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Direct Current Electrical Conduction Mechanism in Plasma Polymerized Pyrrole Thin Films

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The complex direct current (DC) electrical conduction mechanism in plasma polymerized pyrrole (PPPy) thin films has been discussed in this article. PPPy thin films of different thicknesses were deposited at room temperature onto glass substrates by using a parallel plate capacitively coupled glow discharge reactor and their properties were studied in detail. In the study of DC conduction properties, the current density-voltage (J-V) characteristics of PPPy thin films indicated that in the low field region the conduction obeys Ohm's law and J-V relationship is linear but at high field non-linear characteristics were observed. This high field complex nonlinear electrical conduction mechanism can not be described by a single conduction process. Different theories are usually employed to explain the charge transport phenomenon e.g., Schottky-Richardson mechanism, Poole–Frenkel (PF) mechanism, Fowler–Nordheim mechanism and space charge limited conduction (SCLC) mechanism. In this article an attempt has been made to explain the probable conduction mechanism in the dielectric PPPy thin films using existing theories and the experimental data. After analyzing the result it is concluded that the charge transport phenomenon appears to be the space charge limited conduction (SCLC) in the higher voltage region in the PPPy thin films.

Field of Research: Plasma Polymerization, Thin Film Characterization

1. Introduction

Electronic conduction in amorphous organic insulating solids has become a very important topic in recent years because of their versatile applications in electrical and electronic devices. Charge transport measurements in disordered semiconductors and insulators can provide information about the electronic structure of these materials. Polymers are insulators and they are not supposed to conduct electrical current, but the electrical properties of these materials are usually observed to be changed when subjected to high electric fields and temperatures for long time and consequently polymers starts to conduct current. The classical conduction and transport mechanism which is found in conductors and semiconductors are not found in polymers, and therefore different conduction mechanisms are observed in these materials. Charge injection from electrodes into polymer, traps and volumetric conduction, tunneling and hopping conduction etc play important roles in conduction and charge transport process in polymers. Extensive studies on the electrical conductivity of insulating polymer thin films deal mainly with the dependence on parameters like temperature, pressure, voltage and thickness. Valuable insight into the different transport mechanisms can be obtained from such studies, and since

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polymers are, generally, composed of both polycrystalline and amorphous phases [Bunn, 1959], therefore, it is not surprising that several theories such as electron, ion and proton conduction mechanisms are postulated to explain experimental observations in polymer films.

In the study of the dc electrical conduction in the polymer thin films, the current conduction is considered through the film, rather than along the plane of the film and the carriers may either be electronic or ionic in nature. The low field properties are usually Ohmic in nature, but the high field electrical properties cannot be described by a single conduction process. A power law of the form $J \infty V^n$, can express the variation of current density with voltage, where n is a power factor. When n is unity, the conduction is Ohmic, and if the value of n is less or more than unity, then the conduction process is other than Ohmic.

Different types of dc electronic conduction mechanisms by which electrons are transported under the influence of an applied electric field have been investigated in the literature [Kao & Hwang, 1981; Yasuda, 1985]. The conduction mechanism is explained usually in terms of electron emission from cathode by the field assisted thermal excitation, where the electrons are transported from the cathode into the conduction band of the contact barrier i.e. Schottky-Richardson mechanism; or by electron liberation from the traps in the bulk of the material, and/or electron transportation by field-assisted thermal excitation over the lower Coulombic potential barrier i.e. Poole–Frenkel (PF) mechanism. The possibilities of tunneling i.e., Fowler–Nordheim mechanism and space charge limited conduction (SCLC) mechanism etc are also observed in amorphous solid.

This article comprises of five sections. Section 2 deals with Literature Review, section 3 describes the Experimental Details for deposition of the thin films and electrical measurement technique, section 4 discusses the Results including necessary theory to explain them and the article is ended up with its concluding remarks in section 5.

2. Literature Review

Various properties of plasma polymerized thin films such as structural, physical, chemical, optical and electrical properties have been investigated and appeared in the literatures. The development of scientific interest in different technological application of these thin films has drawn much attention of the researchers.

There are many reports found on the investigation of the direct current (DC) electrical properties of plasma polymerized thin films. Akther and Bhuiyan [2005] reported that the plasma polymerized *N,N,*3,5-tetramethyaniline (PPTMA) thin films of different thicknesses showed Ohmic behavior at the lower voltage region and SCLC dominated by exponential trap distribution at the higher voltage region. Kamal and Bhuiyan studied on the optical characterization [2011] and direct current electrical characterization [2012] of the plasma polymerized pyrrole-*N,N,3,5* tetramethylaniline (PPPy-PPTMA) bilayer thin films. The optical characterization [2013] and direct current electrical characterization [2013] of the PPPy monolayer thin films were also reported by Kamal and Bhuiyan. Valaski et al. [2001, 2002] 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 consequently in its electrical conductivity [Valaski et al, 2001]. From the study on the influence of the film thickness on the conductivity [Valaski et al , 2002], 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 ≤ 300 nm), the charge transport was limited by thermoionic emission. Sajeev & AnantharamaN [2010] studied on the carrier transport mechanism of polyaniline (PA) thin films prepared by plasma polymerization and found space charge limited conduction mechanism in these films. Sakthi Kumar et al. [2003] 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. The preparation and characterization of PPPy thin films has been studied by Joseph John et al. [2010]. The electrical conductivity studies of the aluminium/ polymer/ aluminium structure have been carried out and an SCLC mechanism is identified as the most probable conduction mechanism in those polymer films.

This paper discusses the high field non-linear characteristics of DC electrical conduction by using different theories on the conduction mechanism for insulating materials. The *J*-*V* characteristics of PPPy thin films of different thicknesses were investigated which were characterized by two different slopes in the low and high voltage region respectively and the complex behavior were explained in detail.

3. Experimental Details

The plasma polymerized pyrrole thin films were deposited on to chemically cleaned glass substrates at room temperature by using a capacitively coupled glow discharge plasma reactor. The monomer pyrrole was collected from Aldrich-Chemie D-7924, Steinheim, Germany. The vapor of the monomers 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 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 by a rotary pump (Vacuubrand GMBH & Co, 97877 Wertheim, Germany) and plasma was generated around the substrates with a power of about 30 W.

For electrical measurements, the Al/ PPPy/ Al sandwich configuration were formed by using an Edward vacuum coating unit E-306A (Edward, UK) at a pressure of about 1.33×10^{-3} Pa with an effective area of about 10^{-4} m^2 of Al electrode. The *J*-*V* characteristics of thin films of different thicknesses were studied in the voltage range of 1.0 - 30.0 V at room temperature. 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 chromelalumel thermocouple connected to a digital microvoltmeter 197A (Keithley Instruments, Inc., USA).

4. Results and Discussion

4.1 Current density–Voltage (J-V) Characteristics

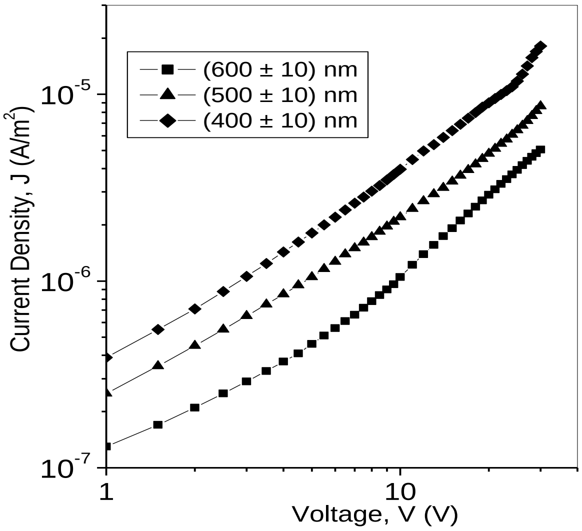
The *J-V* characteristics for PPPy thin films of thicknesses about 400, 500, and 600 nm were recorded at room temperature in the voltage region 1.0 V to 30 V, and are presented in Fig. 1.

It is seen that, the curves in Fig. 1 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 that the transport is not limited by the polymer/electrode interface, and the current density *J* is the given by the following equation,

$$J = Ne\mu \frac{V}{d} = \sigma \frac{V}{d} \qquad (1)$$

where *e* is the elementary electric charge, *N* is the free charge carriers density (in this case, assumed to be positive), μ is the carrier mobility in the transport band, *d* is the film thickness, *V* is the applied voltage, and σ is the conductivity [Kao & Hwang, 1981].

Figure 1: J-V Characteristics for PPPy Thin Films of Different Thicknesses at Room Temperature.



In the Fig. 1, the value of slopes at the lower voltage region (1 ~ 7 V) is found to be 0.85<n<1.15, indicating a probable Ohmic conduction, while at the higher voltages (15 ~ 27 V) the slopes 1.67<n<2.45 represent the non-Ohmic conduction. The voltage dependence of current density at the higher voltage region suggests that the current may be due to space charge limited conduction (SCLC) or Schottky–Richardson mechanism or Poole–Frenkel (PF) conduction mechanisms or Fowler–Nordheim mechanism in PPPy thin films [Kao & Hwang, 1981; Yasuda, 1985].

The Fowler–Nordheim mechanism or tunneling effect is usually observed in very thin films. The Schottky emission is defined only when the carriers are injected from the electrode by means of thermal or field assisted emission. The other process in which carriers are produced by the dissociation of donor-acceptor centers in the bulk of the material is called PF generation. If the generation process is slower than transport by the carriers through the material, the conduction is controlled by generation, specifically by either the Schottky or PF mechanisms. Conversely, when the transport is slower than generation, it constitutes the rate-determining step and the conduction is described by the theory of SCLC.

However, the direct current conduction mechanisms for the PPPy thin films are discussed in the light of the following mechanisms.

4.2 Tunneling or Fowler–Nordheim Mechanism

If the applied voltage is not too high and the film is extremely thin or contains a large number of imperfections, or both, electrons can tunnel directly between the metal electrodes and produces a current without the movement of carriers in the conduction band or in the valence band. This process is known as tunneling or Fowler-Nordheim mechanism [Taylor & Lewis 1971].

In this process, the electron may flow by tunneling from the negative electrode into unoccupied levels of the positive electrode; but if the voltage is higher or the film is thicker the tunnel transfers or conveys the electrons into the conduction band of the dielectric rather than directly to the second metal. If the dielectric contains a large number of traps, the tunneling can take place through some of the traps.

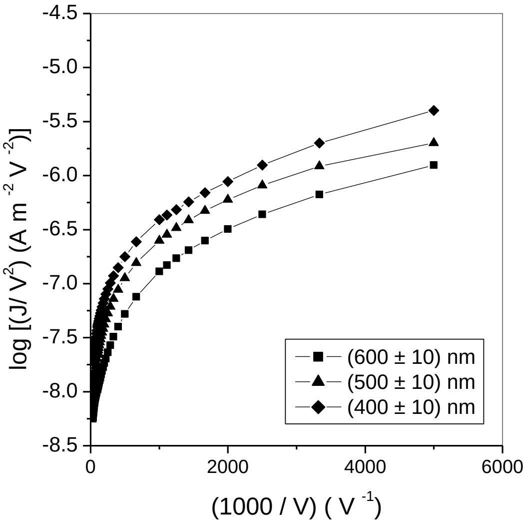
The Fowler–Nordheim relation [Kao & Hwang, 1981] for J can be expressed as,

$$\log \frac{J}{V^2} = \log A - \frac{\varphi}{V} \tag{2}$$

i.e., if the log J/V^2 vs. $1/V$ plot shows a linear relationship with a negative slope, the conduction is then designated as tunneling effect.

In the Fig. 2, the Fowler–Nordheim plots, i.e., log J/V^2 vs. $1/V$ plots for PPPy thin films of thicknesses 400, 500 and 600 nm are shown. It is seen from the figure, that the curves are not at all linear and all of them have positive slopes, indicating the absence of tunneling effect in PPPy thin films.

Figure 2: Fowler–Nordheim Plots for PPPy Thin Films of Different Thicknesses.



4.3 Schottky–Richardson Mechanism

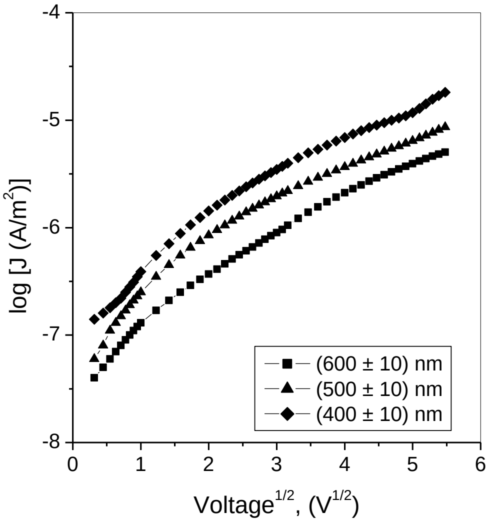
The Schottky–Richardson current voltage relationship is expressed as,

$$\log J = \log AT^2 - \frac{\varphi}{kT} + \beta_s F^{1/2} \qquad (3)$$

where F is the electric filed, and therefore *log J* vs. $F^{1/2}$ (or *log J* vs. $V^{1/2}$) plot is referred to as Schottky plots, and should be a straight line with a positive slope to become Schottky mechanism operative.

The Schottky plots i.e., log J vs. $V^{1/2}$ plots for PPPy thin films of thicknesses 400, 500 and 600 nm have been shown in Fig. 3. It is seen from the figure, that the curves in this case are not also linear though all of them have positive slopes. This result also indicates the absence of Schottky mechanism in PPPy thin films.

Figure 3: Schottky Plots for PPPy Thin Films of Different Thicknesses



4.4 Poole–Frenkel Mechanism

The PF effect is sometimes called the internal Schottky effect, since the mechanism of this effect is associated with the field enhanced thermal excitation (detrapping) of trapped electrons or holes, which is very similar to the Schottky effect in the thermionic emission. It is a bulk-limited conduction process, in which the emission of electrons occurs from trapping centers in thin films by the joint effect of temperature and electric field. It is also called the field-assisted thermal ionization.

The PF field-dependent conductivity can be expressed as,

$$\sigma = \sigma_o \exp\left[\frac{\beta_{PF} F^{1/2}}{2kT}\right] \tag{4}$$

where β_{PF} is the Poole-Frenkel co-efficient and F is the static electric field.

or $$\log\sigma = \log\sigma_0 + \frac{\beta_{PF}}{2kT} F^{1/2} \tag{5}$$

so that the PF mechanism is characterized by the linearity of *log σ* vs. $F^{1/2}$ plots (or *log σ* vs. $V^{1/2}$ plots) with a positive slope.

Figure 4: Poole–Frenkel Plots for PPPy Thin Films of Different Thicknesses

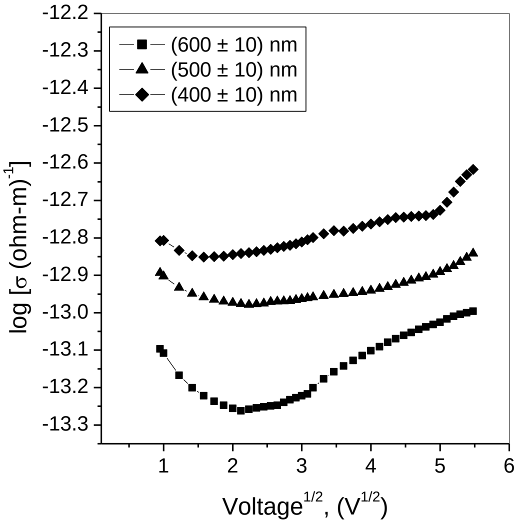


Fig. 4 shows the PF plots for PPPy thin films of thicknesses 400, 500 and 600 nm. It is observed that none of the curves shows linearity and no particular types of slope-character (positive or negative) could be mentioned from the curves, which ruled out the possibility of PF conduction mechanism in PPPy thin films.

4.5 Space Charge Limited Conduction

This bulk-limited mechanism occurs because the rate of carrier injection from the contacts exceeds the rate at which charge can be transported through the film. If the cathode emits more electrons per second than the space can accept, the remainder would form a negative space charge which creates a field to reduce the rate of electron emission from the cathode. Hence the current is controlled not by the electron injecting electrode but by the bulk of the insulator i.e. by the carrier mobility in the space inside the material. This type of conduction is known as SCLC.

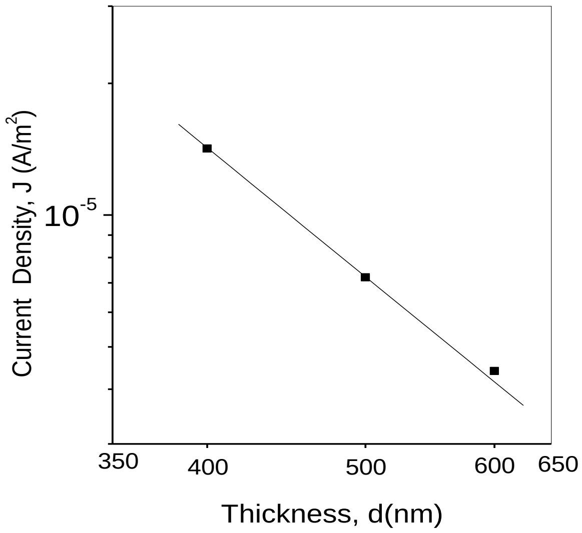
However, If the applied voltage is increased over a certain value, the injected charge carrier density largely exceeds the free charge density under thermal equilibrium and the system transits to SCLC conditions. In this case, the J can be described by the equation [Kao & Hwang, 1981; Yasuda, 1985]

$$J = \frac{9}{8}\varepsilon\mu \frac{V^2}{d^3} \tag{6}$$

where, ε is the permittivity of the material.

This relation indicates that J is inversely proportional to d^3. The thickness dependence of current follows the relation $J \alpha d^{-l}$, 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 thin films at a higher voltage of 27 V, which is presented in Fig. 5. The linear slope derived from Fig. 5 gives a negative value of 3.54, which is much higher than corresponding to Schottky or PF mechanism. Therefore, the conduction mechanism in PPPy thin films is suggested to be SCLC.

Figure 5: Plots of *J-d* for PPPy Thin Films in the Non-Ohmic Region (at 27V).



5. Conclusions

From J-V characteristics of PPPy thin films, a general trend is observed that the current conduction is higher in the films of lower thickness than that of the higher-thickness films at the same voltage. The most probable reason of this behavior may be due to better morphological characteristics of the films of lower thicknesses which causes increased charge mobility. Thinner films present more structural order due to more homogeneous surfaces, decreased grain size and improve interchain conduction, and as a result, an increased conductivity could be observed.

The J-V characteristics of PPPy thin films were characterized by two different slopes in the lower and higher voltage regions. The slopes at lower voltage region indicate a probable Ohmic conduction, while at higher voltages a non-ohmic conduction is observed. This complex conduction behavior has been explained in terms Schottky–Richardson mechanism, Poole–Frenkel mechanism, tunneling or Fowler–Nordheim mechanism and space charge limited conduction mechanism, and it is found that the current conduction in PPPy thin films follow an SCLC mechanism.

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