties than the thin films prepared from their component monomers.

This article describes the preparation of PPPy-PPTMA bilayer thin films and discusses the chemical structure investigated by Fourier Transform Infrared (FTIR) spectroscopy and DC electrical properties of the thin films. The  $J$ - $V$  characteristics of bilayer thin films of different thicknesses at different temperatures with Al electrodes were investigated to study the conduction mechanism in the bilayer thin films. The change in the conductivity for the different compositions of the bilayer structure was also studied. The results that were obtained for PPPy-PPTMA bilayer thin films were compared to those of the PPPy and PPTMA thin films.

## EXPERIMENTAL DETAILS

The PPPy-PPTMA bilayer thin films were deposited on to chemically cleaned glass substrates at room temperature by using a capacitively coupled glow discharge plasma reactor. To deposit the bilayer films, pyrrole-monomer was used as the mother-material and *N,N,3,5* tetramethylaniline (TMA) monomer was deposited in different deposition time-ratios after the pyrrole thin films were formed. The total deposition time was kept 60 min for all the samples, but the deposition time-ratios of PPPy : PPTMA for the bilayer thin films were (50 min : 10 min), (45 min : 15 min), (40 min : 20 min), (35 min : 25 min) and (30 min : 30 min). The PPPy and PPTMA thin films of different thicknesses were also deposited by keeping the deposition parameters (flow-rate, power, vacuum order, etc.) almost same for all samples so that the comparison of the results can be made for various plasma polymerized samples.

The monomers pyrrole and TMA were collected from Aldrich-Chemie D-7924, Steinheim, Germany. The monomers' vapor was introduced in to the glow discharge reactor through a flow-meter (Glass Precision Engineering, Meterate, England, UK) at the flow rate of about 20  $\text{cm}^3$  (STP)/min. The glow discharge system consists of two parallel plate electrodes of stainless steel of diameter and thickness 0.09 and 0.001 m, respectively, placed 0.035 m apart. The glow discharge chamber was evacuated



**Figure 1** The FTIR spectra of PPPy, PPTMA, and PPPy-PPTMA bilayer samples.

by a rotary pump (Vacuubrand GMBH and Co, 97877 Wertheim, Germany) and plasma was generated around the substrates, which were kept on the lower electrode, with a power of about 30 W. The PPPy, PPTMA and PPPy-PPTMA bilayer thin films of different thicknesses were deposited onto the glass substrates. The thicknesses of deposited thin films were measured by a multiple-beam interferometric technique.

For the FTIR studies, the as-grown PPPy, PPTMA and PPPy-PPTMA bilayer thin film were scraped off from the glass substrates in powder form and were mixed with potassium bromide (KBr). This mixture was then pelletized. These pellets of the mixture were used to record the FTIR spectra at room temperature using an FTIR spectrometer (Shimadzu -IR 470, Shimadzu Corp., Tokyo, Japan). All the spectra were recorded in transmittance (%) mode in the wavenumber region 4000–500  $\text{cm}^{-1}$ .

For electrical measurements, the lower and upper Al electrodes were deposited onto the glass substrate and sample respectively, i.e., after the lower Al electrode deposited on the substrate, the bilayer thin film was formed and then the upper Al electrode was deposited on the film in a similar manner by using an Edward vacuum coating unit E-306A (Edward, UK) at a pressure of about  $1.33 \times 10^{-3}$  Pa with an effective Al electrode area of about  $10^{-4}$   $\text{m}^2$ .

The  $J$ - $V$  characteristics of thin films of different thicknesses were studied in Al/PPPy-PPTMA/Al sandwich configuration in the voltage range of 1.0–30.0 V and in the temperatures of 298, 323, 348, and 373 K. The samples Al/PPPy/Al and Al/PPTMA/Al were also used to perform their  $J$ - $V$  characteristics. The current across the thin films was measured by a high impedance Keithley 614 electrometer (Keithley Instruments, Inc., USA) and the DC voltage was applied by an Agilent 6545A stabilized DC power supply (Agilent Technologies Japan Ltd, Tokyo, Japan). The measurements were carried out under dynamic vacuum of about 1.33 Pa and the temperature was measured by a chromel-alumel thermocouple connected to a digital microvoltmeter 197A (Keithley Instruments, Inc., USA). The capacitance of the samples was measured by a low frequency impedance analyzer (Agilent 4192 LF Impedance Analyzer; Agilent Technologies Japan Ltd, Tokyo, Japan).

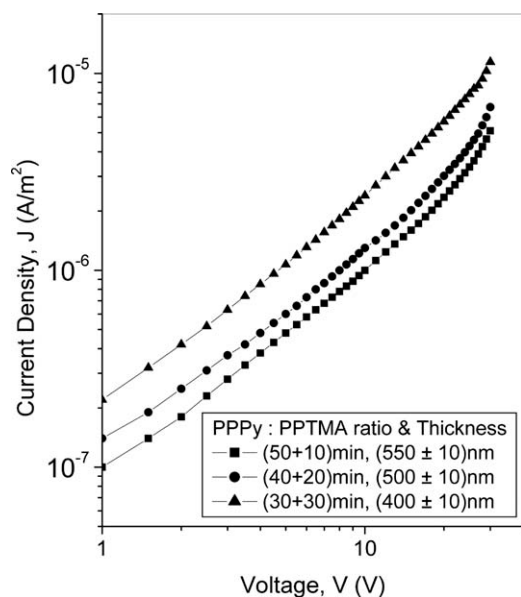
## RESULTS AND DISCUSSION

### Fourier Transform Infrared spectroscopic analyses

The FTIR spectra of PPPy, PPTMA and PPPy-PPTMA bilayer samples are presented in Figure 1 and the peak assignments for the samples are listed in the Table I. From the comparison of the FTIR spectra of PPPy and PPPy-PPTMA bilayer thin films, it is seen that both the spectra exhibit a broad band

**TABLE I**  
Assignments of IR Absorption Peaks for PPPy, PPTMA, and PPPy-PPTMA Bilayer Samples

Vibrations	Wavenumber ( $\text{cm}^{-1}$ )		
	PPPy	PPTMA	PPPy-PPTMA bilayer
N–H stretching vibration of primary and secondary amines	3383	3435	3385
Asymmetric and symmetric C–H stretching vibration of saturated hydrocarbon	2923	2935	2924
–N=C=O	2214	–	2214
C=O	–	1850–1603	–
C=C conjugated and C=N conjugated stretch and N–H deformation vibration	1662–1490	–	1652–1458
C=C stretching vib. in benzenoid and quinoid	–	1570, 1472	1610, 1508
C–N stretching vibration	1124	1340	1128



**Figure 2** J-V characteristics for PPPy-PPTMA bilayer thin films of different deposition timeratios and different thicknesses at room temperature.

between  $3300\text{ cm}^{-1}$  and  $3400\text{ cm}^{-1}$ , which is due to the N—H stretching vibration of primary and secondary amines and imines.<sup>12</sup> In the bilayer film the relative intensity of this peak is higher than that in the PPPy film. The bilayer film has a relatively more intense peak at  $2924\text{ cm}^{-1}$  compared with  $2923\text{ cm}^{-1}$  of PPPy film and  $2935\text{ cm}^{-1}$  of PPTMA films, which is due to the symmetric and asymmetric C—H stretching vibration of saturated hydrocarbons.<sup>2</sup> The absorption peak at  $2214\text{ cm}^{-1}$  in both PPPy and PPPy-PPTMA films suggests the introduction of —N=C=O group<sup>13,14</sup> which is very typical in plasma polymerization.<sup>1</sup> The absorption at  $1508$  and  $1610\text{ cm}^{-1}$  of bilayer films can be assigned to the benzoid and quinoid structures of the benzene rings in TMA. As expected, they are found due to the presence of TMA, because pyrrole does not contain any benzene rings. This study, however, shows that the bilayer thin films contain the characteristics of both the monomers.

### Current density—Voltage characteristics

The J-V characteristics of PPPy-PPTMA bilayer thin films were recorded at room temperature in the voltage region 1.0–30 V and are presented in Figure 2. The bilayer thin films were formed in different deposition time-ratios of PPPy and PPTMA as (50 min : 10 min), (40 min : 20 min) and (30 min : 30 min) with corresponding thicknesses 550, 500, and 400 nm, respectively. From the Figure 2, it is observed that the current conduction in the bilayer thin films is increased with the increase of PPTMA in the bilayer structures. This result could also be explained by considering the thicknesses of the

films. In many investigations<sup>2,3,6</sup> it is already reported that the conduction in the plasma polymerized thin films is thickness dependent and current density is found to be higher for same applied voltage in the films of lower thicknesses. From the study of deposition nature, however, it is observed that the thicknesses of the bilayer thin films were reduced as the proportion of PPTMA was increased in the bilayer structure. This is because, the deposition rate of TMA is lower than that of the pyrrole, i.e., if the deposition parameters are remained same then PPTMA thin films are found to be thinner than PPPy thin films. Since the increase in PPTMA in the bilayer thin films causes a decrease in the thickness, therefore increase in the current conduction in bilayer thin films with the increase of PPTMA is not unexpected. Moreover, it would also be seen that the conductivity of PPTMA is higher than that of the PPPy, and therefore the increase of the conductivity of bilayer thin films with the increase of PPTMA is also not ambiguous. The conductivity calculation is found to be consistent with this observation. The conductivity of different bilayer thin films of different deposition time-ratios were calculated from Figure 2 at lower voltage region by using the eq. (1) and is presented in Table II. It is clearly seen from Table II that as the deposition time-ratio of PPTMA is increased, the conductivity of the PPPy-PPTMA bilayer thin films is increased.

The curves of Figure 2, however, follow a power law of the form  $J \propto V^n$ , where  $n$  is a power index, with two different slopes in the lower and higher voltage regions. At low voltages the J-V characteristics of thin polymer films may follow Ohm's law, provided the transport is not limited by the polymer/electrode interface, so that

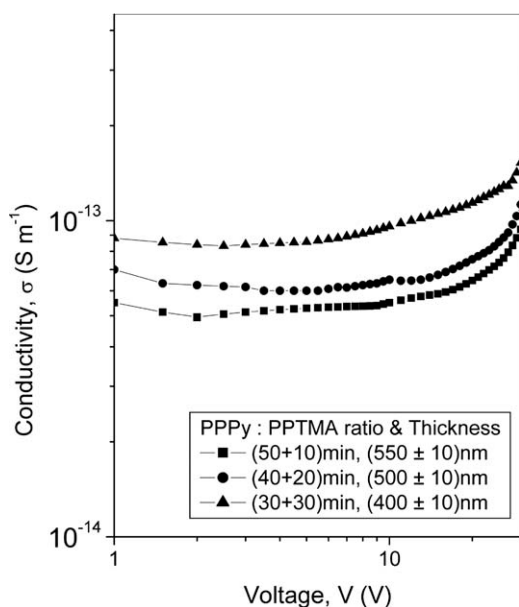
$$J = qp\mu \frac{V}{d} = \sigma \frac{V}{d} \quad (1)$$

where  $q$  is the elementary electric charge,  $p$  is the free charge carrier density (in this case, assumed to be positive),  $\mu$  is the charge carrier mobility,  $d$  is the film thickness,  $V$  is the applied voltage, and  $\sigma$  is the electrical conductivity.<sup>15</sup>

If the applied voltage is increased over a certain value, the injected charge carrier density largely

**TABLE II**  
DC Electrical Conductivity of PPPy-PPTMA Bilayer Films for Different Compositions

PPPy-PPTMA deposition time ratio (min)	Film thickness (nm)	Conductivity, $\sigma$ ( $\text{S m}^{-1}$ )
50 : 10	550	$(5.3 \pm 0.05) \times 10^{-14}$
40 : 20	500	$(6.1 \pm 0.05) \times 10^{-14}$
30 : 30	400	$(8.5 \pm 0.05) \times 10^{-14}$



**Figure 3** Plots of DC electrical conductivity vs. voltage for different deposition time-ratios and different thicknesses for PPPy-PPTMA bilayer thin films.

exceeds the free charge density under thermal equilibrium and the system transits to either Schottky or PF or SCLC conditions. For SCLC, the current density can be described by,<sup>16</sup>

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{d^3} \quad (2)$$

where,  $\varepsilon$  is the permittivity of the material.

From eqs. (1) and (2) the free charge carriers' density  $p$  can be calculated at the transition voltage from the Ohmic to the SCLC regime as follows,<sup>15</sup>

$$p = \frac{9}{8} \varepsilon \frac{V_{\Omega}}{qd^2} \quad (3)$$

where  $V_{\Omega}$  is the transition or threshold voltage from the Ohmic regime to the SCLC regime.

In the Figure 2, the value of slopes at the lower voltage region (1 ~ 6 V) is found to be  $0.85 < n < 1.10$ , indicating a probable Ohmic conduction, while at the higher voltages (15 ~ 25 V) the slopes  $1.65 < n < 2.45$  represent the non-Ohmic conduction.

The DC electrical conductivity of PPPy-PPTMA bilayer thin films for different thicknesses 550, 500, and 400 nm have been calculated at different voltages from Figure 2 by using eq. (1) and are plotted in Figure 3.

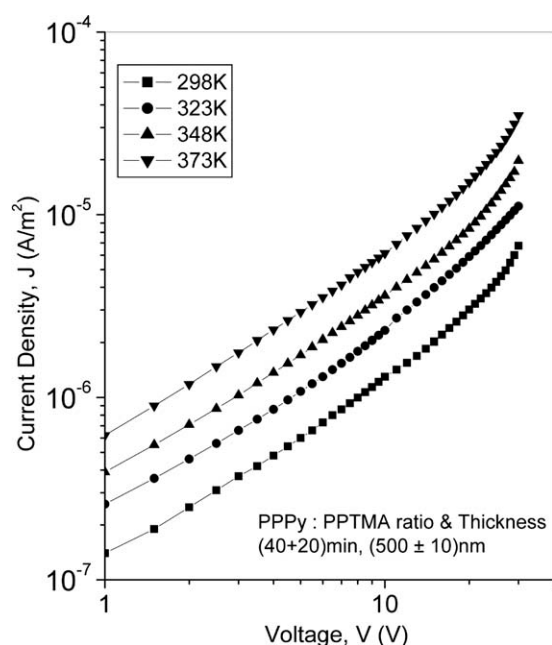
It is observed from the Figure 3 that the electrical conductivity of the bilayer thin films is changed as the deposition time-ratio is changed, though, as expected, for any particular time proportion the conductivity of the thin film remains same. Since the

electrical conductivity is a physical property of a material which should remain constant for any circumstances, therefore, the change in the conductivity for different deposition time-ratios suggests a probable change in physical properties during the formation of the bilayer thin films.

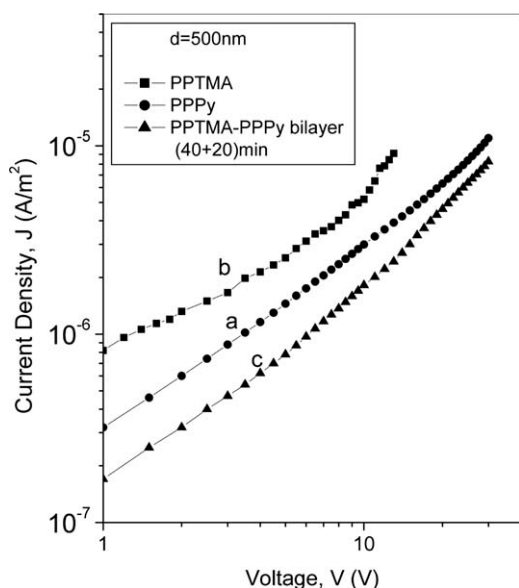
Figure 4 represents the  $J$ - $V$  curves of a PPPy-PPTMA bilayer thin films of deposition time-ratio (40 min : 20 min) for PPPy and PPTMA (thickness,  $d = 500$  nm) at different temperatures of 298, 323, 348, and 373 K. It is observed that the current conduction in the thin films in both the voltage regions is increased slightly with increasing temperature, which may be an indication of temperature dependent conductivity of bilayer thin films. This increase may be due to the increased molecular motion at the higher temperatures.<sup>2</sup>

For a comparative study of the electrical conductivity of PPPy-PPTMA bilayer thin films with those of the PPPy and PPTMA thin films, the  $J$ - $V$  characteristics of these three types of films of nearly equal thickness (about 500 nm) were recorded at room temperature and are presented in Figure 5. It is observed that the current conduction in the PPTMA is higher than that in the PPPy films thin and the conduction in the PPPy-PPTMA thin films is lower than that in its component thin films. The conductivities of different films were calculated at the lower voltage region by using the eq. (1) and are presented in Table III.

From the Table III, it can be noted that the electrical conductivity of the bilayer thin films is less compared with those of the components, which can be



**Figure 4**  $J$ - $V$  characteristics for PPPy-PPTMA bilayer thin films at different temperatures ( $d = 500$  nm).



**Figure 5** J-V characteristics for (a) PPPy (b) PPTMA, and (c) PPPy-PPTMA bilayer thin films at room temperatures ( $d = 500$  nm).

confirmed by estimating the optical band gap of each of the thin films. It is observed that both the direct and indirect energy band gaps are higher for PPPy-PPTMA bilayer thin films than those for PPPy and PPTMA, which has been discussed in a separate communication.<sup>17</sup>

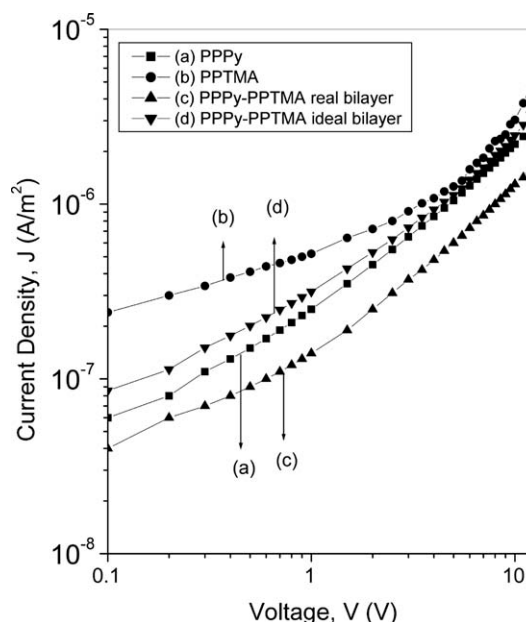
The fact that the physical properties of the PPPy-PPTMA bilayer thin films have been changed due to the formation of the bilayer thin films could be confirmed by considering an ideal situation. In any ideal bilayer of two materials without interface effect, the physical properties of the bilayer usually lie in between those of the constituents, but in the present case, the PPPy-PPTMA bilayer thin films show a different behavior. The current density,  $J'$ , for an ideal PPPy-PPTMA bilayer thin films can be calculated from the current densities of PPPy and PPTMA thin films at a fixed applied voltage by using the following equation,

$$J' = \frac{J_1 J_2}{m_1 J_2 + m_2 J_1} \quad (4)$$

where  $J_i$  and  $m_i$  are the current densities and the fraction of the thicknesses of the components,

**TABLE III**  
Comparison of DC Electrical Conductivity for PPPy, PPTMA, and PPPy-PPTMA Bilayer Films of Nearly Same Thickness (About 500 nm)

Samples	Conductivity, $\sigma$ ( $S\ m^{-1}$ )
PPPy	$(1.1 \pm 0.02) \times 10^{-13}$
PPTMA	$(2.6 \pm 0.02) \times 10^{-13}$
PPPy-PPTMA bilayer thin film	$(0.6 \pm 0.05) \times 10^{-13}$



**Figure 6** J-V characteristics for (a) PPPy (b) PPTMA (c) PPPy-PPTMA real bilayer, and (d) PPPy-PPTMA ideal bilayer thin films.

respectively. It should be noted that the relationship between the thickness of the component has been evaluated from Figure 5 with an approximation of  $m_1 : m_2 = \text{PPPy} : \text{PPTMA} = 0.6 : 0.4$ , with  $m = 1$  as the bilayer thin film thickness, since the bilayer thin film of Figure 5 was prepared by depositing the PPPy and PPTMA thin films with a deposition time ratio (40 min : 20 min). The theoretically calculated values of  $J'$  for the ideal bilayer thin film has been plotted in J-V characteristic curves of Figure 6 to compare with those of the real PPPy-PPTMA bilayer thin films and also with those of the component films.

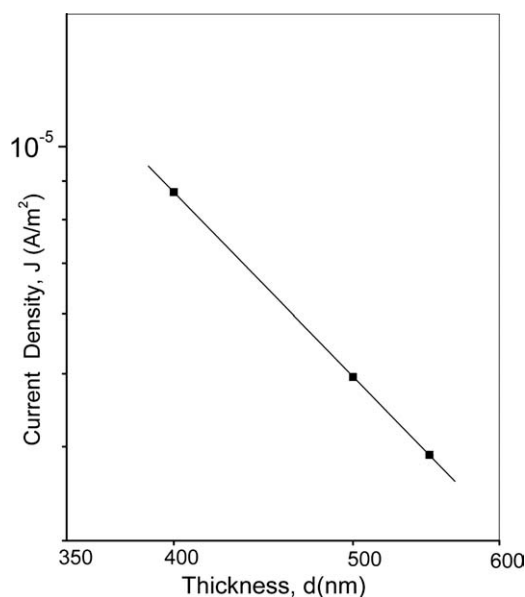
It is observed in Figure 6 that the theoretically calculated values of  $J'$  lie in between the values of  $J$  of two individual components, but the experimental values of  $J$  is found to be reduced than those of its components. This experimental result thus shows a clear departure from the ideal nature as seen from the calculated values of  $J'$  using eq. (4). Since both PPPy and PPTMA layers in the bilayer thin film have the same chemical nature as those of the component thin films, therefore the result that the theoretical values of the  $J'$  of the PPPy-PPTMA ideal bilayer film lie in between those of the components, is not unusual. But when the current density is calculated from the data of the components, the interaction in the interface of the two component thin films is not considered, though this interface might affect the physical properties of the bilayer structure. This type of anomalous effect could give misleading results if they are not recognized or avoided.<sup>18</sup> Therefore, to analyze the electrical behavior of

plasma polymerized bilayer thin films, the effect of the interface should be taken into consideration.

It is known that the incorporation of oxygen in the polymers, even though the monomers do not contain oxygen, is a typical trend of plasma polymer. This incorporation of oxygen in plasma polymer as a contamination may be due to the reaction of trapped free radicals with oxygen from the plasma reactor as well as from the overall environment of the film-formation process. The FTIR analyses of PPPy, PPTMA and PPPy-PPTMA thin films in this study have also indicated the presence of oxygen by the appearance of the absorption bands at 1850-1603 and 2214  $\text{cm}^{-1}$ . Therefore, during the subsequent formation of the thin films by plasma polymerization, there may be adsorbed and/or trapped oxygen in the interface between the PPPy and PPTMA thin film layers. The oxidation in the interface of the bilayer might affect the physical properties of the bilayer thin films. The increase of optical band gap<sup>17</sup> and the decrease of the electrical conductivity of the bilayer thin films may be due to this reason. Furthermore, in the present system, the individual thin films were deposited one over the other to prepare the PPPy-PPTMA bilayer thin films, which may give rise to a system with polymer-polymer complex interface, i.e., the interface between the PPPy and PPTMA thin films may not be homogeneous and therefore there are some possibilities of presence of irregularities in the interface. It should be noted that in most inhomogeneous polymeric systems, the electronic conductivity is affected by the interface. The electrical conductivity depends upon the movement of adventitious ions generated either by impurities centers or induced impurities.<sup>19</sup> The crosslinking in the interfaces should be also taken into consideration in this system, which may cause less electrical conduction.

The thickness and voltage dependence of current density at the higher voltage region suggests that the current may be due to SCLC, Schottky or PF conduction mechanisms in PPPy-PPTMA thin films. If the applied voltage is increased over a certain value, the injected charge carrier density largely exceeds the free charge density under thermal equilibrium and the system transits to SCLC conditions. In this case, the  $J$  can be described by the eq. (2). This relation indicates that  $J$  is inversely proportional to  $d^3$ . The thickness dependence of current follows the relation  $J \propto d^{-l}$ , where  $l$  is a parameter depending upon the trap distribution. A slope  $l < 3$  suggests the possibility of Schottky or PF conduction mechanism and that  $l \geq 3$  reveals the possibility of SCLC.

To study the actual conduction mechanism,  $J$  is plotted against  $d$  of different bilayer thin films at a voltage of 27 V, which is presented in Figure 7. The linear slope derived from Figure 7 gives a negative



**Figure 7** Plots of  $J$ - $d$  for PPPy-PPTMA bilayer thin films in the non-Ohmic region.

value of 3.3, which is much higher than that corresponding to Schottky or PF conduction mechanism. Therefore, the conduction mechanism in PPPy-PPTMA bilayer thin films is suggested to be SCLC.

The free charge carrier density,  $p$ , can be calculated from the eq. (3). The transition or threshold voltage from the Ohmic regime to the SCLC regime has been found to be about 15 V from Figure 2, which can be used to calculate  $p$ . But, to calculate  $p$ , the polymer permittivity  $\epsilon$  needs to be calculated. The permittivity constant of the thin films can be found from the relation  $\epsilon = \epsilon' \epsilon_0$ , where  $\epsilon'$  is the dielectric constant of the material and  $\epsilon_0$  is the permittivity of free space. The capacitance of the bilayer thin films of 500 nm thick was therefore measured at a frequency 20 kHz and the  $\epsilon'$  was found to be about  $(14.25 \pm 0.05)$ . The value of  $\epsilon$  is therefore found to be  $1.26 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ . Using the values of  $\epsilon$ ,  $q$ ,  $d$  ( $= 500 \text{ nm}$ ) and  $V_\Omega = 15 \text{ V}$  from Figure 2 the value of  $p$  is calculated out to be about  $(5.19 \pm 0.02) \times 10^{22} \text{ m}^{-3}$ . The mobility of charge carrier in PPPy-PPTMA bilayer thin films was calculated by fitting the non-Ohmic region of  $J$ - $V$  characteristics of Figure 2 to eq. (2) and was found to be  $(2.1 \pm 0.01) \times 10^{-19} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The quantities  $\epsilon$ ,  $p$ , and  $\mu$  for PPPy thin films were also calculated in a similar manner. The capacitance of the PPPy thin film was measured at the same frequency and the dielectric constant  $\epsilon'$  was found to be about  $(12.20 \pm 0.05)$ , and  $V_\Omega = 12 \text{ V}$  was found from Figure 5. The value of  $\epsilon$ ,  $p$  and  $\mu$  for PPPy thin films were then calculated and found to be  $1.07 \times 10^{-10} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ ,  $(3.56 \pm 0.01) \times 10^{22} \text{ m}^{-3}$  and  $(4.4 \pm 0.01) \times 10^{-19} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively. The values of the quantities  $\epsilon$ ,  $p$ , and  $\mu$  for PPTMA thin film was, however, reported

by Akhter and Bhuiyan<sup>2</sup> as  $2.2 \times 10^{-11} \text{ C}^2\text{N}^{-1} \text{ m}^{-2}$ ,  $2 \times 10^{21} \text{ m}^{-3}$  and  $1.3 \times 10^{-13} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively.

### CONCLUSIONS

The direct current electrical properties of plasma polymerized PPPy-PPTMA bilayer thin films have been investigated with Al/PPPy-PPTMA/Al configuration and the results have been compared with those obtained from its component thin films, i.e., PPPy and PPTMA. From the  $J$ - $V$  characteristics of PPPy-PPTMA bilayer thin films, it is observed that the current conduction is increased with an increased proportion of PPTMA in the bilayer structure. To confirm this observation, the conductivity of PPPy-PPTMA bilayer thin films of different thicknesses and different deposition time-ratios were calculated and were found to be increased with the increase of PPTMA in the films. An Ohmic conduction in the lower voltage and space charge limited conduction in the higher voltages have been observed from the  $J$ - $V$  characteristics curves. The conductivity of PPPy, PPTMA, and PPPy-PPTMA bilayer thin films of nearly same thickness has also been calculated to compare the conduction nature of these films. It is found that the conductivity of PPTMA film is higher than that of the PPPy thin film, but the conductivity of PPPy-PPTMA film was found to be lower than that of its component thin films. This suggests a decrease in the conductivity of the PPPy-PPTMA films during the formation, which might be an effect of inhomogeneous complex interface between the PPPy and PPTMA thin films in the bilayer structure. The values of the quantities  $\epsilon$ ,  $\rho$ , and  $\mu$  for PPPy thin films were found to be  $1.07 \times 10^{-10} \text{ C}^2\text{N}^{-1} \text{ m}^{-2}$ ,  $(3.56 \pm 0.01) \times 10^{22} \text{ m}^{-3}$  and  $(4.4 \pm 0.01) \times 10^{-19} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively, for PPTMA thin films  $2.2 \times 10^{-11} \text{ C}^2\text{N}^{-1} \text{ m}^{-2}$ ,  $2 \times 10^{21} \text{ m}^{-3}$  and  $1.3 \times 10^{-13} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively,<sup>2</sup> and for PPPy-PPTMA bilayer thin films,  $1.26 \times 10^{-10} \text{ C}^2\text{N}^{-1} \text{ m}^{-2}$ ,

$(5.19 \pm 0.02) \times 10^{22} \text{ m}^{-3}$ , and  $(2.1 \pm 0.01) \times 10^{-19} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ , respectively.

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