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Conduction mechanism in plasma polymerized aniline thin films

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Abstract

Electrical properties of ac plasma polymerized aniline thin films are investigated with a view of determining the dominant conduction mechanism. The current–voltage (*I–V*) characteristics in symmetric and asymmetric electrode configuration for polyaniline thin films in the thickness range from 1300 to 2000 Å are investigated. From the studies on asymmetric electrode configuration, it is found that the dominant conduction mechanism in these films is of Schottky type.

Keywords: Plasma polymerization; Polyaniline; Thin film; Conduction mechanism; Schottky mechanism

1. Introduction

Chemical and electrochemical polymerizations are common methods used to obtain polyaniline thin films on metallic electrodes [1,2]. However, the technique of plasma polymerization is increasingly being used as an alternative for obtaining polymer thin films [3]. Polymer thin films obtained by plasma polymerization technique are different from those obtained by the conventional technique. Unlike the films obtained by chemical or electrochemical methods, plasma polymer films are pinhole-free, chemically inert, of uniform thickness and thermally stable [4].

Electronic and photonic properties of polyaniline have attracted considerable research interest due to its potential applications in a wide range of fields such as LEDs, intermetallic dielectric, EMI shielding and in anticorrosion protection layers. Most of the published literature deals with polyaniline prepared by chemical methods. Articles relating to plasma polymerized aniline are less abundant in literature. A few of them relating to plasma polymerized polyaniline are all synthesized by rf plasma [5–7]. The ac plasma polymerization is an effective method for the preparation of polymer thin films. This study particularly focuses on the electrical properties of ac plasma polymerized aniline thin film. This is carried out with a view of determining the dominant conduction mechanism.

2. Experimental

Polyaniline thin films are prepared by ac plasma polymerization technique and the details of this tech-

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nique are cited elsewhere [8]. These thin films of polyaniline are 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 are in the form of metal/polymer/metal of cross-sectional area 2.5×10^{-5} m^2. The thickness of the polymer films is measured by interferometric technique (Tolansky technique) and the thickness values lie in the range from 1300 to 2000 Å. These sandwich samples are placed in a home-built conductivity cell to investigate the dependence of current density on voltage, temperature and thickness. A bias voltage in the range from 1 to 40 V is applied and the current flowing across the sample is measured by a Keithley Picoammeter/Voltage source (Model 487). All the measurements are carried out under dynamic vacuum. The data acquisition and analysis of the data are completely automated by employing the LabVIEW software (National Instruments).

3. Results and discussion

3.1. J–V studies on symmetric electrode configuration

Fig. 1 shows a typical room temperature J–V plot of polyaniline thin film of thickness 1350 Å. The plot

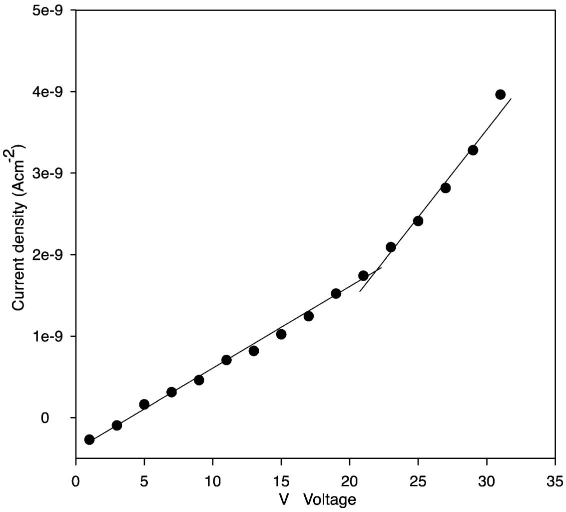

Fig. 1. Current density against applied voltage for Al/polyaniline/Al film of 1350 Å in thickness at room temperature.

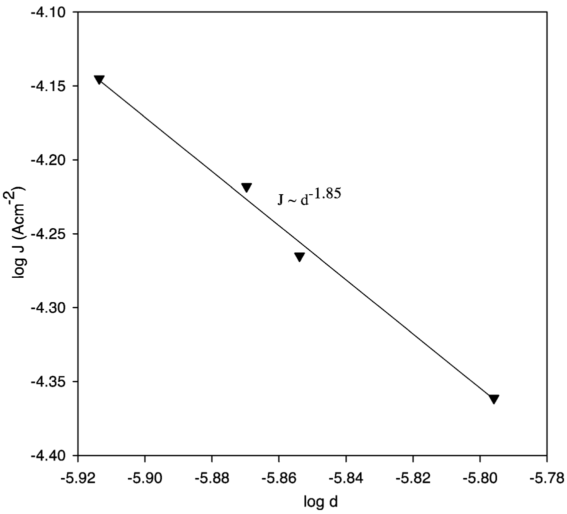

Fig. 2. Thickness dependence on the current density for Al/polyaniline/Al thin film at room temperature.

consists of two regions, in the lower range of the applied voltage, the slope is around 1, and in the higher range, the slope is 2.3. The conduction in the lower region of the applied voltage is found to be ohmic while in the higher range of the applied field, it is found to be non-ohmic. There are three different types of conduction mechanisms, namely, space charge limited conduction (SCLC), Schottky-type conduction and Poole–Frenkel conduction mechanism [9], and one of these mechanisms will be dominant in a given sample.

According to SCLC theory [9], the thickness (d) 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. Fig. 2 shows the dependence of thickness on the current density for polyaniline films and it is found that the current density varies as $d^{-1.85}$. The value of $n \sim 1.85$ is less than that required for space charge limited conduction and so SCLC conduction mechanism is ruled out.

A general expression that holds equally well for both types (Schottky and Poole–Frenkel) of conduction mechanism is of the form [10]

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

where ϕ is the barrier height of electrode–polymer interface, T is the absolute temperature, k is the Boltzmann constant, F is the electric field given by $F=V/d$, where V is the applied voltage and d the thickness of the sample and the constant β is given by

$$\beta = \left(\frac{e^3}{a\pi\varepsilon\varepsilon_0}\right)^{\frac{1}{2}}, \tag{2}$$

where the coefficient $a=1$ for Poole–Frenkel effect and $a=4$ for Schottky emission, ε is the dielectric constant and ε_0 is the permittivity of free space.

According to Eq. (1), a plot of log J versus $V^{1/2}$ should yield a straight line if either of the above mentioned two mechanisms are dominant in plasma polymerized aniline thin films. Fig. 3 shows the log J versus $V^{1/2}$ plot for plasma polymerized aniline thin film of thickness 1350 Å. This further confirms that the conduction mechanism in polyaniline thin films is due to either Poole–Frenkel or Schottky.

To differentiate between the two conduction mechanisms is to compare the theoretical and experimental values of the β coefficients. The experimental value of β ($\beta_{exp}=\alpha kTd^{1/2}$) is obtained from the slope (a) of the linear portion of log J versus $V^{1/2}$ plot and the theoretical coefficients β_s and β_{PF} are calculated by using Eq. (2). Dielectric constant (ε) of plasma polymerized aniline film at high frequency is estimated

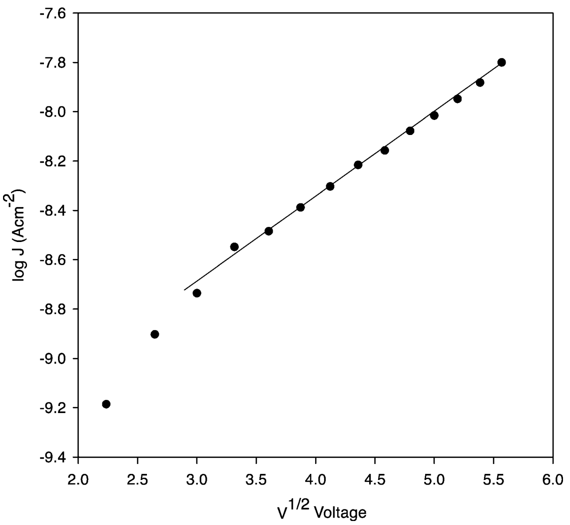

Fig. 3. Schottky plot for Al/polyaniline/Al polymer thin film of thickness 1350 Å.

Table 1
Experimental and calculated values of β coefficients

Film thickness (Å)	Experimental β (eV m$^{1/2}$ V$^{-1/2}$)	Theoretical β_s (eV m$^{1/2}$ V$^{-1/2}$)	Theoretical β_{PF} (eV m$^{1/2}$ V$^{-1/2}$)
1350	3.21×10^{-5}	2.82×10^{-5}	5.64×10^{-5}

from the optical transmission studies in the near IR-visible region and the value is found to be 1.81. This value of dielectric constant is substituted in Eq. (2) to calculate the theoretical β values and is given in Table 1 along with the experimentally obtained β value.

A comparison of the values of the experimental and theoretical β coefficients indicates that in plasma polymerized aniline thin films, the β coefficient value agrees well with the Schottky-type conduction mechanism. However, reports indicate that the mere coincidence of theoretical and experimental β coefficients is not sufficient to establish the dominance of either of the mechanisms [11,12]. Thus, to confirm the dominance of the Schottky-type conduction mechanism in polyaniline thin films, J–V studies for asymmetric electrode configurations are also carried out. These results are discussed below.

3.2. *J–V studies for asymmetric electrode configurations*

Equation for Schottky effect is given by [9]

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

from the above equation, it is clear that the current depends exponentially on the barrier height ϕ. Thus, in an asymmetric electrode configuration, the current should also be asymmetric when the bias polarity is reversed. Fig. 4 shows a typical J–$V^{1/2}$ plot obtained for Au/polyaniline/Al asymmetric electrode configuration for a sample thickness of 1350 Å. The two curves in the plot indicate the two directions of the applied field.

The difference between the work functions of the two metal electrodes in Au/polyaniline/Al asymmetric electrode configuration is about 0.82 eV and hence many orders of change should be observed in the current density values for opposite directions of the applied field. However, the difference in the current density values for opposite polarities of the applied field in Au/polymer/Al asymmetric electrode configuration is quite small as observed in Fig. 4. This small difference in the current density values may be due to the effects of surface states present at the polymer electrode interface, which can change the potential barrier [13]. The difference in the current density values for opposite directions of the applied field, though small, can hence be considered as favouring an electrode-dependent Schottky-type conduction in polyaniline films. The different slopes of the two curves in Fig. 4 for opposite polarizations of the asymmetric electrode configuration clearly indicate that barrier heights play a significant role in the conduction process.

3.3. Activation energy

For Schottky-type conduction mechanism, Eq. (3) requires that the plots of $\ln(J/T^2)$ versus $(1/T)$ for different values of the applied bias voltages should be linear. The activation energies can be obtained from the slopes of the linear portions of $\ln(J/T^2)$ against $(1/T)$ plots that are shown in Fig. 5 for Al/polyaniline/Al of film thickness 1350 Å. As observed in Fig. 5, the plot yields a straight line, which further confirms that the Schottky-type conduction mechanism is dominant in the ac plasma polymerized aniline thin film [14]. The activation energy is found to decrease from 0.73 to 0.65 eV as the biased voltage increases from 5 to 11 V.

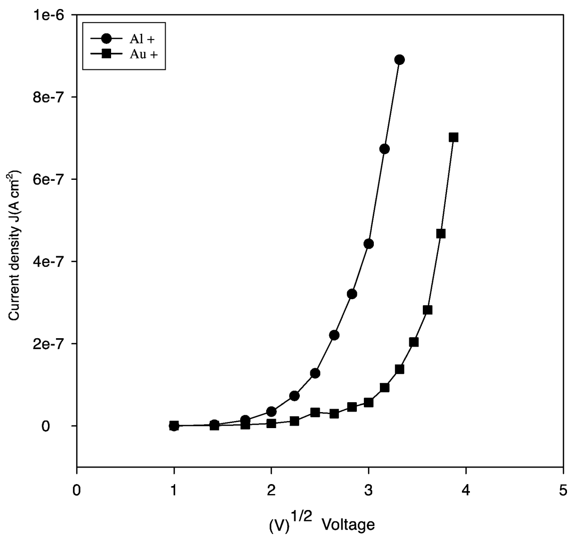

Fig. 4. Schottky plot for Au/polyaniline/Al asymmetric electrode configuration at room temperature.

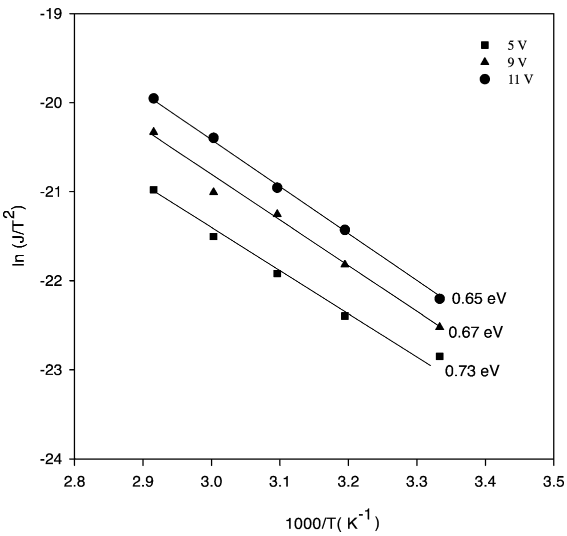

Fig. 5. Plot of $\ln(J/T^2)$ against $1000/T$ for Al/polyaniline/Al structure of film thickness 1350 Å for different applied bias voltages.

4. Conclusion

Polyaniline thin films of different thickness are prepared by ac plasma polymerization technique. Asymmetric electrode configuration studies show that barrier heights play a significant role in the conduction process. It is found that conduction is an activated process with activation energy decreasing from 0.73 to 0.65 eV as the bias voltage is increased. From the above observations, it can be inferred that electrode limited Schottky-type conduction is dominant in plasma polymerized polyaniline thin films.

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