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Mechanism of electrical conduction in plasma polymerized furfural thin films

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Abstract

Polyfurfural thin films lying in the thickness range of 1300–2000 Å were prepared by ac plasma polymerization technique. The current–voltage characteristics in symmetric and asymmetric electrode configuration were studied with a view to determining the dominant conduction mechanism. It was found that the Schottky conduction mechanism is dominant in plasma polymerized furfural thin films. The predominance of Schottky mechanism was further confirmed based on the thermally stimulated current measurements.

Keywords: Plasma processing and deposition; Polymers; Conduction mechanism; TSC

1. Introduction

Plasma polymerization is an inexpensive and promising technique for the preparation of polymer thin films of varying thickness on various substrates from almost any organic vapor [1,2]. The polymers formed by plasma polymerization are different from the polymers formed by other conventional techniques [3,4]. The properties of these films can be altered by varying the deposition parameters like pressure, applied current, monomer flow rate and time of polymerization. By employing this technique it is possible to deposit polymer films which are pin hole free, chemically inert, adhesive and thermally stable.

Polymer films have been extensively investigated in the recent past due to their potential applications in LEDs, Sensors, EMI shielding and in Photovoltaic devices [5–9]. However, applications of these films in commercial processes have been rather slow. Additional fundamental understanding of electrical properties is essential before extensive use is made of plasma polymerized films in these devices. Many researchers have carried out studies on the conduction mechanism of plasma polymerized thin films. For example, Boben et al. [10] have observed Schottky mechanism in plasma polymerized thiophene films, Jacek Tyczkowski et al. [11] have reported that the conduction mechanism in plasma polymerized hexamethylcyclotrisilazane is electrode limited Schottky conduction while Szeto et al. [12] have reported Poole–Frenkel conduction in plasma polymerized tetramethylsilane films, Suleimanov et al. [13] investigated the electrical properties of plasma polymerized acetonitrile in the high and low conduction states and found that in high conduction state it is predominately Schottky and in the low conduction state it is the Poole–Frenkel type, Sakthikumar et al. [14] in their studies conducted on plasma polymerized lemon grass oil have come to a conclusion that Schottky type conduction is predominant. The structure and properties of polyfuran thin films synthesized by plasma polymerization techniques have also been reported [15]. Sharma et al. [9] have reported the preparation of a furfural resin thin film device by thermally induced polymerization and its photovoltaic behavior has been studied. In the present study furfural is chosen as the monomer because, furfural being a derivate of furan, is expected to yield polymer films with interesting properties in a

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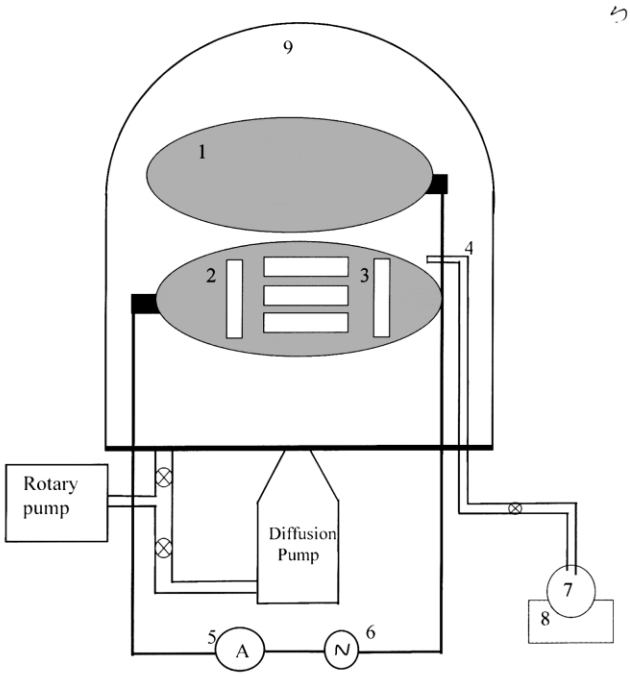

Fig. 1. Ac plasma polymerization setup (1 and 2) Stainless Steel Electrodes, (3) Substrates, (4) Sprayer, (5) Ammeter to Control Current (6) AC Power Supply, (7) Monomer Holder (8) Monomer Heater, (9) Glass Bell Jar.

plasma discharge. Moreover, to our knowledge reports on the preparation and electrical properties of ac plasma polymerized furfural thin films are scanty. In the present investigation, the preparation of ac plasma polymerized furfural thin films and their electrical and thermal characterization are reported. These studies are carried out in order to understand the mechanism involved in the conduction process.

2. Experimental

Polyfurfural thin films were prepared by ac plasma polymerization technique. The experimental setup is as shown in Fig. 1. It consists of two parallely placed stainless steel electrodes of diameter 0.23 m each and 2×10^{-3} m thick, which are placed 0.05 m apart. Chemically and ultrasonically cleaned glass substrates, some of them pre-coated with Al/Au/Ag were placed on the lower electrode for plasma polymer deposition. The glow discharge chamber was evacuated and monomer furfural is injected in between the electrodes by means of a sprayer at a monomer vapor pressure of 0.2 torr. The plasma discharge is obtained between the electrodes by applying a low frequency (50 Hz) ac voltage (500–800 V) controlled by the current in the range of 40–80 mA. The conditions for depositing plasma polymer films on substrates were standardized and optimized [16].

Polymer thin films were grown under optimum conditions on the substrates kept on the lower electrode. These polymer coated substrates were then transferred with appropriate masks into a conventional metal coating unit for coating the second electrode (Al/Au/Ag) under a pressure of 7×10^{-6} torr. These films were in the form of Metal/polymer/Metal of cross sectional area 2.5×10^{-5} m^2. The thickness of the polymer films was measured by interferometric techniques (Tolansky technique) [17] and the thickness values lie in the range of 1300–2000 Å.

For conduction mechanism studies, these sandwich samples were placed in a home built conductivity cell in which the temperature could be varied from 300 to 423 K by a digital temperature controller and the temperature was measured by a Fe–K thermocouple kept on the sample. A bias voltage in the range 0–60 V was applied and the current flowing across the sample was measured by a Keithley Picoammeter/Voltage source (Model 487). All the measurements were carried out under dynamic vacuum. The acquisition and analysis of the data were completely automated by employing the LabVIEW software (National Instruments).

FTIR spectra of these samples were recorded by a Nicolet Avatar 360 FTIR spectrophotometer and these results have been cited elsewhere [16]. Thermally stimulated current (TSC) measurements were carried out on a polyfurfural thin film of thickness 1750 Å sandwiched between two Al electrodes in Al/polyfurfural/Al configuration. The sample was cooled to 77 K in a cryostat (CTI-Cryogenics), subjected to illumination and then heated linearly at a rate of 5 K/min. An electric field was applied on cooling, illumination and heating. As the temperature (measured by Lakeshore temperature controller 321) was linearly increased the current across the sample was measured by a Keithley 236 SMU.

3. Results and discussion

3.1. J–V studies on symmetric electrode configuration

Various mechanisms have been suggested for the carrier transport in insulating polymer thin films based on the dependence of current density on voltage, temperature and thickness. To establish the predominance of a particular mechanism it is necessary to analyze the dependence of current density on the above mentioned parameters.

A typical room temperature *J–V* plot of polyfurfural thin film for different thickness values is shown in Fig. 2. The plot consists of two regions; in the lower range of applied voltage the slope is approximately 1.1 and in the higher range of applied voltage the slope is approximately 1.6. The conduction in the lower region of the

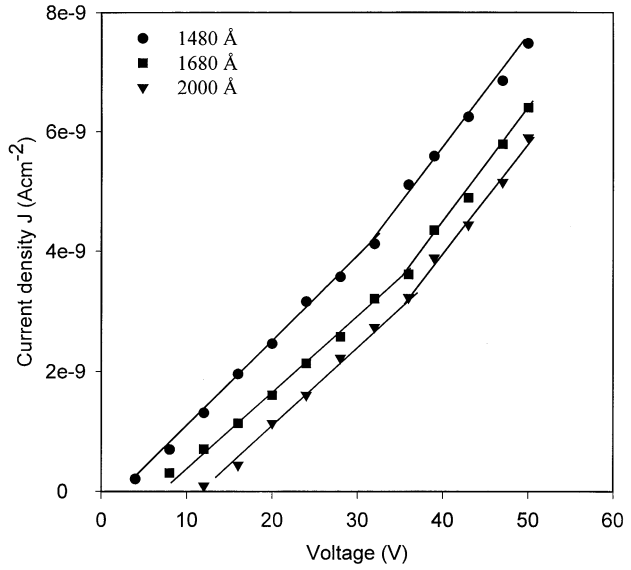

Fig. 2. Current density against applied voltage for Al/polyfurfural/Al of different thickness at room temperature.

applied voltage is found to be ohmic. Normally for space charge limited conduction, the slope in the non-ohmic region should be equal to or greater than two. In the present case the values of slope are smaller than those required for space charge limited conduction (SCLC).

According to SCLC [18] theory, the thickness dependence of the space charge limited current follows the relation of $J\alpha d^{-n}$, where n is a parameter which depends on the trap distribution and is equal to or greater than three in the presence of traps. The thickness dependence of the current density for plasma polymerized furfural thin films is shown in Fig. 3 and the current density varies as d^{-2}. The value two is much less than the required exponent value for space charge limited conduction and so SCLC conduction mechanism is ruled out. Having eliminated the occurrence of SCLC, an alternate assumption is that the conduction mechanism may be either due to Poole–Frenkel or Schottky.

The Poole–Frenkel effect [18] involves the emission of trapped electrons or holes. On applying an external field, the potential barrier at the trap is lowered and the carriers escape easily, giving rise to a bulk conductivity governed by the relation,

$$\sigma = \sigma_o F \exp\left(\frac{\beta_{PF} F^{1/2} - E_d}{kT}\right) \quad (1)$$

where $\sigma_o = e\mu n_{o,}$ is the low field conductivity, μ is the low field mobility, n_o is the carrier concentration, E_d is the ionization potential of the Poole–Frenkel centers, F is the field applied ($F = V/d$, where V is the applied voltage and d the thickness of the sample) and β_{PF} is Poole–Frenkel coefficient given by

$$\beta_{PF} = \left(\frac{e^3}{\pi \varepsilon \varepsilon_o}\right)^{1/2} \quad (2)$$

where ε is the high frequency dielectric constant and ε_o is the permitivity of free space.

In the Schottky type conduction the electrode effects limit the conduction current. The expression for the current density for the electrode limited Schottky type conduction is given by

$$J = AT^2 \exp\left(\frac{\beta_s F^{1/2} - \phi}{kT}\right) \quad (3)$$

here F is the applied field, ϕ is the electrode–polymer interface barrier height and β_s is the Schottky coefficient given by

$$\beta_s = \left(\frac{e^3}{4\pi \varepsilon_o \varepsilon}\right)^{1/2} \quad (4)$$

A general expression which holds equally well for both types of conduction mechanisms is of the form [10]

$$J = J_o \exp\left(\frac{\beta F^{1/2} - \phi}{kT}\right) \quad (5)$$

A plot of log J vs. $V^{\frac{1}{2}}$ yielded a straight line as shown in Fig. 4. This further confirms that the conduction mechanism is due to either Poole–Frenkel or Schottky.

The easiest way to differentiate between the two mechanisms is to compare the theoretical and experimental β values. The experimental value of β (β_{exp} =

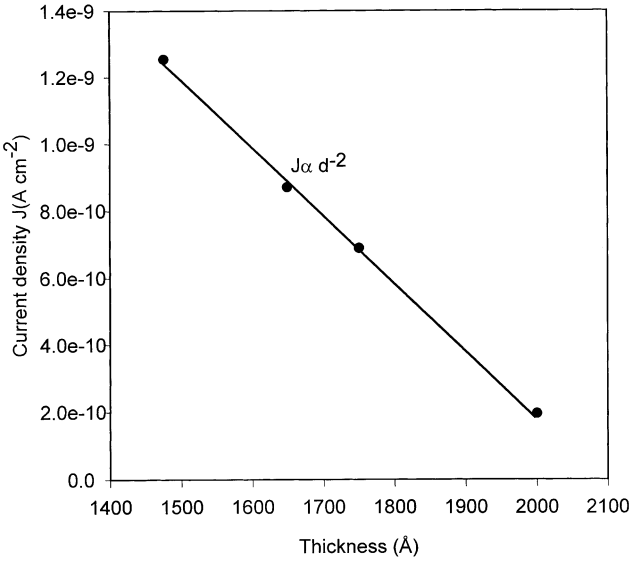

Fig. 3. Thickness dependence of current density for Al/polyfurfural/Al at room temperature.

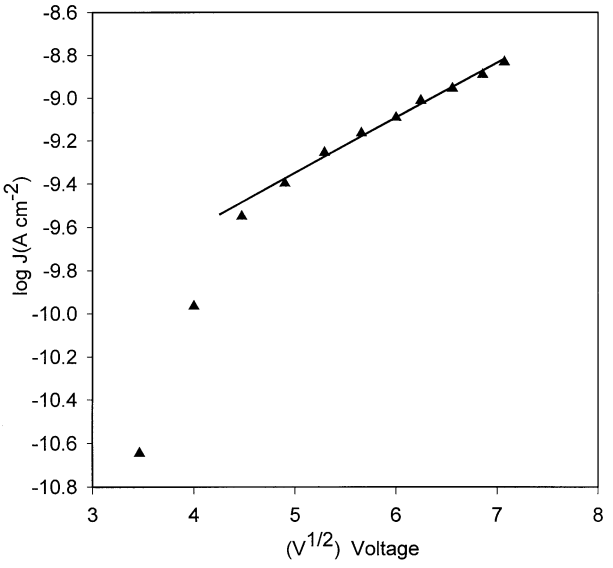

Fig. 4. Schottky plot of Al/polyfurfural/Al sandwich structure polymer film thickness 2000 Å at room temperature.

$\alpha kTd^{1/2}$) can be obtained from the slope(α) of the linear portion of log J vs. $V^{1/2}$ plot and the theoretical coefficients β_s and β_{PF} can be calculated by using Eqs. (2) and (4), respectively. High frequency dielectric constant(ε) of plasma polymerized furfural film was estimated from optical transmission studies in the near IR-visible region and the value was found to be 2.25. This value of ε was substituted in Eqs. (2) and (4) for evaluating the theoretical β values and are tabulated in Table 1 along with the experimentally obtained β value.

A comparison of the values of the β coefficients indicates that in the present case the possibility for Schottky type conduction is more probable. However, reports [19,20] indicate that the differentiation between the two conduction mechanisms is not easy and the difference of a factor of two between the β_s and β_{PF} is not sufficient enough to prove the dominance of either Poole–Frenkel or Schottky type conduction mechanism [21]. Thus, to confirm the dominance of the Schottky type conduction, two different sets of experiments: (i) TSC studies and (ii) J–V characteristics for asymmetric electrode configuration were carried out. These results are discussed below.

3.2. Thermally stimulated current studies

The presence or absence of Poole–Frenkel type trapping centers in the sample can be confirmed by TSC measurements. When a field is applied the potential barrier at the trap is lowered and due to heating the trapped carriers are liberated and a maximum current is produced in the TSC plot of current vs. temperature. It has been reported [11,22] that when the trapped centers are of Poole–Frenkel type the temperature T_m corresponding to the maximum current is field dependent and is given by

$$T_m = \frac{E_o}{kC} - \frac{\beta_{PF}}{kC} F^{1/2} \quad (6)$$

where E_o is height of the unaffected barrier, k a constant and the factor C varies weakly with field and thus it is neglected. Schottky effect also results in a field dependence of the conductivity, but it has only a minor effect on the position of TSC peak and it cannot be detected by this technique. TSC studies were carried out at different fields in the range of 8.5×10^7–2.8×10^8 V/cm. Zielinski et al. [23] have carried out TSC measurements on poly *N*-vinylcarbazole and found that the temperature T_m corresponding to the maximum current shifts with applied field and therefore concluded that Poole–Frenkel effect is dominant in poly *N*-vinylcarbazole. In our case, in the whole range of field studied the field dependence of the temperature(T_m) corresponding to the maximum current was negligible, thus eliminating the presence of Poole–Frenkel centers in plasma polymerized furfural thin films.

3.3. J–V studies on asymmetric electrode configuration

Eq. (5) indicates that for both type of conduction mechanisms the current depends exponentially on the barrier height ϕ. Thus, the current should also be asymmetric when the bias polarity is reversed in an asymmetric electrode configuration. The J–$V^{1/2}$ characteristics are therefore plotted for an asymmetric electrode configuration. This provides valuable information regarding the electrode dependence of the conduction current. Fig. 5 is a typical plot obtained for Au/polyfurfural/Al asymmetric electrode configuration of the sample thickness 2000 Å. The two curves in the plot indicate the two directions of the applied field.

When a polymer film is inserted between two different metal electrodes, the barrier heights at the two polymer–metal electrode interface differ by the difference between the workfunctions of metal electrodes. Theoretically for Schottky type conduction [23] a workfunction difference of approximately 0.06 eV between the metal electrodes should result in a decade difference in the current levels, measured for opposite polarity of the applied field. The difference between the workfunctions of the two metal

Table 1
Theoretically calculated and experimentally obtained β cofficients values

Film thickness in Å	Experimental β ($eVm^{1/2}V^{-1/2}$)	Theoretical β_s ($eVm^{1/2}V^{-1/2}$)	Theoretical β_{PF} ($eVm^{1/2}V^{-1/2}$)
1480	1.83×10^{-5}	2.53×10^{-5}	5.06×10^{-5}
1650	2.39×10^{-5}		
2000	2.73×10^{-5}		

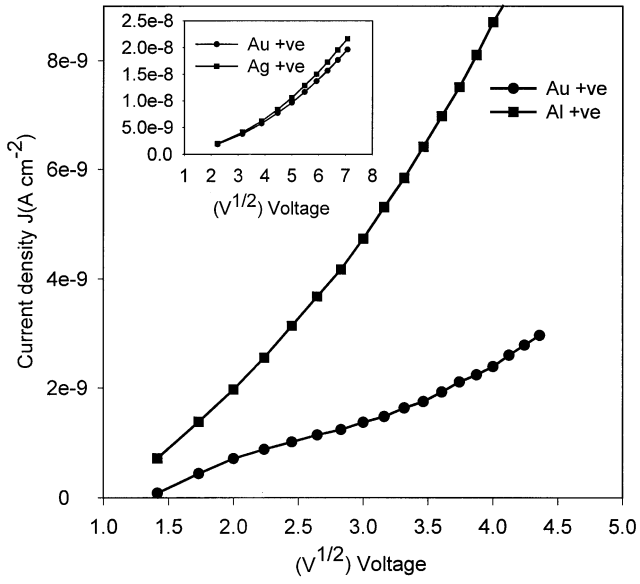

Fig. 5. Schottky plot for asymmetric electrode configuration Au/polyfurfural/Al of thickness 2000 Å at room temperature. Insert graph is for Au/polyfurfural/Ag asymmetric electrode.

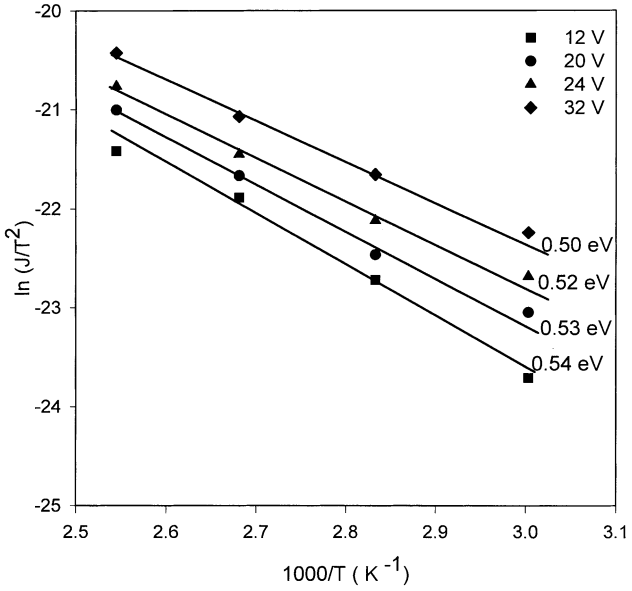

Fig. 6. Plot of $\ln(J/T^2)$ against $1000/T$ for Al/polyfurfural/Al structure of film thickness 1480 Å for different applied bias voltages.

electrodes in Au/polyfurfural/Al asymmetric electrode configuration is approximately 0.82 eV, hence many orders of change should occur in the current density values for opposite directions of the applied field. However, in Fig. 5 the difference in the current density for opposite polarity of the applied field in Au/polymer/Al asymmetric electrode configuration is quite small. This small difference in the current density may be due to the surface states present at the polymer and electrode interface, which can change the potential barrier.

According to Mizutani [24] when asymmetric electrode configuration is employed, the small difference in the barrier heights may be due to the phenomenon of equalization of metal polymer contact barriers. The difference in the current density values for opposite directions of the applied field can hence be related to electrode dependent Schottky type conduction. The different slopes of the two curves in Fig. 5 for opposite polarization of the asymmetric electrode configuration clearly indicate that barrier heights play a significant role in the conduction process.

3.4. Activation energy and barrier height

From Eq. (3), the Schottky type conduction mechanism requires that the plots of $\ln(J/T^2)$ vs. $(1/T)$ for different bias voltages should be linear. The activation energies can be obtained from the slope of the linear portion of $\ln(J/T^2)$ against $(1/T)$ plot as shown in Fig. 6 for Al/polyfurfural/Al of film thickness 1480 Å. From Fig. 6, it is observed that the activation energy decreases from 0.54 to 0.50 eV, as bias voltage is increased from 12 to 32 V. On extrapolating to zero bias the plot between the activation energies and the square root of the applied voltage, will provide the barrier height and it is shown in Fig. 7. The value of Al/polymer interface barrier height obtained on extrapolating to zero bias is 0.61 eV.

4. Conclusion

Polyfurfural films with different thickness values were prepared by ac plasma polymerization technique. The

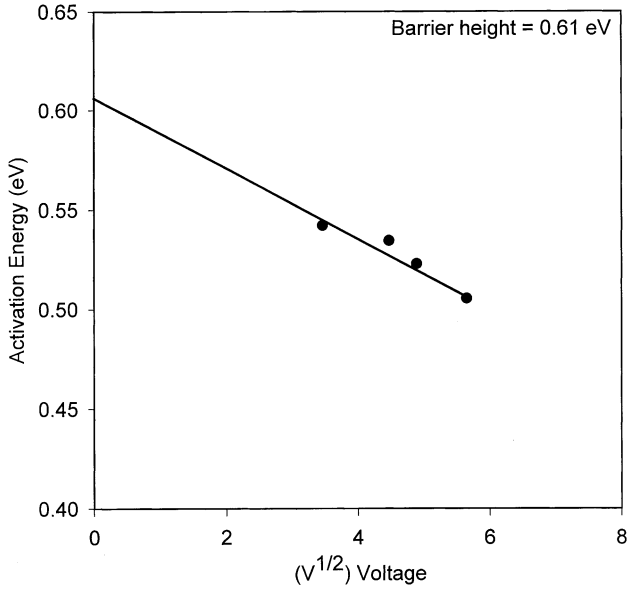

Fig. 7. Activation energies obtained from Fig. 6 plotted against the square root of the applied voltage for Al/polyfurfural/Al of film thickness 1480 Å.

possibility of SCLC was eliminated on the basis of the thickness dependence of the current density. From TSC measurements, Poole–Frenkel conduction was ruled out. Asymmetric electrode configuration studies show that barrier heights play a significant role in the conduction process. It was found that the conduction is an activated process with activation energy decreasing from 0.54 to 0.50 eV as the bias voltage is increased. From the above observations it can be inferred that Schottky type conduction is dominant in plasma polymerized polyfurfural thin films.

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