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# Determination of charge carrier transport in radio frequency plasma polymerized aniline thin films

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## Abstract

The carrier transport mechanism of polyaniline (PA) thin films prepared by radio frequency plasma polymerization is described in this paper. The mechanism of electrical conduction and carrier mobility of PA thin films for different temperatures were examined using the aluminium–PA–aluminium (Al–PA–Al) structure. It is found that the mechanism of carrier transport in these thin films is space charge limited conduction.  $J$ – $V$  studies on an asymmetric electrode configuration using indium tin oxide (ITO) as the base electrode and Al as the upper electrode (ITO–PA–Al structure) show a diode-like behaviour with a considerable rectification ratio.

## 1. Introduction

Recently, polyaniline (PA) has captured the attention of the scientific community due to its high electrical conductivity, ease of synthesis, environmental stability and simple doping/dedoping chemistry [1]. PA is one of the most studied conducting polymers of the past two decades [2]. The synthesis of PA thin films is widely described in the literature [3]. Among them plasma polymerization is considered to be an excellent tool for the preparation of pinhole-free and thermally stable PA thin films of uniform thickness [4]. It is a simple and cost effective technique for the synthesis of polymer thin films on various substrates. A plasma polymerization apparatus generally consists of a vacuum system, a plasma source and a monomer delivery system. As the monomer molecules flow through the plasma chamber, a plasma discharge energizes and dissociates the monomer molecules into neutral particles, ions, free radicals and electrons. The product of the recombination of these fragments on a substrate forms a highly branched and cross-linked three-dimensional network, namely a plasma polymer. Depending on the type/frequency of the plasma source used for the polymerization, the process is termed dc (direct current), ac (alternate current), rf (radio frequency)

microwave or pulsed [5]. By tuning the plasma parameters, namely the *Yasuda parameters*, used for the synthesis of polymer thin films, such as plasma power, electrode distance and monomer flow rate, the optical and electrical properties of the polymer thin films can be monitored. Applications of plasma polymers include surface modification, barrier coatings, dielectric, photo resist and wave guiding films for microelectronics and photonics [6].

Extensive studies have been carried out by our group on various properties of PA thin films in its rf and ac plasma polymerized forms. It is found that PA thin films prepared by ac and rf techniques are excellent *low k* materials [7, 8]. The photoluminescent property of PA thin films in their pristine as well as swift heavy ion (SHI) irradiated forms was reported [9]. A study on the conduction mechanism of PA thin films prepared by ac plasma polymerization is already reported by Mathai *et al* [10]. This paper focuses on the study of the charge carrier transport properties of PA thin films with a view to determining the dominant charge transport mechanism of the PA thin films, because the performance of an organic device relies on the charge carrier injection and transport of the active material. It is widely accepted that charge carrier transport in a conducting polymer occurs by variable hopping with polarons as the actual carriers [11]. Recently the fabrication of a quantum well hetero-structure based on PA films has been reported by Narayanan *et al* [12]. The mechanism of conduction in an organic device depends on the traps present in the polymer and

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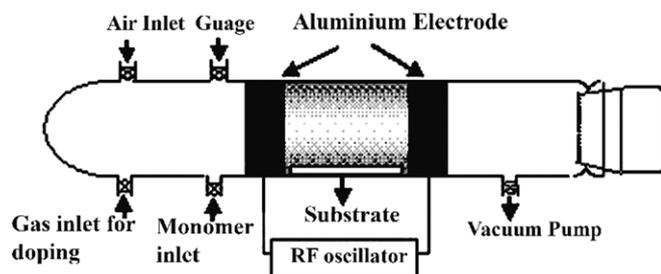


Figure 1. The rf plasma polymerization setup.

the metal polymer interface. Many experimental techniques are in existence for the determination of trap states in an organic device. The current–voltage ( $I$ – $V$ ) characteristics in the space charge limited conduction (SCLC) regime is one among them. This technique provides information on the energy density and density of traps as well as the charge carrier mobilities [13]. This paper deals with the  $I$ – $V$  characteristics of PA thin films and the study on the carrier transport properties. A simple design of a diode structure with a single polymer layer with considerable rectification ratio is reported.

## 2. Experimental

The rf plasma polymerization unit used for the preparation of PA thin films is given in figure 1. It consisted of a glass tube of length 50 cm and diameter 8 cm, with provisions for evacuation and for admitting monomer vapours and dopants in their vapour forms. Ultrasonically cleaned glass substrates were placed inside the glass tube under the space separated by aluminium foil electrodes which were wrapped around the glass tube. The spacing between the electrodes was 5 cm. The chamber was evacuated to a pressure of 0.1 Torr with the help of a rotary pump and a glow discharge was obtained in between the electrodes by applying a radio frequency (rf) of 13.5 MHz, plasma power of 20 W and a current of 70 mA. The monomer was injected into the chamber in a controlled manner by means of a needle valve in the form of vapours. The flow rate was optimized such that vapours of 5 ml of monomer would enter into the chamber in 60 min. The film thickness was optimized as a function of deposition time. In this study, no precursor gas was used. The substrates were not biased during the polymer deposition.

The film thickness was measured using a Detach 6M stylus Profilometer. The electrical conductivity measurements of the PA thin films were carried out by employing a metal–polymer–metal (M–P–M) sandwich configuration. In symmetric electrode configuration studies, aluminium (Al) was used as the electrode material. The Al thin film electrodes were coated on a glass substrate by vacuum thermal evaporation at a pressure of  $10^{-6}$  Torr. Al–PA–Al sandwich structures with an effective area of  $2.5 \times 10^{-5}$  m<sup>2</sup> were used to study the  $J$ – $V$  characteristics. The lower and upper aluminium electrodes (99.99% pure) were deposited onto the glass substrate and on the sample, respectively. The samples for electrical conductivity studies on the asymmetric electrode configuration were prepared by the deposition of PA thin films

on commercially available indium tin oxide (ITO) glass slides. ITO–PA–Al structures were fabricated by the deposition of Al counter electrodes by vacuum thermal evaporation.

For the measurement of electrical conductivity of thin films, the metal–PA–metal sandwich samples were placed in a homemade conductivity cell which was evacuated to a dynamic vacuum of  $2 \times 10^{-2}$  Torr. A bias voltage in the range 1–30 V (step 0.5 V and an interval of 0.5 s between two measurements) was applied and the current flowing through the films was measured using an automated Keithley 236 SMU (source measurement unit). The SMU was automated to a data acquisition system using Interactive Characterization Software (ICS) Version 3.4.1 developed by Metrics Technology Inc. The temperature of the sample was controlled by a Lakeshore temperature controller during the measurements. The voltage versus current graph was plotted and the current density was calculated by using the formula current density  $J = \text{current}/\text{effective area of the device structure}$ . The dielectric constant of the polymer structure was measured using the capacitive method. The dielectric constant of PA films is found to be 2.2 at 10 kHz with a bias voltage of 1 V.

## 3. Results and discussion

### 3.1. Characterization of PA thin films

From the atomic force microscopy (AFM) results, it is found that the PA thin films were optically smooth with a surface roughness of 4.25 Å [12]. This value is also consistent with the surface roughness value calculated from variable angle spectroscopic ellipsometry (VASE) measurements [14]. The film thickness was found to be uniform for the effective area of M–P–M, the thin film sandwiched structure. The optical absorption and FTIR spectrum of PA films have already been reported [12]. The thickness of the films was monitored as a function of deposition time. In this study, we optimized the rate of deposition to be  $8 \pm 1$  nm min<sup>-1</sup>.

### 3.2. Electrical conductivity studies on PA thin films

The device for the electrical conductivity study consisted of a single PA layer sandwiched between two electrodes. Al–PA–Al symmetric structures were employed for the evaluation of the  $J$ – $V$  characteristics in the symmetric electrode configuration and ITO–PA–Al configuration was utilized for the  $J$ – $V$  measurements in the asymmetric electrode configuration. A detailed study on the  $J$ – $V$  characteristics of the PA thin films was carried out to establish the conduction mechanism of these thin films.

*3.2.1.  $J$ – $V$  studies on PA thin films in symmetric electrode configuration.* Under normal circumstances the mechanism of conduction in the polymerized thin films falls under three categories. They are Schottky [15, 16], Pool–Frenkel and SCLC. The complete  $J$ – $V$  characteristics of a polymer device are determined by four parameters. They are the carrier mobility  $\mu$ , the equilibrium density of carriers  $n_0$ , the trap density  $N_t$  and the trap distribution parameter  $T_t$ . The current

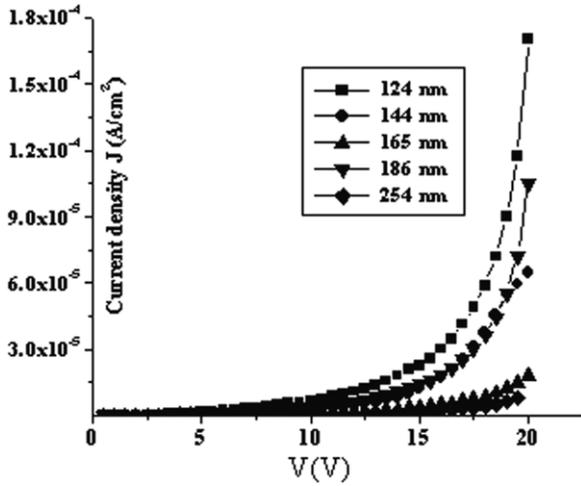


Figure 2.  $J$ - $V$  plot of Al-PA-Al structure. The thicknesses of the films are shown.

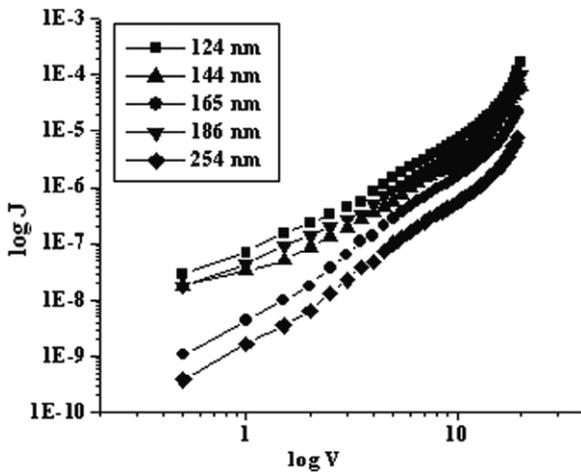


Figure 3.  $J$ - $V$  characteristics of PA (double log plot).

density ( $J$ ) versus applied potential ( $V$ ) of the Al-PA-Al thin films of different thicknesses is given in figure 2. The double log plot of ( $J$ - $V$ ) in the forward direction is shown in figure 3 to get a clear idea of the variation of current density as a function of applied voltage.

The dependence of conductivity on the film thickness is depicted in figure 4. It is found that the current density decreases when the thickness of the film increases. From figures 2, 3 and 4 it can be found that in the low voltage region the current density ( $J$ ) exhibits an ohmic dependence with the applied voltage ( $V$ ) described by the relation

$$J = \mu n_0 e \frac{V}{d}, \quad (1)$$

where  $e$  is the charge of the carriers and  $d$  is the film thickness. As the applied potential exceeds 3.6 V, the slope of the graph is found to be 2 which indicates SCLC [17]. In this region  $J$  is governed by the Mott-Gurney relation [18].  $J$  varies quadratically with  $V$  in this region:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu_p \frac{V^2}{d^3}, \quad (2)$$

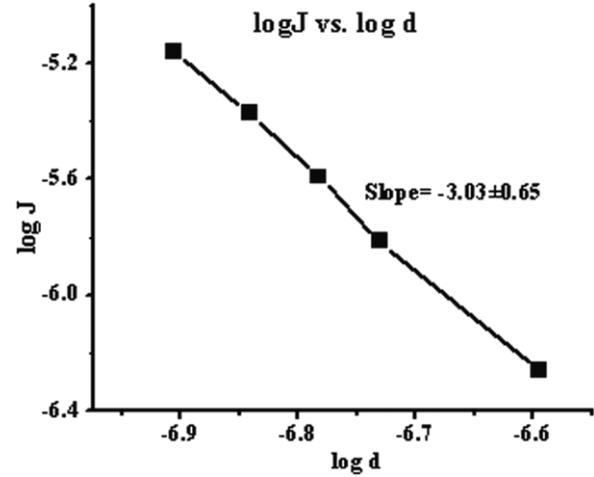


Figure 4. The  $\log J$  versus  $\log d$  plot of PA films. The slope of the  $\log J$ - $\log d$  plot  $3.03 \pm 0.65$  shows a space charge limited current.

where  $\epsilon_0 \epsilon_r$  is the permittivity of the polymer and  $\epsilon_r$  is the relative permittivity of the sample = 2.2. The value of  $\epsilon_r$  is obtained from the dielectric measurements.  $\mu_p$  is the hole mobility. In the space charge region described by the Mott-Gurney relation, the mobility can be calculated directly from the current density. It is found that the mobility in the SCLC region is in the order of  $3 \times 10^{-10} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . At low voltages, the mobility is a constant and independent of the electric field and carrier density. But it is a function of temperature. In the present case the  $\log J$  versus  $\log d$  graph (figure 4) has a slope of  $-3.03 \pm 0.65$ . The values of current density at 10 V for different thicknesses were taken to plot the  $\log J$  versus  $\log d$  graph. It is evidenced from this result that the dependence of  $J$  on  $d$  is according to equation (2). This observation is clear evidence of the existence of the SCLC conduction mechanism and the possibility of Schottky or Pool-Frenkel mechanisms in PA thin films [19] can be discarded.

From the slope of the  $\log J$ - $\log V$  plot (figure 4), it can be seen that [20] beyond the SCLC region, the quadratic dependence of  $J$  on  $V$  changes to a trap filled limit (TFL) with a slope of  $>2$ . In the present case this change is found to occur at an applied potential of 13.5 V. The slope of graph 3 in the high voltage region is found to be 4, which is an indication of the presence of traps.

As a representative sample, the temperature dependence of the  $J$ - $V$  characteristics of the PA thin film (124 nm) is shown in figure 5. The temperature dependence of  $J$  obeys the relation

$$J = e \mu N_v \left( \frac{V}{d} \right) \exp \left( -\frac{E_a}{kT} \right). \quad (3)$$

This expression is characteristic of an exponential trap distribution, where  $N_v$  is the effective density of states in the valence band,  $k$  is the Boltzmann constant,  $E_a$  is the activation energy which is obtained from the  $\ln J$  against the  $1/T$  plot given in figure 6. The plot is a straight line and from this the activation energy is obtained as  $E_a = 0.81 \text{ eV}$ . The linear dependence of the slope of the graph with inverse temperature underlines the validity of the SCLC model for the device structure described here. Here the trap distribution obeys a

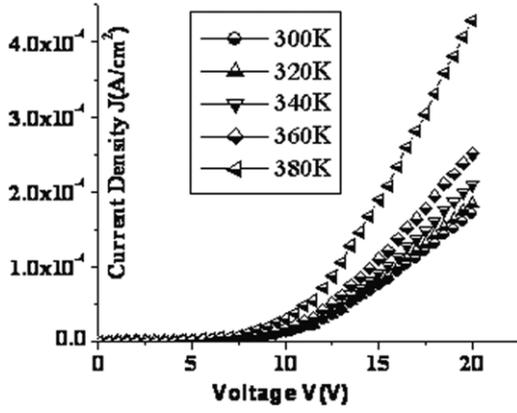


Figure 5. The temperature dependence of the  $J$ - $V$  characteristics of PA thin films (124 nm).

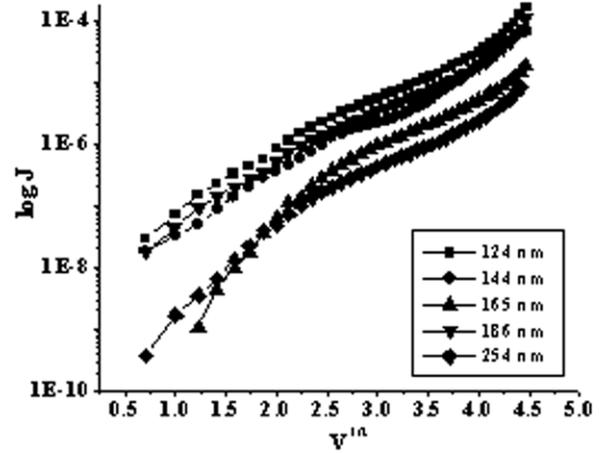


Figure 7. Log  $J$  versus  $V^{1/2}$  plot of PA thin films in the symmetric electrode configuration.

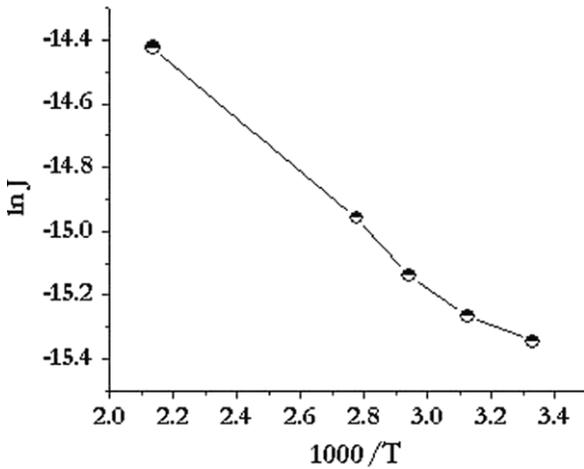


Figure 6. The log  $J$  versus  $1000/T$  plot of PA thin film (124 nm). The activation energy is calculated as 0.81 eV.

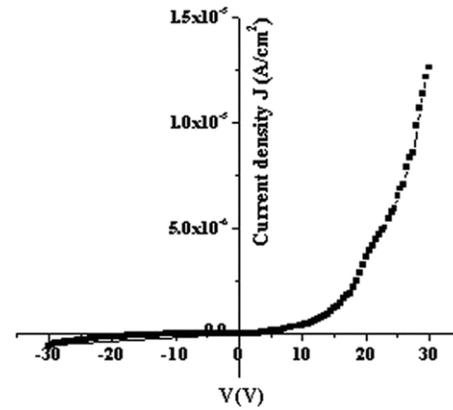


Figure 8.  $J$ - $V$  plot of ITO-PA-Al structure; forward bias ( $Al^-$ ) and reverse bias ( $Al^+$ ).

Mayer-Neidel [21] observation and within the SCLC region the current density  $J$  is given by the relation

$$J = e\mu N_v \left( \frac{\epsilon_r \epsilon_0}{ePkT_t} \right)^L \frac{V^{L+1}}{d^{2L+1}}, \quad (4)$$

where  $P$  is the trap density per unit energy range at the valence band edge. At high voltages it is observed that the current increases more steeply than a quadratic relation. This increase in current density is due to an electric field induced enhancement of mobility of the carriers in the polymer. Here  $L$  is a ratio  $T_t/T$ ,  $T$  is the ambient temperature and  $T_t$  is the temperature parameter described by the trap distribution. The exponential trap distribution may be described in terms of  $T_t$  as

$$P_{(E)} = P \exp\left(\frac{-E}{kT_t}\right), \quad (5)$$

where  $P_{(E)}$  is the trap concentration per unit energy range at an energy  $E$  above the valence band edge. The total concentration of the traps is given by the equation [22]

$$N_t = PkT_t. \quad (6)$$

The value of  $N_t$  can also be calculated from the relation

$$N_t = \frac{3}{2} \frac{\epsilon_r \epsilon_0 V_{TFL}}{ed^2}, \quad (7)$$

where  $V_{TFL}$  is the voltage where the trap filled region is observed (here 13.5 V). With this, the value of  $N_t$  will be numerically equal to  $1.06 \times 10^{19} \text{ cm}^{-3}$ . From the slope of the double log plot given in figure 3, in the TFL regime  $T_t$  is obtained and is equal to 900 K since the slope of the trap filled region is calculated as 4.

To confirm the conduction mechanism of the thin films log  $J$  versus  $V^{1/2}$  is plotted and given in figure 7. The dependence of log  $J$  on  $V^{1/2}$  is not linear and the presence of a Schottky mechanism is ruled out.

### 3.2.2. $J$ - $V$ studies on asymmetric electrode configuration of PA.

In this case all the measurements were taken at room temperature (300 K). The current density versus applied potential for the asymmetric configuration is shown in figure 8. The reverse  $J$ - $V$  characteristics give information about the metal-semiconductor contact. It is found that the asymmetric  $J$ - $V$  characteristics exhibit a diode-like behaviour. The reason for this asymmetry could be the difference in work function of the two electrodes and the ionization potential of the organic film [23]. The work function for ITO is 4.7 eV and for aluminium it is 4.2 eV. Figure 8 shows a rectification curve with a considerable rectification ratio. This rectification behaviour is obtained under the low field bias condition which results

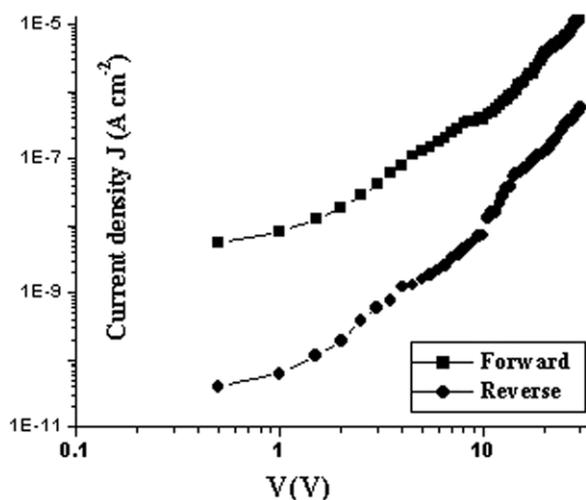


Figure 9. The log  $J$  versus log  $V$  plot for forward and reverse bias.

from the Schottky junction at the interface of PA/Al, and the ohmic contact at the PA/ITO junctions for the asymmetric electrode configuration. The rectification ratio of the diode, the ratio of the magnitude of forward to reverse current at a high voltage, is calculated as 40 at a potential of 20 V.

From figure 8 it can be observed that the rf plasma polymerized PA is p-type. The conduction in the asymmetric electrode configuration is explained as follows. At the Schottky junction, electrons are presumed to transfer from Al to the p-type semiconductor of PA until the electronic potentials reach equilibrium due to the difference in work functions of the Al electrode and PA thin film. The electron transfer fills the p-type acceptors and forms an insulating depletion layer, resulting in the formation of a negative space charge and a built-in field at the depletion layer [24, 25]. When the double log  $J$ - $V$  plot (figure 9) of the asymmetric electrode configuration is analysed, it can be found that in the ohmic region the slope of the graph is 1.11 (below 2 V), in the SCLC region the slope is 1.94 (2–10 V) and in the high voltage region it is found to be 3.3 under the forward bias condition. Under the reverse bias condition it is 0.98, 2.09 and 3.41, respectively, for similar regions.

After a particular biasing voltage the electrode independent SCLC [26, 27] mechanism dominates over the electrode dependent or ohmic contacts formed at the electrode/polymer interface [28]. To check the plausibility of a Pool-Frenkel or Schottky type conduction mechanism, the log  $J$  versus  $V^{1/2}$  graph of the asymmetric electrode configuration of PA films is plotted and is given in figure 10.

The graph is not found to be a straight line and thus it is found that the mechanism of conduction is not Schottky or Pool-Frenkel type but the chances for SCLC behaviour are evident [10, 29]. When compared with the Schottky plot in the symmetric configuration, the Schottky plot for the asymmetric configuration varies much in the low voltage region. The structural properties of PA thin films based on FTIR spectra have already been reported [12]. However, a complete structural characterization for elucidating the molecular structure of these thin films, which leads to the

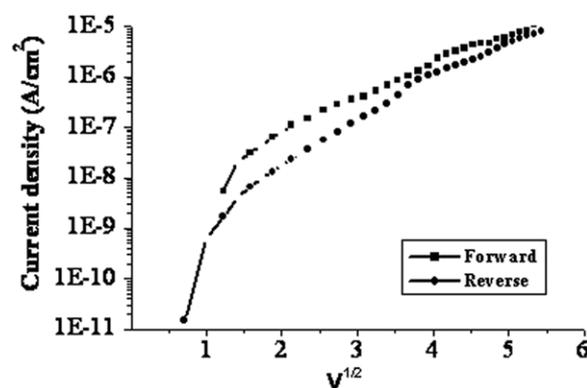


Figure 10. Log  $J$  versus  $V^{1/2}$  plot of PA thin films in asymmetric electrode configuration.

conduction mechanism of the plasma polymer films, is beyond the scope of this paper.

#### 4. Conclusion

Good quality thin films of PA were prepared by a rf plasma polymerization process. The conduction mechanism studies on PA thin films showed that the dominant carrier transport mechanism is SCLC. Field induced enhancement of the mobility of PA thin films is observed and the carrier mobility  $\mu$ , the equilibrium density of carriers  $n_0$ , the trap density  $N_t$  and the trap distribution parameter  $T_t$  of the thin films are calculated from the  $J$ - $V$  characteristics. A diode structure based on the asymmetric electrode configuration, ITO-PA-Al structure, is fabricated and the rectification ratio is calculated. The asymmetric electrode configuration shows a considerable difference in the  $J$ - $V$  characteristics when compared with the symmetric electrode configuration of Al-PA-Al structure. The asymmetric electrode configuration forms a diode-like structure with a considerable rectification ratio.

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