Temperature Dependence of DC Electrical Conduction in Plasma Polymerized Pyrrole Thin Films

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The temperature dependence of direct current (DC) electrical conduction in plasma polymerized pyrrole (PPPy) thin films has been discussed in this article. A parallel plate capacitively coupled glow discharge reactor was employed to deposit PPPy thin films and different properties of the films were studied in detail. In the study of DC conduction properties, the current density-voltage (J-V) characteristics of PPPy thin films at room temperature indicated that in the low field region the conduction obeys Ohm's law but at high field non-linear characteristics were observed. The J-V characteristics at different temperatures showed that the current density in both the voltage regions is increased slightly with increasing temperature which indicated the temperature dependence of the conductivity. From the Arrhenius plots activation energies were calculated in both the low and high temperature region. It is observed that activation energy is decreased with the decrease of temperature which was an indication of a gradual transition to the hopping regime. The change in activation energy at higher temperature in comparison to that at lower temperature has been attributed to a considerable temperature-dependence of SCLC mechanism.

Field of Research: Material Science

1. Introduction

Material preparation and processing have received significant attention in the academic and industrial research community in last few decades. Organic thin films, especially plasma polymer thin films, due to their excellent properties have been undertaken very actively 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. Traditional involvement of polymer thin films in microelectronics was as element with excellent insulating properties.

Electrical properties of polymer thin films are very important from both the theoretical and practical point of view. Since polymers are insulating materials they are not supposed to conduct electrical current, but when subjected to high electric fields and temperatures for long time the electrical properties of these materials are usually observed to be changed. Extensive studies on the electrical conductivity of insulating polymer thin films deal mainly with the dependence on parameters like temperature, pressure, voltage and thickness.

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Polymer conductivity is very low, usually less than 10^{-13} (Ohm-m)$^{-1}$ [Dissado and Fothergill, 1992]. In amorphous solids the band structure is not well-defined and explanation of conduction mechanisms in these materials is very complicated. When electronic conduction is considered in polymers, band theory is not at all suitable because the atoms are covalently bonded to one another, forming polymeric chains that experience weak intermolecular interactions. But macroscopic conduction requires electron movement not only along the chain but also from one chain to another. This changes the classic band theory and limits the movement of charge. However the band gap is very large in polymer material and it is very difficult to create mobile charge [Ieda 1984; Das-Gupta 1987].

In polymer system, the conductivity is influenced by the factors such as dopant level, morphology of polymer, concentration of conducting species, temperature, etc. It is difficult to generalize the temperature dependence of dc conduction whether it is ionic or electronic, since so many processes are possible. As the temperature is increased the charge carrier concentration increases strongly with temperature. This dominates the temperature dependence of the conductivity giving it an Arrhenius-like character i.e., exponential temperature dependence as,

$$J = J_0 \exp \frac{-\Delta E}{kT} \qquad (1)$$

Where J_0 is a constant and ΔE is the activation energy for carrier generation. Whatever the Ohmic mechanism, a *log J* vs. *1/T* plot (Arhennius plot) will usually exhibit increasing linear slopes (activation energies) as T is raised [Maisel and Glang, 1970].

This paper discusses the temperature dependence of DC electrical conduction in PPPy thin films. The *J-V* characteristics of PPPy thin films of different thicknesses were investigated at different temperatures. To investigate the nature of dependence the Arrhenius plots (*log J* vs. *1/T* plot) were made and activation energies were calculated in both low and high temperature region.

This article comprises of five sections. Section 1 is the introduction, 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

Many reports on the investigation of the structural, optical, direct current (DC) and alternating current (AC) electrical properties of plasma polymerized thin films are found in the literature. The optical characterization and direct current electrical characterization of the plasma polymerized pyrrole-*N,N,3,5* tetramethylaniline (PPPy-PPTMA) bilayer thin films were studied by Kamal and Bhuiyan [2011, 2012]. The optical characterization and direct current electrical characterization of the PPPy monolayer thin films were also reported by Kamal and Bhuiyan [2013a, 2013b]. They also investigated on the direct current electrical conduction mechanism of the PPPy monolayer thin films [Kamal and Bhuiyan, 2014] and reported space charge limited

conduction (SCLC) dominated by exponential trap distribution at the higher voltage region. Akther and Bhuiyan [2005a, 2005b, 2005c] 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 at the higher voltage region. From the UV-vis absorption spectra, allowed direct transition (E_{qd}) and indirect transition (E_{qi}) energy gap were determined and it was seen that while E_{qd} increases a little, E_{qi} decreases, on heat treatment of PPTMA. It was then concluded that PPTMA thin film with conjugation can be produced by plasma polymerization and the structural order can be improved by heat treatment. The influence of temperature and humidity on the electrical conductivity of polyaniline (PAn) and polypyrrole (PPy) thin films were studied [Morales et al., 2000]. To study the temperature dependence of the conductivity the polymers were submitted to heating–cooling cycles. In the heating step of the cycles, the polymers with greater humidity contents did not have the behavior proposed in the Arrhenius model because the loss of water molecules affected the shape of the curve. During the cooling step, the plots showed good agreement with the Arrhenius model. These behaviors suggested that in the absence of humidity, the electric conductivity was dominated by 1-D conducting character of the polymeric systems. Chowdhury and Bhuiyan [2000] investigated the dielectric relaxation behavior of the as-deposited and heat treated plasma polymerized Diphenyl (PPDP) thin films over the frequency range from 10^{-1} to 10^{6} Hz and temperature range from 223 to 423 K. It was observed that the ac conductivity was more dependent on temperature in the low frequency region than in the high frequency region. El-Nahass et al. [2006] investigated the dependence of the dc and ac electrical conductivity of thermally deposited N-(p-dimethylaminobenzylidene)-p-nitroaniline (DBN) thin films on the temperature and frequency. The dc conductivity showed an increasing rate of thermally activated carrier hopping with increasing temperature.

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 electrode area of about 10^{-4} m^2. The *J-V* characteristics of PPPy thin films of different thicknesses were studied in the voltage range of 1.0 - 30.0 V, first at room temperature and then at different higher temperatures ranges from 298 to 398 K. 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 thermally activated current or the temperature dependence of current across the thin films was measured at different applied voltages using the above mentioned electrometer. For these measurements the samples were heated by a heating coil which was wrapped around the specimen chamber. The temperature was measured by a chromel-alumel 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 [Kamal and Bhuiyan, 2013b]. It is seen that, the curves follow a power law of the form $J \propto V^n$, where n is a power index. By characterizing the curves with two different slopes in lower and higher voltage region 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 SCLC mechanism [Kamal and Bhuiyan, 2014].

Figure 1: J-V Characteristics for Pppy Thin Films of Different Thicknesses at Room Temperature
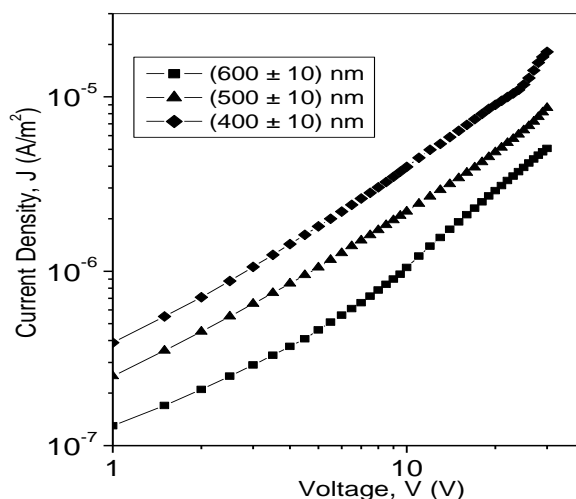
4.2 Temperature Dependence of Current

Fig. 2, Fig. 3, and Fig. 4 represent the *J-V* characteristics of PPPy thin films of thicknesses about 400, 500, and 600 nm respectively at different temperatures of 300, 323, 348 and 373 K. It is observed that the current density of all the samples for both the voltage regions is increased slightly with increasing temperature. This increase may be due to the increased molecular motion at higher temperatures, and indicates probable temperature dependence of the conductivity.

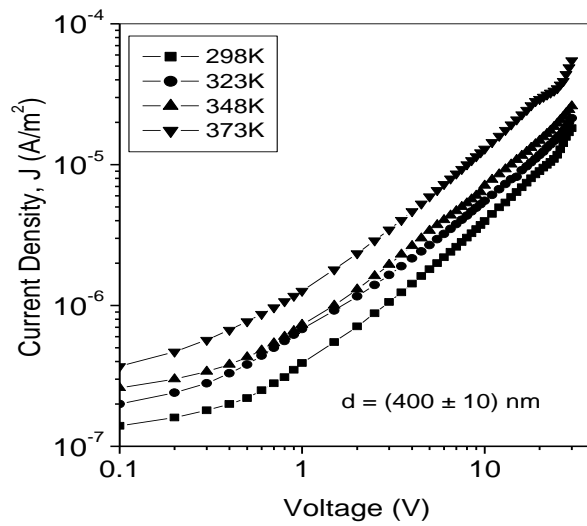**Figure 2: The J-V Characteristics for Pppy Thin Film of Thickness 400 Nm at Different Temperatures**

Figure 3: The J-V Characteristics for PPPy Thin Film of Thickness 500 Nm at Different Temperatures
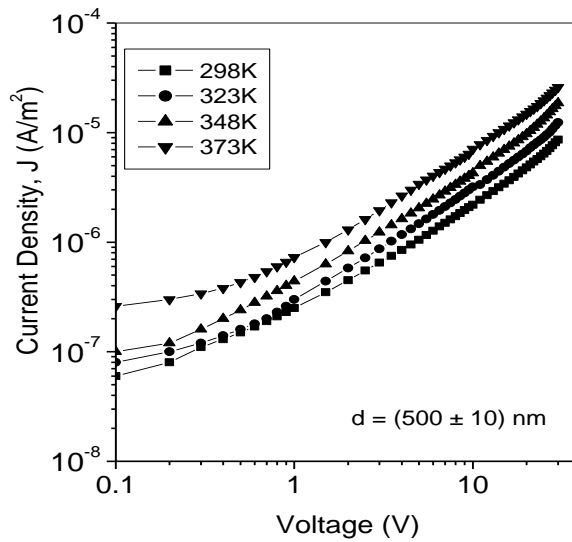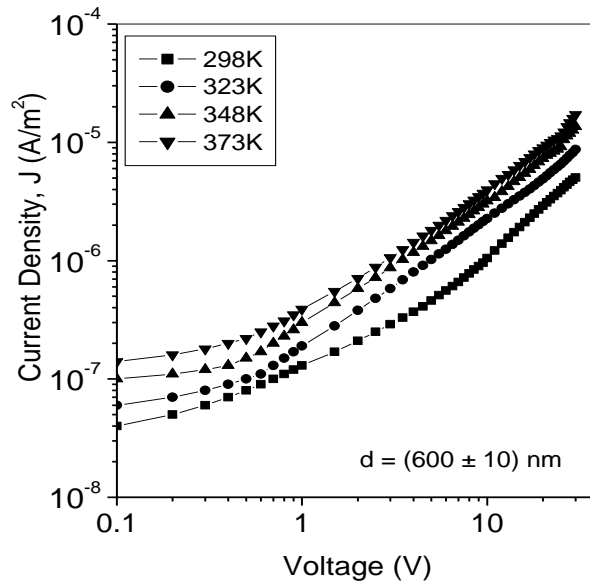
Figure 4: The J-V Characteristics for PPPy Thin Film of Thickness 600 Nm at Different Temperatures

4.3 Arrhenius Plots

Fig. 5, Fig. 6 and Fig. 7 represent the plots of *J* with inverse absolute temperature $1/T$ for the PPPy thin films of thicknesses about 400, 500, and 600 nm respectively. Every figure having two curves in two different voltage regions, one in the Ohmic region with an applied voltage, 5V, and other in the SCLC region with an applied voltage, 20V. Moreover, each of the curves has two different slopes in the low and high temperature regions. The activation energies are calculated from the slopes of the curves from Fig. 5 – Fig. 7 and are listed in Table 1.

Figure 5: Plots of J vs. 1/T for Pppy Thin Films of Thickness 400 Nm in ohmic and Non-ohmic Regions
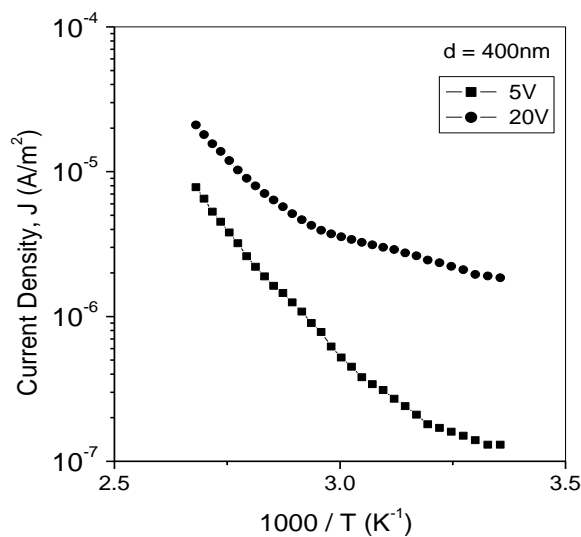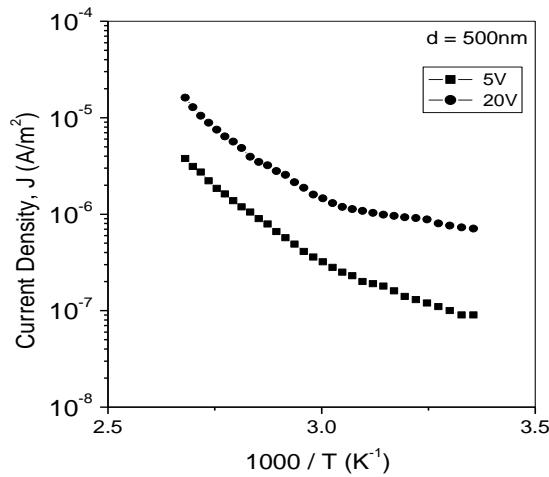
Figure 6: Plots of J vs. 1/T for Pppy Thin Films of Thickness 500 Nm in Ohmic and Non-Ohmic Regions

It is known that, the trapped charges can lead to the polarization and distortion of the lattice structure and could result in local energy band deformation, which makes it very hard for trapped charge to be free. However, charge carriers in polymer thin films may move from one site to another by hopping over a potential barrier [Taylor 1971]. Hopping is the transfer of a thermally activated charge carrier between localized states. Carriers acquire enough energy from the lattice by means of thermal fluctuations to overcome the potential barrier. Here the ΔE values at lower and higher temperature regions suggest that there may not be any transition of the conduction process from the hopping regime to a regime dominated by distinct energy levels. Therefore the carrier may take part in the conduction process throughout the bulk of the material. The low temperature activation energy suggests drawing a correlation with the hopping behavior. Moreover the decrease in activation energy with decreasing temperature also indicates a gradual transition to the hopping regime [Mott and Davis 1979].

Figure 7: Plots of J vs. 1/T for Pppy Thin Films of Thickness 600 Nm in Ohmic and Non-Ohmic Regions
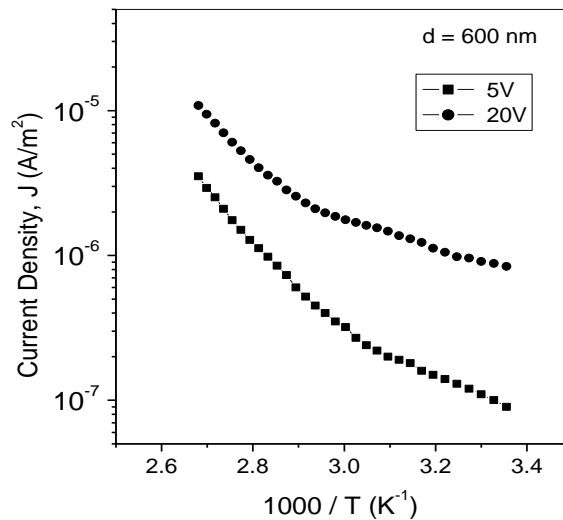
Table 1: Values of Activation Energy, ∆E, For Pppy Thin Films of Different Thicknesses

Thickness d (nm)	Activation energy ∆E (eV)			
	5 V		20 V	
	Temperature (K)		Temperature (K)	
	low (298-323)	high (348-323)	low (298-323)	high (348-398)
400±10	0.062±0.002	0.145±0.002	0.035±0.002	0.123±0.002
500±10	0.075±0.002	0.175±0.002	0.025±0.002	0.115±0.002
600±10	0.041±0.002	0.116±0.002	0.051±0.002	0.135±0.002

The theory of SCLC in defect insulators, which contains traps, was developed by Rose [1955]. In the presence of traps, a large fraction of the injected space charge will condense therein, which means that the free-carrier density will be much lower than in a perfect insulator. The conduction mechanisms in PPPy thin films, it is observed that at higher voltage a trap-mediated SCLC mechanism is shown by the thin films [Kamal and Bhuiyan, 2014], and since the occupancy of traps is a function of temperature, the SCL current will be temperature-dependent. The change in activation energies at higher temperatures in comparison to those at lower temperatures also suggests a considerable temperature-dependence of SCLC mechanism.

5. Conclusions

The temperature dependence of direct current electrical properties for PPPy thin films has been studied in this article. From *J-V* characteristics of PPPy monolayer 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. This change in the conductivity for different thicknesses suggests a probable change in physical properties during the formation of the plasma polymerized thin films. The most probable reason of this behavior may be due to better morphological characteristics of the films of lower thickness 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 curves at room temperature were characterized by two different slopes in lower and higher voltage region. It is observed that in low field region the curves follow Ohm's law but in high field region a non-linear non-Ohmic SCL conduction mechanism was found. From J-V plots at different higher temperatures the current density in all the samples were found to be increased slightly with increasing temperature for both the voltage regions. This increase may be due to the increased molecular motion at higher temperatures and indicates temperature dependence of the conductivity. The Arhennius plots (*log J* vs. *1/T* plot) were made and activation energies were calculated in both low and high temperature region and a trend of decreasing activation energy with decreasing temperature has been observed which indicates a gradual transition to the hopping regime. Moreover from the low temperature

activation energy a correlation with the hopping behavior was also suggested. However, the change in activation energy at higher temperature in comparison to that at lower temperature has been attributed to a considerable temperature-dependence of SCLC mechanism.

This paper is a part of a research work where an attempt was made to investigate the structural, optical and the electrical properties of PPPy, PPTMA and PPPy-PPTMA bilayer composite thin films. Some papers about this research have also been published earlier which are mentioned in the literature review. In this research it was observed that both the optical and electrical properties are thickness dependent. An intimately arising question from this observation is: how to describe the thickness dependence of these physical processes in thin polymer films? Our result was explained by using existing theories, but the reports on thickness-dependent optical and electrical properties were found to be less abundant in literature. To study the thickness dependence more precisely the Fourier Transform Infrared (FTIR) spectra could be taken and analyzed for the films of different thickness separately to know the probable structural change due to the change of the thickness. The x-ray diffraction (XRD) analysis could also be done for each thickness to get information about the chemical structure of the materials. The x-ray photoelectron spectroscopy (XPS) investigation which provides quantitative information of the element present could be carried on to study the bonding of different functionalities and chemical states in the thin films of different thickness. The scanning electron microscopy (SEM) analysis could provide information about the morphological change with the change of the thickness. The electron spin resonance (ESR) study may also be carried out to see the nature and source of radicals in this material. All the results of the above analysis could then be correlated with the thickness dependent optical and electrical properties of the thin films of different thickness.

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