8. BREAKDOWN STUDIES

8.1. INTRODUCTION

Today, much of our industrial progress is based on the use of organic materials such as polymers, as insulators for both heat and electricity. In all these applications, it is mandatory that the polymeric films retain their insulating properties with time and stress. Consequently, breakdown strength measurements have received much attention. Breakdown, results in the catastrophic formation of a narrow discrete channels or a tree like pattern of channels of destruction in what might appear to be initially a homogeneous medium.

Detail studies have been made on the breakdown properties of insulating polymer films by various investigators [1-11]. The criterion that determines breakdown is a form of self healing [1-8] or the onset of a negative differential resistance range in the voltage current characteristics. The instability in non-thermal breakdown is explained, as in thermal breakdown, on the basis of positive feedback effects. These effects are frequently ascribed to mutual enhancement of current by processes at the electrodes. Films of polymeric materials are mechanically and chemically stable and hence they have attracted attention for device applications. The knowledge of their dielectric strength (breakdown voltage) is important for the design of thin film capacitors and also in the field of active devices, where a good quality dielectric is needed to avoid the leakage of current to the gate. Some investigators have been carried out on the breakdown properties of polymeric materials like styrene [1-5], polyethylene [9] and polyimide [8] thin films. However, no investigations have been carried out on the breakdown properties of pure and nickel doped CA films. Therefore, in the
present investigation, an attempt has been made to study the breakdown properties of pure and nickel doped CA films.

8.2. THEORY

In this section the breakdown theories proposed by Forlani and Minnaja [12-13], O'Dwyer [14-15] and Klein and Gafni [16] have been discussed. The first two are based upon the ideas of electron avalanche developed by Von Hippel [17], Frohlich [18], Seitz [19], Callen [20] and Franz [21]. The treatment of Klein and Gafni is based upon the thermal breakdown.

8.2.1. Theory of Forlani and Minnaja

Forlani and Minnaja [12-13] described the onset of breakdown in an ionic crystal by considering the injected electrons from the cathode as free electrons in the conduction band of the dielectric. The acceleration of these electrons in a field is impelled by electron-phonon collisions. Electrons with energy larger than the unstable equilibrium energy, gain energy from this field till they attain the ionisation energy of the dielectric crystal. The current is then enhanced by ionising collisions. The thickness dependence of the breakdown field strength ($F_b$) can be obtained from the electron current equation. The field $F_b$ varies as $d^\alpha$, where $d$ is the film thickness and $\alpha$ varies from 0.25 to 0.5. The different exponentials are justified by two mechanisms, namely the tunnel injection of electrons from the cathode and the electron-phonon scattering. Also $F_b$ is independent of thickness comparable to the hole electron recombination distance. Theories based on the electron-phonon scattering state that the dielectric field strength increase as the temperature increases. Also the decrease of dielectric field strength with increasing temperature is obtained provided the electron-electron scattering is taken into account [22]. Experiments have shown that there exists a transition temperature between a breakdown dominated by
photon scattering and a breakdown affected predominantly by electron-electron scattering [23-24].

8.2.2. Theory of O'Dwyer

The theory of O'Dwyer [14-15] incorporates a condition of current continuity during avalanche process that causes the field to be heterogeneous, being considerably larger at the cathode than elsewhere. The breakdown mechanism is associated with impact ionisation. The instability is due to the positive feedback between the holes that are trapped by impact ionisation and the electrons that are injected from the cathode. The injection is enhanced by trapped holes owing to the increase in field at the cathode. This results in increase in impact ionisation and hole trapping, when these rises cannot be balanced by hole drift, current run away and breakdown follows.

8.2.3. Klein theory

This theory proposed by Klein and Gafni [16] is based on a succession of electron avalanche processes due to impact ionisation and the injection of electrons into the conduction band when an electric field is applied across the thin film capacitor. An electron produced at the cathode produces an avalanche of free electrons by impact ionisation and the positive charges are left behind in the insulator. These positive charges have a very low mobility and hence drift slowly to the cathode forming a positive charge cluster. This results in the enhancement of field at the cathode. The local injection rate of electrons increases and a finite probability is reached for an electron to hit the tiny charge cluster during transit through the insulator. The average cathode field during the transit of the charge cluster increases with film thickness. Hence the formation of large avalanche also depends on the film thickness, in addition to other parameters involved.
The breakdown, according to this theory follows in a sequence of stages. In the initial stage harmless avalanche occurs in the whole of the specimen causing the temperature to rise significantly. This enhances the critical conductivity leading to a thermally unstable state at the breakdown spot in the specimen that finally results in a voltage collapse through current run-away. Impact ionisation may stop during voltage collapse, but the breakdown events continue until destruction occurs because of the thermally unstable state, due to the temperature rise at the site. Thus a complete breakdown event comprises of the initiation of breakdown, instability due to heating and finally the destruction of the capacitor with voltage collapse.

8.3. MEASUREMENTS

The breakdown studies have been made on pure, 0.05%, 0.1% and 0.15% nickel doped CA films prepared by solution growth technique. The electrode overlapping area of the MPM sandwich structure of the present study was in the range of $3 \text{ to } 5 \times 10^{-6} \text{ m}^2$. To have self-healing breakdown, one of the contacting electrodes has been deposited with thickness less than 100 nm. The breakdown studies were performed using a D.C stabilised power supply in series with the film specimens. A limiting resistor in the circuit helped to avoid massive destruction by propagating breakdown. In order to determine breakdown voltage, equal incremental steps of voltage were applied to the capacitor. The leakage current through the capacitor was recorded by a nano ammeter and digital multimeter. The onset of breakdown in these structures was characterised by a sudden and sharp current upsurge at the breakdown voltages. In MPM structures with large area, the phenomenon initiated with emission of light and spreads as a spider pattern. In some structures, a flash of light is emitted during breakdown that resulted in the complete damage of the film. Further the prominence of the breakdown phenomenon could also be observed at the edges of the electrodes. The breakdown patterns were observed through an optical microscope and photographed.
8.4. RESULTS AND DISCUSSION

Fig. 8.1(a-d) shows the doubly logarithmic plot of self healing breakdown field against film thickness for solution grown pure, 0.05%, 0.1% and 0.15% nickel doped CA films. The breakdown field strength is observed to vary from $23 \times 10^6$ to $9.4 \times 10^6$ V/m, $18.8 \times 10^6$ to $8.45 \times 10^6$ V/m, $13.7 \times 10^6$ to $7.1 \times 10^6$ V/m and $9.6 \times 10^6$ to $5.3 \times 10^6$ V/m in the thickness range approximately from 10 µm to 18 µm for the pure, 0.05, 0.1 and 0.15% nickel doped CA films respectively. The values of slope are found to be 0.44, 0.53, 0.45 and 0.33 respectively at room temperature for the above said films. As the temperature increases from 303 to 423 K the slopes vary randomly in between 0.25 to 0.5 (Table 8.1) for pure, 0.05, 0.1 and 0.15% nickel doped CA films.

The observed breakdown field strength is of the same order as that obtained by Segui et al [5] and Sawa et al [1] on thin polymer films and other dielectric materials [25-32]. The thickness dependence observed in these films can be explained on the basis of existing theories. Theories based on the impact ionisation predicts a breakdown field independent of film thickness. Hence these theories cannot be applied here. Forlain-Minnaja theory [12-13] however agrees with the observed results. As mentioned in the section 8.2.1, this theory predicts a thickness dependence of the form $F_b \propto d^{-\alpha}$, where $\alpha$ varies from 0.25 to 0.5. This theory also predicts that the higher value 0.5 holds good for higher energy gap dielectrics. In the present case, most of the values obtained vary from 0.25 to 0.5 and hence it can be predicted that the thickness dependence of the breakdown field in the pure, 0.05, 0.1 and 0.15% nickel doped CA films obey Forlain-Minnaja theory. The electrons injected into the conduction band of the dielectric cause ionisation. The current density increases rapidly with the applied field at some critical field where the self healing of electrons occurs. This grows as a core with it’s maximum cross-section towards the anode. Joules heat produced by electron avalanche of breakdown field has been observed and
Fig. 8.1 (a) Log $F_b$ versus log $d$ of pure 4% CA at various temperatures.
Fig. 8.1(b) Log $F_b$ versus log $d$ of 0.05% nickel doped CA at various temperatures.
Fig. 8.1 (c) Log $F_B$ versus log $d$ of 0.1% nickel doped CA at various temperatures.
Fig. 8.1 (d) Log $F_b$ versus log $d$ of 0.15% nickel doped CA at various temperatures.
| Table 8.1: The values of slope from Figs 8.1(a) to (d) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                  | at 303 K        | at 348 K        | at 373 K        | at 398 K        | at 423 K        |
| Pure 4% CA       | 0.44            | 0.33            | 0.25            | 0.33            | 0.5             |
| 0.05% Ni-doped CA| 0.53            | 0.53            | 0.32            | 0.46            | 0.51            |
| 0.1% Ni-doped CA | 0.45            | 0.33            | 0.25            | 0.43            | 0.26            |
| 0.15% Ni-doped CA| 0.33            | 0.32            | 0.44            | 0.54            | 0.39            |

Table 8.2 Results of DSC studies

<table>
<thead>
<tr>
<th>Film</th>
<th>T_g From (°C)</th>
<th>T_g To (°C)</th>
<th>On Set (°C)</th>
<th>T_g (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure 4% CA</td>
<td>88.71</td>
<td>176.64</td>
<td>91.2</td>
<td>106.95</td>
</tr>
<tr>
<td>0.05% Ni-doped CA</td>
<td>74.61</td>
<td>169.51</td>
<td>85.26</td>
<td>99.64</td>
</tr>
<tr>
<td>0.10% Ni-doped CA</td>
<td>72.49</td>
<td>173.4</td>
<td>86.44</td>
<td>95.24</td>
</tr>
<tr>
<td>0.15% Ni-doped CA</td>
<td>65.1</td>
<td>150.89</td>
<td>127.84</td>
<td>98.24</td>
</tr>
</tbody>
</table>
reported by earlier workers on thin polymer materials like polystyrene [1-5], polyimide [8] and other dielectric materials.

In the case of nickel doped samples, the field strength values are low when compared to pure films. The formation of charge transfer complexes, as reported in previous chapters, causes the breakdown of the polymer films at lower applied fields as compared to the pure films. Also light emission is observed during dielectric breakdown measurements in the open atmosphere. This may be attributed to the recombination of carriers produced by impact ionisation, indicating that breakdown starts by avalanching. Using a multimeter, the discontinuity in the top electrode and the continuity in the bottom electrode have been observed.

8.4.1. Temperature dependence of onset breakdown field.

Fig. 8.2 (a-d) represents the variation of self healing breakdown field with temperature (303 - 423 K) for solution grown pure, 0.05, 0.1 and 0.15% nickel doped CA films of 3μm thickness each. It is observed that in all these films, the breakdown field remains almost constant upto a certain temperature (varies from film to film), after which it decreases suddenly with further rise of temperature.

A number of theories have been proposed to explain the temperature dependence of breakdown field. According to the theory of O'Dwyer, electrons are assumed to be distributed over numerous energy levels in the valence band gap and a few electrons are in the conduction band due to thermal excitation. When these electrons have subjected to the applied field they gain energy and due to their finite life time, then fall into the shallow traps very near to the conduction band. According to this theory, the breakdown field should show a strong temperature dependence at all temperatures. However, in the present study, the temperature dependence has been observed only after a certain
Fig. 8.2 (a) Variation of self healing breakdown field with temperature for pure 4% CA film.
Fig. 8.2 (b) Variation of self healing breakdown field with temperature for 0.05% nickel doped CA film.
Fig. 8.2 (c) Variation of self healing breakdown field with temperature for 0.1% nickel doped CA film.
Fig. 8.2 (d) Variation of self healing breakdown field with temperature for 0.15% nickel doped CA film.
temperature, viz., 360 K for pure, 348 K for 0.05%, 343 K for 0.1% and 323 K for 0.15% nickel doped CA films. Hence this theory is inadequate to explain the observed behaviour. According to the intrinsic breakdown theory, the breakdown field strength should increase with temperature i.e., the slope of the breakdown field versus temperature curve should be positive. But the observed experimental slope is negative. Therefore the intrinsic breakdown field theory cannot be applied to explain the temperature dependence of in these films.

Forlani and Minnaja's field emission theory [13], suggests that at low temperature the breakdown occurs by an avalanche initiated by tunnel emission of electrons at the cathode into the conduction band of the dielectric. Hence, at lower temperatures, the breakdown field is independent of temperatures. This concept explains the experimental observation in which the breakdown field remains constant up to certain temperatures ($T_c$) in these films. At high temperatures, the electron injection is governed mainly by Schottky emission [12] rather than tunnel effect. As a consequence, the breakdown field strength decreases with increase of temperature, provided the electron-electron collision is taken into account. Due to dominant roles of the electron image force on the shape of the potential barrier, the decrease of breakdown field with the increase of temperature can be explained by the relation

$$F_b = \frac{\phi_{eff}}{E} \frac{E}{K} T q d$$

where $\phi_{eff}$ is the effective height of the potential barrier at the metal-insulator interface and $E$ is the difference between the mean energy of the electrons required to ionise the dielectric and the mean energy of the emitted electrons. A decrease in the breakdown voltage can occur due to the lowering of bonding strength with the increase of temperature. But in the case of nickel doped films, the breakdown voltage values are low as compared to that of pure samples. The decrease in the field may be due to the formation of charge transfer complexes between the polymer matrix. The sudden decrease in the breakdown field is
observed in all these films above certain temperature ($T_c$). This may be due to the deformation of both the pure and nickel doped films around the temperature where the glass transition ($T_g$) of the material begins with. The detailed Differential Scanning Calorimetry (DSC) spectra for these samples are shown in Fig. 8.3 (a-d). Important data obtained from these spectra are given in table 8.2. On comparing our $T_c$ values with the $T_{gform}$ values, it is obvious that the material undergoes deformation right from the beginning of the glass transition ($T_{gform}$) temperature and hence the sudden decrease in the breakdown field $F_b$ with the increase in temperature above $T_c$.

### 8.4.2 Breakdown patterns

Breakdown patterns have been classified into three types, viz.,

(i) Single hole
(ii) Propagating and
(iii) Maximum

by Klein and Burstein [33] after their studies on SiO capacitors. The first two kinds are attributed to the localised flaws in the dielectric destroying a small area (single hole) or a large area (propagating) of the dielectric. The third one is regarded as characteristic of the ultimate breakdown strength of the film material.

The breakdown patterns of solution grown pure and nickel doped CA films under transmitted light are shown in Figs. 8.4 (a–d) and 8.5 (a–d). These figures show the single hole patterns for pure and nickel doped CA films. The single hole breakdown originates from the cathode due to electronic impact ionisation and terminates at the anode, due to successive avalanche in the same spot thereby increasing the local temperature. Due to the low thermal conductivity of the dielectric material, the dissipation of the thermal energy is low and hence
Fig. 8.4 Break down patterns of pure 4% CA films.
(A) Single hole (B) Propagating (C) Complete and spreading of break down to electrodes through edges (D) Complete break down.
Fig. 8.5 Break down patterns of nickel doped CA films
(A) Single hole (B) Propagating (C) Complete and spreading of break down to electrodes through edges (D) Complete break down.
Fig. 8.3 (a) DSC Spectra of pure 4% CA film.

- Tg from: 88.71°C to 176.64°C
- Onset: 91.20°C
- Tg: 106.95°C
Fig. 8.3 (b) DSC Spectra of 0.05% nickel doped CA film.

Tg from: 74.61°C to: 169.51°C
Onset: 85.26°C
Tg: 99.64°C
Fig. 8.3 (c) DSC Spectra of 0.1% nickel doped CA film.

0.1% Ni DOPED CA

Tg from: 72.49°C to 173.40°C
Onset: 86.44°C
Tg: 95.24°C
Fig. 8.3 (d) DSC Spectra of 0.15% nickel doped CA film.

Temperature (°C)

Heat flow (mW)

0-15 % Ni DOPED CA

Tg from : 65.10 °C
to : 150.89 °C
Onset : 127.84 °C
Tg : 98.24 °C
there arises a rise of temperature that ultimately damages the dielectric. When
the field is high at a flaw in the dielectric a large increase in current occurs. A
relatively conducting channel appears then at the flaw through which the
capacitor discharges, causing the observed rapid destruction in an explosive
manner [34].

Figs. 8.4 b and 8.5 b. show the propagating patterns for pure and nickel
doped CA films. The propagating breakdown consists of consecutive repetitions
of many single hole breakdowns. The mechanism for this propagation may be
the following [35]. The breakdown hole periphery is very hot at the end of a
single hole breakdown and the dielectric strength is therefore strongly reduced.
When the series resistor is low and the source voltage is high, the capacitor
recharges before the periphery cools down and a second breakdown occurs
even before the capacitor is fully recharged. This chain continues and the
breakdown propagates further.

Figs.8.4 (c-d) and 8.5 (c-d) show the complete breakdown patterns for
pure and nickel doped films. Also it has been observed that the effect
breakdown is always greater at the edges inspite of the reinforcement of
insulating layer.
References