The results of attempts made to characterize conduction mechanism in polymerized Lemongrass oil are presented in this chapter.
7.1. Experimental details

Plasma polymerized Lemongrass oil films were prepared from locally available Lemongrass oil using the experimental setup described in chapter III and the procedure given in chapter IV. For the studies of electrical conductivity samples in the form M-I-M i.e., metal-insulator-metal sandwich structures of area 0.25 cm$^2$ were prepared. Here for the M-I-M structure we used Al, Ag, Au as the electrodes. The electrode metals were deposited by conventional thermal evaporation technique under a pressure of 2 x 10$^{-5}$ Torr on very well cleaned glass substrates. Electrical measurements were carried out in a metal chamber under vacuum conditions. The sample films loaded in the metal chamber described earlier (In chapter III), were subjected to vacuum annealing cycles to eliminate moisture and monomer vapour. The current flowing through the films were measured using an electrometer amplifier (Keithley model 617). On applying the voltage, the current initially obtained was found to decay with time. Therefore for each value of applied voltage a 2 hours of stabilization time was allowed, to get constant current values. The experiment was repeated in a number of films in the thickness range 855-3100 Å. A copper constanton thermo couple 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. Thickness of the samples were measured using Tolensky technique. The measurements were taken employing Au-PL-Ag and Ag-PL-Al asymmetric electrode configurations also.
7.2. Results and discussion

7.2.a. Current - Voltage characteristics

For the study of the activation energy of the plasma polymerized Lemongrass oil, the electrical resistance measurements with Al electrodes have been made between 303 K (room temperature) and 473 K under vacuum conditions. Annealing of the sample was done in such a way that the temperature was steady for about 2 min. at every stage of 5 K increment. Every reading was taken by giving a biased voltage of 2V to the sample. The results can be discussed on the basis of the Arrhenius relation. Arrhenius relation is

\[ R_{sh} = R_o \exp\left[\frac{-E_a}{kT}\right] \]  

7.01

Where ‘k’ is the Boltzmann constant ‘Ea’ is the activation energy and ‘R_{sh}’ is the sheet resistance of the film. For multiple activation energy the equation is

\[ R_{sh} = R_o \exp\left[-(E_{a1} + E_{a2} + E_{a3} + \ldots \ldots \ldots) / kT\right] \]  

7.02

Graphs are plotted between log $R_{sh}$ and $\frac{1000}{T}$ for the samples with thickness 1550, 3100 Å. Fig. (7.1). For both the films it was observed that there are two straight lines with differing slopes. This means that there are two regions of differing activation energies, one for higher temperature region and the other for lower temperature region. The values of activation energies for different thickness are given in the Table 7.1.
From this observation we conclude that with increasing thickness the activation energy decreases. The same type of behaviour is observed in many other cases also [1,2].
Fig (7.2.) gives a graph plotted between voltage and current for thickness 3100 Å. From this graph it is observed that there is a linear relationship between V and I for this sample. No breakdown has been observed in the sample even at higher voltage (100 V). Which means that it can withstand even high voltage.

![Graph showing current-voltage characteristics](image)

Fig. 7.2
Current-voltage characteristics (3100 Å)

The current-voltage relationship of the polymer film with Aluminium as electrode is represented as log J (current density) against log V (applied voltage) in Fig. (7.3.). The plots are for thickness values 1550 and 3100 Å. Slope of these plots are 0.9563, 1.006 respectively. Generally such a plot between current density and applied voltage, with a slope equal to or greater than 2, suggests the possibility of space-charge-limited
conduction [3]. But here the slopes are smaller than the required value for space charge limited conduction.

The thickness dependence of the current density for Al-Polymer - Al system in shown in Fig. (7.4) for films in the range 855 - 3100 Å. The straight line plot shows that J is inversely proportional to thickness. The slope is nearly 1.89. For space charge limited conduction thickness dependence with current density is $J \propto d^{-n}$ where 'n' is a parameter depending upon the trap distribution and want to be equal to 3. But the value 1.89 is much less than that of the required value. From this observation and the observation from the Fig.(7.3.), we can rule out the possibility of space charge limited conduction.
The possibility of the tunneling mechanism is also limited, because we have performed experiments on the films with thickness ranging from 855-3100 Å. This is very high for tunneling mechanism. Tunneling usually takes place at lower thickness of the sample (about 100 Å).

The graph between $J$ and $d^{-1/2}$ where ‘$d$’ is the thickness is a straight line graph (Fig. 7.4) indicating that the conduction mechanism is either Schottky or Poole-Frenkel.

Comparison of the experimentally obtained $\beta$ coefficient values is the easiest method to differentiate between Schottky and Poole-Frenkel mechanisms [4].
The dependence of current density on the square root of film thickness

Fig (7.6.) which is a plot between log \( J \) vs \( V^{1/2} \) for the film of thickness 3100 Å. Beyond the ohmic region, a straight line portion is obtained, indicating that log \( J \) is proportional to \( V^{1/2} \) in this region. Taking the slope of the straight line we can calculate the experimental \( \beta \) coefficient value, with the help of the equation

\[
\beta_{\text{exp}} = \alpha \ k \ T \ d^{-1/2}
\]

The theoretical coefficients \( \beta_s \) and \( \beta_{PF} \) are obtained from the equations (7.04) and (7.05) taking the high frequency dielectric constant of plasma polymerized Lemongrass oil film 5.2 as obtained from optical transmission studies in the VIS - NIR region.

\[
\beta_s = \left( \frac{e^3}{4\pi \varepsilon \varepsilon_0} \right)^{1/2}
\]
Experimental and Theoretically obtained values of $\beta$ coefficients are given in the Table (7.2)

**Table 7.2**

<table>
<thead>
<tr>
<th>Film thickness</th>
<th>$\beta$ experimental</th>
<th>$\beta$ theoretical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>eV m^{-3/2} V^{-1/2}</td>
<td>Schottky</td>
</tr>
<tr>
<td>3100 Å</td>
<td>$1.23 \times 10^5$</td>
<td>$1.66 \times 10^5$</td>
</tr>
</tbody>
</table>
A comparison shows that the theoretical and experimental $\beta$ coefficient values agree better for the Schottky conduction mechanism.

But the mere coincidence of the experimental and theoretical $\beta$ coefficients is not a sufficient proof of the occurrence of either mechanism, because the difference of a factor of 2 in the values $\beta_s$ and $\beta_{PF}$ may not be adequate to prove the dominance of either mechanism [5].

Generally accepted and reliable method for the confirmation of the conduction mechanism experimentally is the asymmetric electrode method.

![Graph showing $J$ vs $V^{1/2}$ for Au-PL-Ag](image)

*Fig. 7.7*

$J$ vs $V^{1/2}$ (Au-PL-Ag)

○ Au + ve, ● Ag + ve
The \( J \) versus \( V^{1/2} \) plots for the Au - PL - Ag, Ag - PL - Al asymmetric electrode system for a polymer films of thickness 3100 Å is shown in Fig. (7.7.) and Fig. (7.8.) respectively. In the Fig. (7.7.) the two plots represent opposite polarizations of the asymmetric electrode system. That is the two plots are obtained for two directions of the applied field; first with Au positively biased and then with Ag positively biased. The plots do not coincide but show a significant and reproducible difference in the current density values for opposite directions of the applied field. Similarly in the Fig. (7.8.) also the two straight lines
represent two directions of the applied field, first with Ag positively biased and than Al positively biased. Here also the plots do not coincides; but gives 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 differ by the work function difference between the two metals.

Theoretically conduction, when a work function difference of about 0.06 eV between two electrode metals should result in many order difference in current levels, measured for opposite directions of the applied field [6]. Here we have employed Au and Ag electrodes, which differ by 0.25 eV in work functions [7,8]. In such an asymmetric electrode systems many orders of change can be expected in the current density values for the opposite directions of the applied field. However in Fig. (7.7.) and Fig. (7.8.) it is not observed, which is contrary to the expected one. This phenomenon can be explained by the equalization of the metal polymer contact barriers, because of the presence of surface states [3,4,9]. Therefore the small but significant difference in current density values for opposite directions of the applied field can be related to electrode dependent Schottky type conduction.

7.2.b. Temperature effects

The thermal variation of the current flowing through Al- Poly Lemongrass oil - Al
symmetric structures has investigated in the temperature range 300 - 423 K for different fixed values of applied bias voltages in a number of polymer films in the thickness range 855 - 3100 Å. Since the results do not show any appreciable variation, the results obtained for a typical film of thickness 3100 Å are only given.

\[ \log \left( \frac{I}{T^2} \right) \text{ against } \frac{1000}{T} \text{ (Al - PL - Al)} \]

The metal polymer barrier height can be determined by plotting \( \log \left( \frac{I}{T^2} \right) \) against \( \frac{1000}{T} \), where \( I \) corresponds current density for different biased voltages. From the slope of the resulting straight line, the barrier height can be determined. Fig. (7.9) shows plot
log \left( \frac{1}{T^2} \right) \text{ against } 1000/T \text{ for different biased voltages. This plot yield a straight line.}

This is further indication of Schottky type mechanism. The activation energy decreases from 0.60 eV to 0.55 eV as biased voltage increases from 4 V to 16 V.

7.3. Conclusions

From the above observations the following conclusions are arrived.

(i) The conduction current varies as the field direction and the nature of the electrode metal

(ii) It shows a rapid increase with temperature

(iii) The conduction is an activated process, with the activation energy decreasing with increasing field. In the light of the above conclusions the dominance of Schottky conduction can be confirmed.
References:

8. O. Klein and E. Lange, Zeits. F. Electrochemie, 44 (1938) 542