

The dc electrical conduction mechanism of heat-treated plasma-polymerized diphenyl (PPDP) thin films

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Abstract Thin, uniform and pinhole-free plasma-polymerized diphenyl (PPDP) films were deposited using a capacitively coupled glow discharge reactor. The infrared (IR) analysis reveals that the heat-treated PPDP film structure is different from that of the monomer diphenyl. Study on dc electrical conduction mechanism has been performed on heat-treated PPDP films of different thicknesses. It is seen that Poole-Frenkel mechanism is found to be operative in the heat-treated PPDP films.

Keywords Electrical conduction, infrared spectroscopy, plasma polymerization

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1. Introduction

The production of polymer thin films of organic vapours by glow discharge techniques has been known for many years [1-3]. The plasma polymers and plasma-modified surfaces [4, 5] have gained considerable interest among the researchers. Plasma polymers have few additional advantages compared to the conventionally synthesized polymers, like excellent adhesion to the substrate, ease of preparation in completely dry atmosphere and possibility of preparing extremely thin, uniform and pinhole-free films. Owing to the wide range of possible technological applications of these films in various electronic devices, an elucidation of the underlying carrier generation and transport processes in them is important. Because of their high resistivity, high dielectric breakdown strength and cost effectiveness, these materials have found important applications as thin film insulators and capacitors in integrated microelectronics, passivation layers for integrated circuits, dry lithography for VLSI, electron beam or X-ray lithography, protective coatings and photoconductive devices [6-8].

Many scientists have investigated the electrical properties of various organic compounds produced by the glow discharge

technique. They have observed that three different conduction processes are involved. The first one is the injection of carriers from the electrode by means of thermal and field assisted emission, and is referred to as Schottky mechanism. The second process, in which the carriers are produced by the dissociation of donor-acceptor centres in the bulk of the material, is called Poole-Frenkel (P-F) conduction. If the generation processes are slower than the transport of carriers through a dielectric, the conduction is controlled by either the Schottky or the P-F mechanism. On the other hand, when the transport is slower than the generation of carriers, it constitutes the rate-determining step and the conduction can then be described as a space charge limited (SCL) conduction mechanism. A procedure commonly used to distinguish among these mechanisms is to examine the dependence of the current (I) or current density (J) on the applied voltage (V) and the sample thickness (d) and to compare these relationships with those predicted by the respective theories [9-14].

Particular interest has been established in the phenyl oligomers since the discovery that poly-p-phenylene could be made conducting by doping with acceptor or donor [15]. It may be noted that the reported intrinsic dc conductivity value of poly p-phenylene is of the order of $10^{-12} \Omega^{-1} \text{ m}^{-1}$ that could be

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increased to over $10^4 \Omega^{-1} \text{ m}^{-1}$ by doping. Although, interest has been shown on diphenyl [16, 17] there are scanty of reports on synthesis and characterization. Recently, the optical [18], chemical composition [19] and dielectric properties [20] of PPDP thin films have been investigated. In this paper, an attempt is made to elucidate the probable dc conduction mechanism of PPDP thin films heat-treated at 423 K.

2. Experimental details

2.1. Sample preparation :

Monomer diphenyl (C_6H_5)₂ of BDH Chemicals Ltd., England was purchased from local market. The PPDP thin films were prepared using a bell-jar type capacitively coupled glow discharge system. Chemically cleaned microscope glass slides were used as substrates. The film deposition conditions utilized in this investigation are (i) substrates were placed on the top of the bottom electrode, (ii) maximum deposition time was 1 hour, (iii) electrode separation was 0.04 m, (iv) deposition power was about 40 W at 50 Hz, and (v) pressure during deposition was about 30 Pa. The more details of plasma polymerization system and the control of deposition parameters used in this study has been reported elsewhere [21].

Transparent light yellow colour PPDP thin films up to a few hundred nm thick were deposited onto the glass substrates. Samples were prepared under the same deposition condition. The thickness was determined by producing a well-defined film outline using mask and then measuring the step height by interferometry technique.

2.2 IR Spectroscopy :

The PPDP deposited on to the substrates was collected by scrapping off from the substrate before heat treatment. The KBr pellets of monomer diphenyl and PPDP films heat-treated at 473 K (for two hours) prepared and IR spectra were recorded at room temperature on an IR spectrometer (IR-470, Shimadzu Corporation, Japan) All the spectra were recorded in transmittance (%) mode in the wave number region 4000 to 400 cm^{-1} .

2.3 dc measurements :

Aluminium (Al of purity 4N (British Chemical Standard) was coated by vacuum evaporation at about 10^{-4} Pa to act as lower electrode onto chemically cleaned glass substrates by Edward's coating unit (model E-306). The PPDP thin films were deposited over the lower electrode and finally Al was evaporated on PPDP thin film as before to act as upper electrode. A number of PPDP films were heat-treated at 423 K for a period of two hours in a furnace.

For dc measurement, samples of sandwiched (Al/PPDP/Al) structure with vacuum evaporated Al metal thin film electrodes on both sides were used. The electrical measurements were carried out in a stainless steel chamber under inert (argon)

atmosphere to avoid oxidation. The circuit diagram for current-voltage measurements is shown in Figure 1. The current across the heat-treated PPDP thin films was measured at different temperatures by a digital Keithley electrometer 614, and the voltage was supplied using a stabilized dc power supply (PS : 5000N of Ogawa Seiki Co. Ltd., Japan).

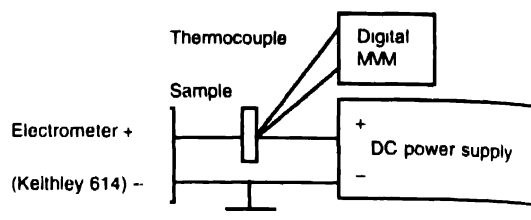


Figure 1. A schematic circuit diagram of dc measurement

The samples were heated by heating the specimen chamber externally by a heating coil during measurement. A variable resistance was used to control the current through the coil. The temperature was recorded by a Cr-Al thermocouple placed very close to the sample which was connected to a Keithley 197A digital multimeter.

3. Results and discussion

3.1 IR spectroscopy .

The IR spectra of monomer (diphenyl) and PPDP heat treated at 473 K for two hours are presented in Figure 2. The IR spectra of diphenyl and heat-treated PPDP film are represented by spectra A and B, respectively. These spectra reveal the heat-treated PPDP structure is different from that of monomer.

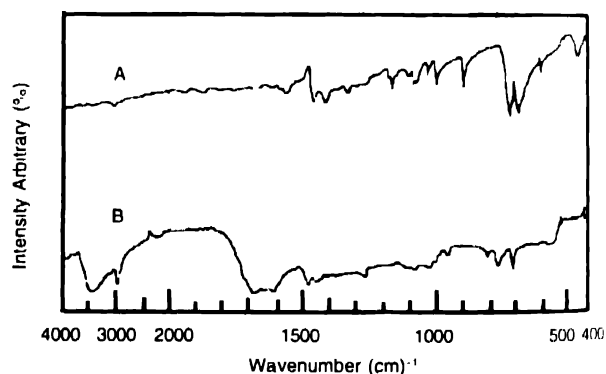


Figure 2. The IR spectra of monomer (C_6H_5)₂ and PPDP films heat treated at 473 K

The spectrum A is well matched with the standard IR spectrum of diphenyl [22]. The band assignments of monomer diphenyl are depicted in Table 1. In the spectrum B of heat-treated PPDP, a broad band around 3450 cm^{-1} is due to the presence of O-H stretching vibration for absorbed water in the PPDP film. The vibration at 2915 cm^{-1} is owing to the C-H stretching of aromatic ring structure. The wide band at $1850\text{--}1450 \text{ cm}^{-1}$ can be assigned to aromatic ring stretching vibration for C=C in the structure and to the stretching vibration of C=O

Table 1. IR band assignment of monomer $((C_6H_5)_2)$.

Peak position (cm^{-1})	Band assignment
2915	$\nu(C-H)$ of aromatic ring
1900-1667	Over tones of aromatic ring
1650-1450	$\nu(C=C)$ of aromatic ring
1170-1040	$\delta(C=H)$ in-plane
740-680	$\delta(=C-H)$ out-of-plane

ν -stretching, δ -bending

group which is typical for plasma polymer. The weak bands at $1140-950\text{ cm}^{-1}$ correspond to the C = H in-plane bending and bands $800, 760$ and 700 cm^{-1} correspond to the = C-H out-of-plane phenyl ring bending. Thus, the IR spectrum of heat-treated PPDP shows the main absorption band features of the monomer diphenyl except for bands corresponding to C = O and O-H [18]. The above observations reveal that the PPDP films contain an aromatic ring structure with CH side groups. Thus, the heat-treated PPDP thin film composed not only of the corresponding monomer bands but also of new bands which were absent in the monomer spectrum, namely C = O and O-H stretching vibration. The band assignments of heat-treated PPDP film are summarized in Table 2.

Table 2. IR band assignment of heat-treated PPDP film

Peak position (cm^{-1})	Band assignment
1450	$\nu(O-H)$ [new]
2915	$\nu(C-H)$ of aromatic ring
1850-1450	$\nu(C=C)$ of aromatic ring and $\nu(C=O)$ [new]
1110-950	$\delta(C=H)$ in-plane
800	$\delta(=C-H)$ out-of-plane
760	$\delta(=C-H)$ out-of-plane
700	$\delta(=C-H)$ out-of-plane

ν -stretching, δ -bending

The formation of carbonyl group is usually attributed to the oxidation of the hydrocarbon part of the PPDP after exposure to air owing to oxygen reactions with a radical species (dangling bonds) trapped in the structure of plasma polymer. Cross-linking may also occur between different carbons of the chains due to the loss of hydrogen, particularly in the plasma-polymerized films because of the impact of energetic particles within the plasma during deposition.

3.2 Electrical properties :

For the modes of carrier transport in insulating polymer films, various mechanisms has been suggested based on the current density dependence on voltage, temperature, film thickness,

etc. The criterion for establishing the predominance of a particular mechanism is to analyze the dependence of the current density on these parameters.

The detailed information about the transport mechanism through the heat-treated PPDP may be obtained from the current density vs. applied voltage ($J-V$) characteristics analysis. The $J-V$ characteristics of heat-treated PPDP thin films of different thicknesses and at different temperatures were investigated in the dc voltage range 0.2-15.0 V. The voltage dependence of current density or current can be expressed as

$$J \propto V^n \quad (1)$$

where n is a power factor. When $n \equiv 1$, the conduction is ohmic and $n \geq 2$, the conduction is non-ohmic.

Typical $J-V$ characteristics of these samples are presented in Figure 3. In these plots, two different voltage regions are observed with slopes $n \sim 1$ and $n \sim 2$ in the lower (ohmic) and higher voltage regions (non-ohmic), respectively. In the first region, current density is observed to be proportional to the applied voltage (ohmic region). In the second region, a power dependence of current density on the applied voltage *i.e.* $J \propto V^n$ occur with $2.02 < n < 2.33$. This is a common feature of most organic layers with low mobility and high resistivity. It is observed that the value of the exponent n decreases with increasing temperature.

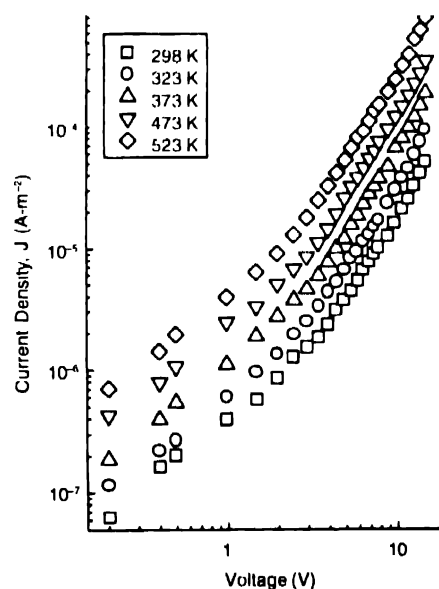


Figure 3. Plots of current density against applied voltage at different measurement temperatures for heat-treated PPDP film ($d = 200\text{ nm}$)

The slopes are found to decrease with increasing thickness in both regions. This type of change in conduction process is not unusual because of the carrier motion may be thickness dependent, *i.e.*, the conduction current in the heat-treated PPDP films may be inversely proportional to the power of the sample thickness; this will be discussed below. A slope $n \geq 2$ suggests

the possibility of space charge limited (SCL) conduction [23] and the current density can be presented as :

$$J = \frac{9}{8} \mu \epsilon \epsilon_0 \frac{V^2}{d^3} \tag{2}$$

where μ is mobility of charge carriers, ϵ is permittivity of the dielectric material, ϵ_0 is permittivity of free space, V is the applied voltage and d is the thickness.

The voltage dependence of current suggests that the current may be SCL in the heat-treated PPDP films above 5.0 V. The thickness dependence of the current in the SCL region follows the relation

$$J \approx d^{-1} \tag{3}$$

where 1 is a parameter depending upon the trap distribution; in the presence of traps, $1 \geq 3$.

In Figure 4, the J at room temperature is plotted against d . The slopes are found to be 1.25 and 1.63 in the first and second

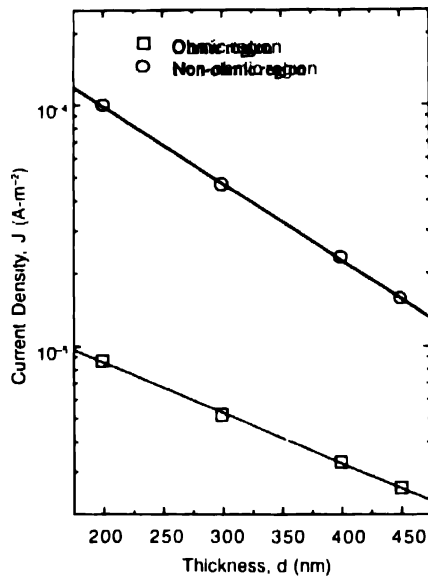


Figure 4. Plots of current density against thickness for the heat-treated PPDP films in the ohmic and non-ohmic regions

voltage regions, respectively. In the second region, the slope is much less than that corresponding to SCL conduction. These observations suggest that the conduction in heat-treated PPDP may be different from SCL conduction. As the PPDP were grown in a plasma discharge, they are likely to contain a high concentration of trapping sites. Since SCL conduction does not occur in this material, an alternative assumption is that the conduction mechanism may either be Poole-Frenkel (P-F) or Schottky type. The general expression for the J that is equally valid for both the P-F and Schottky mechanism is of the form

$$J = J_0 \exp \left(\frac{\beta F^{1/2} - \phi}{k T} \right) \tag{4}$$

where J_0 is the low field current density; β is the coefficient; F is the static electric field and is equal to V/d ; V is the applied voltage, d is the film thickness; ϕ is the ionization energy of the localized centres in Poole-Frenkel conduction and Coulombic barrier height of the electrode-polymer interface in Schottky conduction; T is the absolute temperature, and k is the Boltzmann constant. The coefficient β for the Schottky-type mechanism is known as Schottky coefficient, β_s , and is defined as

$$\beta_s = \frac{e^{1/2}}{4\pi \epsilon_0 \epsilon} \tag{5}$$

For the P-F mechanism, it is called Poole-Frenkel coefficient, β_{PF} , and is defined as

$$\beta_{PF} = \left(\frac{e^3}{\pi \epsilon_0 \epsilon} \right)^{1/2} = 2\beta_s, \tag{6}$$

where e is the electronic charge, ϵ is the high frequency dielectric constant (4.71 for heat-treated PPDP sample having thickness, $d = 200$ nm) and ϵ_0 is the permittivity of free space

For a constant applied voltage at a particular temperature the current density expression (eq. (4)) can be written as

$$\log J = d^{-1/2} \text{ or } \approx V^{1/2}. \tag{7}$$

Thus, for the P-F or the Schottky mechanism, the plot of the $\log J$ against the square root of the film thickness, $d^{1/2}$, should be a straight line. Figure 5 shows a plot of J versus $d^{1/2}$ for heat-treated PPDP thin films. It is observed that the experimental points fit a straight line, in accordance with eq. (7).

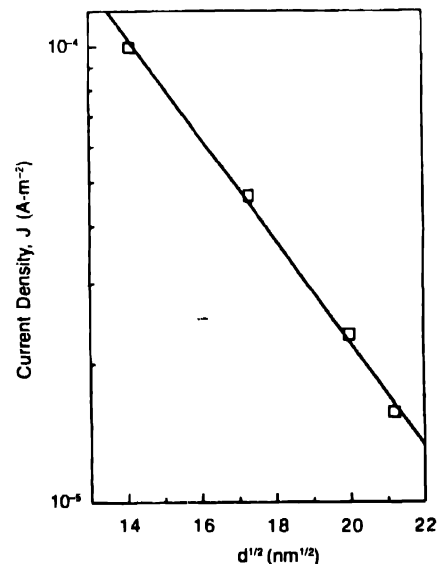


Figure 5. The dependence of current density J on square root of sample thickness $d^{1/2}$ for the heat-treated PPDP films in the non-ohmic region.

Furthermore, in order to ascertain the most probable conduction mechanism in heat-treated PPDP films, plots of J versus $V^{1/2}$ at different temperatures are shown in Figure 6. It

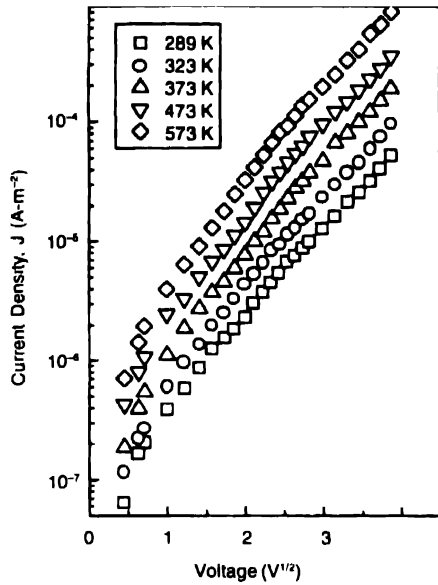


Figure 6. Variation of current density J with square root of applied voltage $V^{1/2}$ for the heat-treated PPDP films at different temperatures ($d = 200$ nm)

matching between the values of β (experimental) is observed with the β_{PF} (theoretical). This again indicates the dominance of P-F type conduction in the heat-treated PPDP films.

4. Conclusions

The IR analysis and electrical conduction mechanism of heat-treated PPDP have been discussed. The IR analysis indicates that the structure of heat-treated PPDP thin film deposited by glow discharge technique is different from that of monomer because of possible cyclization/aggregation and cross-linking in the film structure. On heat treatment, cyclization/aggregation may occur by the removal of radicals and/or dangling bonds. The study of the current-voltage characteristics reveals that the dc conduction of heat-treated PPDP thin film is governed by Poole-Frenkel mechanism.

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Table 3. Values of d , ϵ' , T , β , β_s and β_{PF} for heat-treated PPDP thin films

Film thickness d (nm)	Dielectric constant ϵ'	Measurement temperature T (K)	Experimentally observed β ($eV \cdot m^{1/2} V^{-1/2}$)	Values of β_s from eq 3 ($eV \cdot m^{1/2} V^{-1/2}$)	Values of β_s from eq 4 β_{PF} ($eV \cdot m^{1/2} V^{-1/2}$)
450			2.83×10^{-5}		
400			3.16×10^{-5}		
300			2.62×10^{-5}		
200	4.71	298	2.60×10^{-5}	1.74×10^{-5}	3.48×10^{-5}
200	4.78	323	2.72×10^{-5}	1.73×10^{-5}	3.46×10^{-5}
200	4.85	373	2.80×10^{-5}	1.72×10^{-5}	3.44×10^{-5}
200	4.93	473	2.98×10^{-5}	1.71×10^{-5}	3.42×10^{-5}
200	5.10	523	3.29×10^{-5}	1.68×10^{-5}	3.36×10^{-5}

can be seen that these curves are linear, again indicating the presence of P-F or Schottky type mechanism. To identify the dominant mechanism, the values of β (experimental) were obtained from the slopes of the plots in Figure 6. The values of β_s (theoretical) and β_{PF} (theoretical) are calculated using eq. (5) and (6), respectively. The experimental β values of different film thicknesses at different temperatures are compared with the theoretical β_s and β_{PF} values in Table 3. From the different values of β (experimental) and β (calculated from eq (4)) as depicted in Table 3 that the β (experimental) is in between the β_s and β_{PF} value. But β (experimental) values increases with both thickness and measurement temperature. Better

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