JOURNAL OF MATERIALS SCIENCE **35** (2000) 4427 – 4430

On the mechanism of electrical conduction in plasma polymerized furan films

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Dark conduction in radio frequency plasma polymerized Furan thin film is reported. A contact limited Schottky mechanism is found to predominate. A comparison of the value from different experimental studies and the value from theoretical studies confirm the Schottky type mechanism in Furan thin film.

1. Introduction

Polymers formed by plasma polymerization demonstrate unique chemical and physical properties. Plasma polymers are amorphous, hard, tough, insoluble in organic solvents and resistant to high temperatures. The unique properties result mainly from the chemical structure of the plasma polymer chains, which are highly crosslinked and branched. For tailoring these polymers for different uses in the electronics industry it is essential to determine the conduction mechanism in their films. This report is an attempt to analyze the electrical conduction in plasma polymerized Furan films. As an electrical property, Abraham *et al*. have reported switching in plasma polymerized Furan [1]. In this paper we are reporting the mechanism of conduction in plasma polymerized Furan film. Using the technique of radio frequency plasma polymerization, we have obtained comparably good, slightly brown coloured polymer films from Furan.

2. Exprimental details

Polymer films of Furan were obtained by polymerizing monomer Furan in a radio frequency discharge plasma. The experimental set up is shown in the Fig. 1. In this experimental set up, the polymerization section consists of a deposition cell made of borosilicate glass tube and is about 0.5 m. long and has an outer diameter of 0.035 m. The monomer vapour container with the monomer is attached to the deposition chamber through a vacuum cock and needle valve. Power from the radio frequency oscillator power supply is capacitively coupled to the deposition chamber by means of copper foils wrapped around. The monomer obtained from Aldrich (AR grade) was used without further purification. Polymer films in the thickness range 100 nm. to 500 nm. were grown under a plasma current density of 200 A/m^2 and at a monomer vapour pressure of 26.7 Pa. Electrical studies were carried out on metal - polymer - metal sandwich structures of area 0.25×10^{-4} m^2. Metal electrodes of thickness about 200 nm of Al, Ag, Au were deposited by the conventional thermal evaporation technique under a pressure of 2.7×10^{-3} Pa. Samples for the electrical studies were prepared in the following way. After the deposition of the first electrode, polymer was deposited on the electrode, and before depositing the counter electrode the samples were dried at a pressure of 1.3 Pa at 150°C for 1 hour. Electrical measurements were carried out in a metal chamber under vacuum conditions (1.3 Pa). The current flowing through the films was measured using an electrometer amplifier (Keithley model 617). Unless otherwise specified, readings were taken with an applied voltage of 2V in each case. A copper constantan thermocouple mounted on the sample holder, with the fused end in contact with the polymer film, permitted temperature measurements using a APPA Classic 108 digital multimeter. The thicknesses of the samples were measured using the Tolansky multiple beam interferometer technique [2]. We have done optical transmission studies in the VIS - NIR region to obtain high frequency dielectric constant of plasma polymerized films.

3. Mechanism of electrical conduction in plasma polymerized Furan thin films

Towards establishing the predominance of a particular mechanism of conduction, analysis of the dependence of current density on voltage with variation of temperature, thickness, electrode materials etc. has been suggested [3]. For all these studies we have used vacuum annealed samples.

The current - voltage relationship of the polymer film with Aluminium as electrode is represented in J (current density) against V (applied voltage) in Fig. 2. The plots are for thickness values 165, 220 and 325 nm. The plots consists of two regions and have the same slope in the first region for all the three films (0.79). In the second region the slope varies from 0.99 to 1.05 depending on polymer film thickness. The first region corresponds to the ohmic region. Generally such a plot between current density and applied voltage, with a slope equal to, or greater than 2, in the region beyond the ohmic region suggests the possibility of space - charge - limited conduction [3, 4]. However, the present slope values (1.02, 0.99, 1.05) are smaller than 2 and hence we can rule out

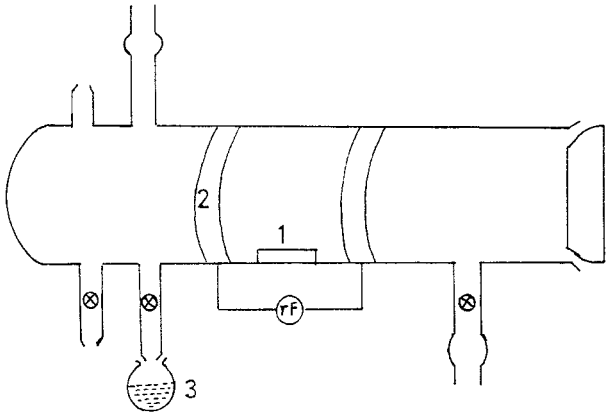

Figure 1 Plasma polymerization set up. 1-substrate 2-Copper foils 3-Monomer.

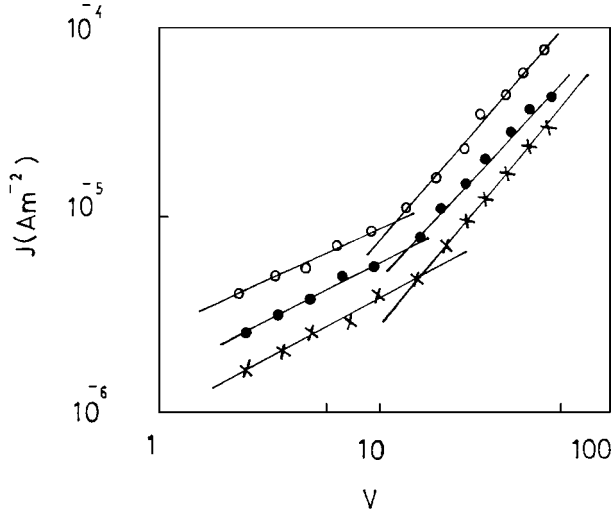

Figure 2 J (Current density) vs V (Applied voltage) for different thicknesses. × 325 nm ● 220 nm ○ 165 nm.

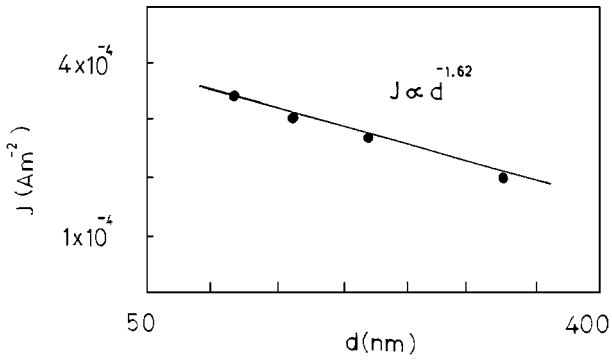

Figure 3 Thickness depends of conduction current in Al-PF-Al.

the possibility of the space charge limited conduction mechanism.

The thickness dependence of the space - charge - limited current is expressed as $J \propto d^{-n}$ where 'n' is a parameter depending upon the trap distribution and is equal to, or greater than 3 in the presence of traps. In Fig. 3, which illustrates the thickness dependence of the current density for plasma–polymerized Furan films, with Aluminium electrodes, the current density varies as $d^{-1.62}$. Since polymer films were grown in a plasma discharge, they are most likely to contain a high concentration of trapping sites. Hence the value, 1.62 of n is much less than that expected for space charge

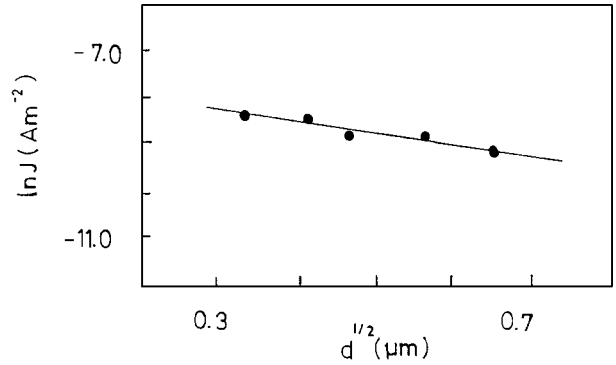

Figure 4 The dependence of the current density on the square root of the film thickness.

limited conduction. This observation also supports the elimination of space charge limited conduction [3].

The possibility for a tunneling mechanism is also limited, since the film thicknesses involved here are higher (150–350 nm.) than those allowing tunneling to take place (tunnelling usually happens at <10 nm.).

If a Poole - Frenkel or Schottky type conduction mechanism is assumed, the current density is required to depend on the thickness at a fixed voltage as $\ln J \sim d^{-1/2}$ [3] which is found to hold in the present case (Fig. 4).

The expression for the current density for the electrode limited Schottky type mechanism is given by

$$J = AT^2 \exp\left(\frac{\beta_s F^{1/2} - \phi_0}{kT}\right) \tag{1}$$

Where F is the applied field (given by $F = (V/d)$, where 'V' is the applied voltage and 'd' the thickness of the film), ϕ_0 is the electrode polymer interface barrier height and β_s is the Schottky coefficient, given by

$$\beta_s = \left(\frac{e^3}{4\pi\varepsilon\varepsilon_0}\right)^{1/2} \tag{2}$$

where 'ε' is the high frequency dielectric constant of the material and 'ε_0' is the permitivity of free space.

In the bulk limited Poole - Frenkel mechanism the thermal emission of trapped carriers from within the bulk material gives rise to a conductivity

$$\sigma = \sigma_0 F \exp\left(\frac{\beta_{PF} F^{1/2} - \phi_c}{kT}\right) \tag{3}$$

Here ϕ_c is the ionization potential of the Poole - Frenkel centers and β_{PF} is the Poole - Frenkel coefficient given by

$$\beta_{PF} = \left(\frac{e^3}{\pi\varepsilon\varepsilon_0}\right)^{1/2} = 2\beta_s \tag{4}$$

Consequently a general expression of the form

$$J = J_0 \exp\left(\frac{\beta F^{1/2} - \phi}{kT}\right) \tag{5}$$

holds equally well for Schottky and Poole - Frenkel mechanisms, where 'J' is the current density at a biased

voltage. By taking logarithms, of Equation 5 and after modification we can arrive on the equation

$$\beta = \alpha k T d^{1/2} \tag{6}$$

where $\alpha = (\ln J / V^{1/2})$ i.e., slope of the graph plotted between ln J and $V^{1/2}$

From the Fig. 4, we have already got information that the mechanism is either Schottky or Poole - Frenkel. A comparison of the theoretical and experimental β coefficients values provides the easiest means to differentiate between the two. The theoretical coefficients β_S and β_{PF} are obtained from the Equations 2 and 4, taking the high frequency dielectric constant of plasma - polymerized Furan film as 4.54, which has obtained from optical transmission studies in the VIS -NIR region. We have used the relation $\varepsilon = n^2$ to get the high frequency dielectric constant of the film, where 'n' is the refractive index of the material [5]. To calculate the refractive index of the material we have adopted Manifacier's method [6].

Fig. 5 shows the plot of ln J against $V^{1/2}$, where beyond the low voltage Ohmic region a straight line is obtained, confirming that either a Schottky or a Poole - Frenkel mechanism is present [3, 7]. From the slope of the straight line an experimental value of β may be obtained.

The experimentally obtained β coefficient value for the samples of thickness 165 nm and 325 nm is compared with the theoretical β_S and β_{PF} values in Table I. The comparison shows that the theoretical and experimental β coefficients agree for the Schottky type mechanism.

TABLE I

		β theoretical	
Film Thickness (nm.)	β experimental (eV m$^{-1/2}$ V$^{-1/2}$)	Schottky	Poole Frenkel ((eV m$^{-1/2}$ V$^{-1/2}$)
165	1.21×10^{-5}	1.78×10^{-5}	3.56×10^{-5}
325	1.05×10^{-5}		

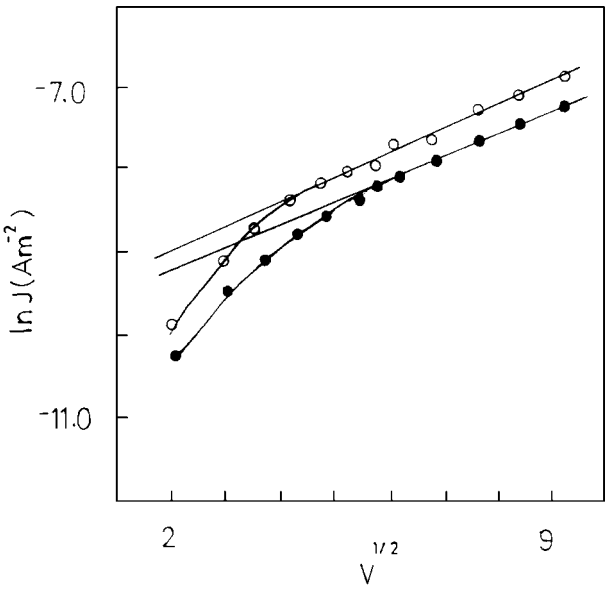

Figure 5 ln J vs $V^{1/2}$ (Al-PF-Al) ● 325 nm ○ 165 nm.

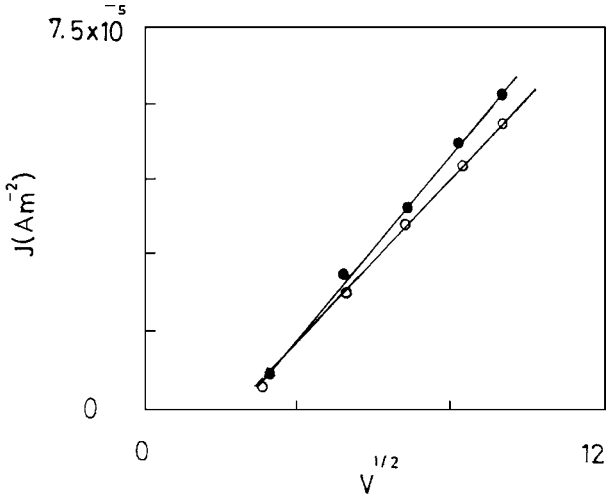

Figure 6 J vs $V^{1/2}$ (Au-PF-Al) ● Au+ve ○ Al+ve.

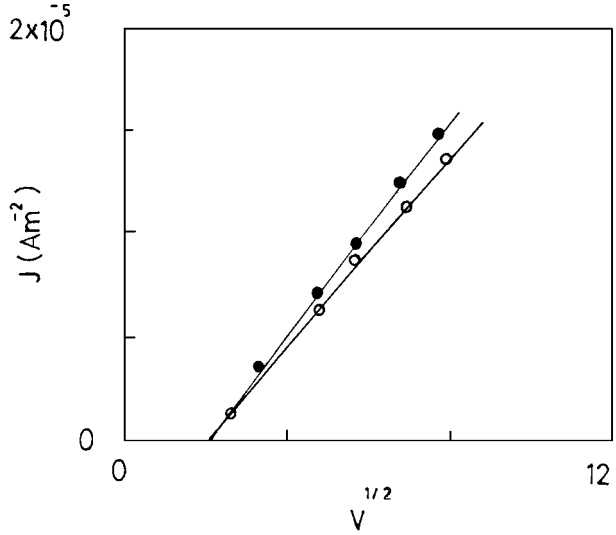

Figure 7 J vs $V^{1/2}$ (Ag-PF-Al) ● Ag+ve ○ Al+ve.

A generally accepted and reliable way to distinguish between Schottky and Poole - Frenkel mechanisms experimentally is the asymmetric electrode method. The J against $V^{1/2}$ plots are hence plotted for asymmetric - electrode configuration, which usually give information regarding the electrode dependence of the conduction current. Figs 6 and 7 show the plots of J against $V^{1/2}$ for Au - PF - Al, Ag - PF - Al asymmetric structure of polymer of film thickness 165 nm respectively. In Fig. 6 the two curves represents two directions of the applied field, first with Au and then with Al positively biased. Similarly in Fig. 7 the two curves represents two directions of the applied field, first with Ag and then with Al positively biased. The plots do not coincide, but they give a significant and reproducible difference in the current density values for opposite directions of the applied field.

When a polymer film is inserted between two different metal films, the barrier heights at the two polymer metal interfaces differ by the work function difference between the two metals. Theoretically for Schottky type conduction [3] a work function difference of about 0.06 eV between the two electrode metals should result in a decade difference in current levels, measured for

opposite directions of the applied field. In an Au - PF - Al asymmetric electrode configuration, where there is a metal work function difference of about 0.82 eV, and in Au - PF - Ag asymmetric system where there is a work function difference of about 0.25 eV, for these values many orders of change should occur in the magnitude of the current density values for opposite directions of the applied field. However in Fig. 6 and in Fig. 7 the difference in current levels for opposite polarization of the Au - PF - Al and Au - PF - Ag structures are quite small, contrary to the expected result.

The presence of surface states at the polymer electrode interface can change the potential barrier [8]. As suggested by Mizutani *et al.* [9], owing to the presence of surface states the phenomenon of equalization of the metal - polymer contact barriers may take place, which results in the small difference in barrier heights when different electrode systems are employed. The small but significant difference in 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 J against $V^{1/2}$ plots for opposite polarization of the asymmetric systems in Figs 6 and 7 clearly indicates that barrier heights play a significant role in the conduction process.

4. Temperature effects

The thermal variation of the current flowing through Al - PF - Al symmetric structures has been investigated in the temperature range 300–423 K for different fixed values of applied bias voltage, in a number of polymer films in the thickness range 105–325 nm. Since the results do not show any appreciable variation with thickness, the results obtained only for a typical film of thickness 325 nm are given.

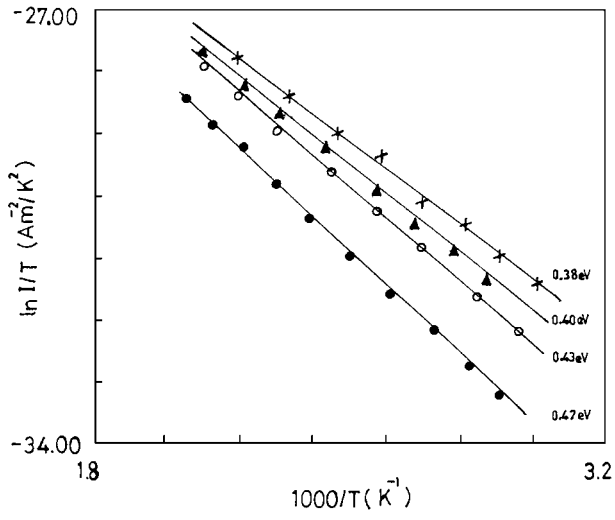

Figure 8 $\ln(I/T^2)$ against $(1000/T)$ for different voltages (Al-PF-Al) ● 4 V ○ 9 V ▲ 16 V + 25 V.

The metal polymer barrier height can be determined by plotting $\ln(I/T^2)$ against $(1000/T)$, where 'I' corresponds current density for different biased voltages. From the slope of the resulting straight line, the barrier height can be determined. Fig. 8 shows the plot $\ln(I/T^2)$ against $(1000/T)$ for different biased voltages. This plot yields a straight line. This is further indication of Schottky type mechanism as suggested by Thomas *et al.* [3]. The activation energy decreases from 0.47 eV to 0.38 eV as biased voltage increases from 4 V to 25 V.

5. Conclusions

The foregoing observations and studies indicate the following:-

1. In plasma polymerized Furan films it has been clearly observed that the conduction current varies with field direction, nature of electrode metals and temperature.
2. The temperature effect studies proved that conduction is an activated process, in which the activation energy decreases with increase in field and temperature. The decrease in activation energy represents extrinsic conduction where the change in activation energy is determined by the number of extrinsic carriers.

Thus with these substantiative evidences and observations, it can be predicted that there is a clear dominance of Schottky conduction in the plasma polymerized Furan films.

6. Acknowledgement

The author thanks U.G.C., New Delhi for financial assistance.

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Received 13 January
and accepted 6 December 1999