9. LASER DAMAGE STUDIES

9.1. INTRODUCTION

The requirement of system reliability and the quest for increased efficiency are the major reasons for the sustained efforts in studying the damage threshold of different materials. Experimental studies on the damage thresholds have been carried out in different types of films, viz., dielectric [1-2], transparent conducting [3], polymer [4], organic [5], and rare earth [6-7] thin films. Cellulose Acetate (CA) is an important polymer, which has got potential use in electronic industries. Almost no work is reported on laser damage studies in pure and doped CA thin films. The Laser Induced Damage Threshold Energy Density (LIDTED) and Threshold Optical Field (TOF) of pure and nickel (Ni) doped cellulose acetate thin films were studied and the results are discussed in this chapter.

9.2. THEORY

9.2.1. Damage mechanism

Laser induced damage can be defined as a permanent induced damage in a coated optical surface, when exposed to a pulse of laser. This degrades the merit of the surface with regard to the specifications such as scattering, reflection or transmission. There is no direct relation between an observed damage centre and the degradation in laser performance. Hence it is generally agreed upon to define the damage threshold as the energy or power density at which a change in the physical appearance of the test component has been observed. The
Laser induced damage may occur either internally or at the surface of the optical component. Internal damage is caused by particulate inclusion, small inhomogeneities, absorption or self-focusing in the material and surface damage is caused by impurities, imperfections, inclusions or irregularities on the surface of transparent dielectrics [8]. Of the two, the effect of the surface damage is more serious since it occurs at smaller values of incident beam energy. In a well designed laser, the main drawback is the surface of the optical component which serve as reflecting or anti-reflecting coatings to reduce transfer losses. This is because, due to surface imperfection and contamination, it is the surface which generally fails first [4]. The requirement of system reliability and the quest for increased efficiency are the two reasons for the continuing efforts to raise the damage threshold of laser materials [9]. Raising the damage threshold of hosts, windows and coatings reduces the probability of failure of the laser system. To develop quality coatings, one need to understand the fundamental damage processes and their dependence of frequency and pulse width [11]. The three most frequently proposed processes of laser induced damage mechanism in thin film materials are, avalanche ionisation, multi-photon ionisation and absorption by impurities within the film. A brief description of the above processes is given in the following sections.

9.2.2. Avalanche ionisation

This model states that avalanche ionisation occurs when an electron in the conduction band of the material absorbs sufficient energy from the electromagnetic fields to impact ionise a valance electron. The electrons then undergo the same process to produce four electrons and so on. The density of the electrons in the conduction band thus grows exponentially with time, forming an absorbing plasma. The plasma absorbs energy from the electromagnetic...
fields and catastrophic damage of the material occurs from the locally deposited electrons [11].

It has been well established [12] that when the conduction electron density reaches a value of the order of $10^{18} / \text{cm}^3$, the absorption of the residual laser becomes appreciable, leading to localised heating and subsequently irreversible damages to the optical materials. Hence the appearance of $10^{18} / \text{cm}^3$ conduction electrons is taken as the criterion for laser induced damage.

9.2.3. Multiphoton ionisation

Multiphoton ionisation occurs when the electrons are promoted from the valance to the conduction band by direct absorption of two or more photons resulting in a plasma. The number of photons required for each ionisation depends on the material and the laser wavelength. This model is based on the postulate that when the photon energy of the incident light was about one third of the band gap energy ($E_g$) of the solid, multiplication absorption would contribute significantly to the break down process. The analytical difficulty in treating multiphoton absorption in dielectrics is the lack of detailed knowledge of the band structure. The most widely used treatment of photon absorption is that of Keldysh [13], which gives meaningful results for the first order as well as higher order photon process. According to this theory, the dependence of critical energy per unit area on the pulse width reveals that if $E_g < h\omega$, the break down process is independent of time, where $E_g$ is the photon frequency. for very high order photon process $E_g >> h\omega$, and the process depends linearly on time.

9.2.4. Impurity dominated breakdown

The main cause for this type of breakdown are the impurities that are embedded in the films. This kind of damage is a thermal process and takes place when an impurity in the film absorbs enough laser radiation to produce melting or
fracture of the host material. There has been sustained interest in the area of fundamental mechanism of laser induced damage produced by impurities in dielectric host materials [14-15]. The impurity dominated breakdown mechanism assumes importance in the case of surfaces and thin films. This is due to the large absorption coefficients in thin films which range from 10 to 1000 cm⁻¹. For the same material in bulk form, the range is several orders of magnitude smaller. The high absorptivity in thin films is generally attributed to impurities which are included during the deposition process are infiltrate into the film during exposure to the environment.

The unique feature of the impurities dominated model is that it predicts an inverse dependence of damage threshold on film thickness. This results from the reasonable assumption that the maximum size of the impurity is limited by the film thickness i.e., as the film thickness increases, so does the impurity size.

9.2.5. Choice of the mechanism

Extensive research has been carried out on laser induced damage as a function of film thickness [3, 5-7,16-21], wavelength [22 - 32] and pulse width [8,33 -36]. Avalanche and multiphoton ionisation theories predict conflicting laser wavelength dependence, while the impurity dominated theory predicts little or no wavelength dependence. However if the Mie absorption coefficient [12] is included in the impurity model, there is no distinction between the wavelength prediction of the multiphoton and the impurity models. This is because the film can be tested only at a few discrete available frequencies across the frequency spectrum. Further more both theories predict an inverse dependence of damage threshold on laser frequency.

In general, studies of damage as a function of only one parameter cannot be expected to reveal the dominant damage mechanism and often lead to controversial results [37-38]. Also it is not possible to correlate the results of the
past research efforts on a multi parameter study of the breakdown process. This is because the each individual experiment will be performed on a different set of films and usually under different conditions. The investigated film may also differ in parameters like film thickness, quality of starting materials and deposition technique, which are important in determining the size, type and distribution of impurities in a film. The calculation of both avalanche and multiphoton ionisation require complicated parameters such as the material band structure and the effective mass of electrons which are not usually available for many dielectrics. The impurity model requires a detailed knowledge of the size, type and distribution of impurities. Hence the only practical way to determine the most appropriate model is to examine their predictive ability in describing the variation of damage with easily controlled experimental or material variables such as pulse width, wavelength and film properties.

Neither the avalanche nor the ionisation model can individually explain the experimentally observed features of laser induced damage. These two mechanisms when combined into a single formation may offer a better fit to the experimental data. The inclusion of the effect of the multi-phonon ionisation in the avalanche ionisation brings the theoretical prediction closer to the experimental results [39]. However contradictions are observed when the data is dealt with as a whole. Also, neither the avalanche nor the ionisation model can account for the observed thickness dependence [12]. Hence the impurity dominated mechanism gains importance and is successful in describing the scaling of the damage threshold with respect to pulse duration and the thermal properties of the film.

9.3 DAMAGE THRESHOLD MEASUREMENTS

There are three stages in the measurement of laser damage threshold. First, the sample is irradiated at several flux levels, some of which induce
Fig. 9.1 Experimental setup.

1. Nd:YAG Laser
2. Mirror
3. Lens
4. Beam Splitter
5. Sample
6. Energy meter
damage. Next the absolute characteristics of the pulse are measured and finally, the shot in the sequence which causes damage is determined.

The schematic of the experimental setup for damage studies is shown in Fig. 1. DCR-11 quanta ray (Q-switched mode) emitted by a Nd:YAG laser was employed. The laser output at 1.06μm had a pulse width of 10 ns. The beam structure was multimode and was approximately Gaussian in profile with a beam diameter of about 3 mm. A biconvex lens of 19 cm focal length was used to focus the laser output onto the thin film samples at normal incidence. The sample was mounted on a platform which could be moved easily to vary the position so that consecutive pulses fall on new adjacent sites. The energy incident on the sample was measured by a pulsed energy meter (Delta Developments, England). A measurement of damage threshold with a pulsed energy laser is brought about by determining the highest energy pulse that can be incident on the sample without producing damage. The true damage threshold lies in between these two values.

Throughout a particular set of experimental study, the distance between the sample and the lens was kept constant. Initially the laser output energy was varied such that the shot impinging on the film sample damages it. The laser output energy is decreased a little bit and the next shot was made to impinge on a site adjacent to the previous one. The experiment was repeated several times by decreasing the laser output energy. The density at which the film gets damaged gives the damage threshold. Once the damage threshold is reached, the subsequent shots will not cause damage as the film is moved as before. At energy densities sufficiently above the damage threshold, crazing or cracking of the film surface is observed with little removal of the material. Bright light sparks are observed to emanate from the film surface when damage is produced.
On completion of the test run, the damage sites were examined with a metallurgical microscope (Versmet-2, Union 7596, Japan) and the threshold damage location was identified.

9.4. RESULTS AND DISCUSSION
9.4.1 Damage threshold energy density

The LIDTED for various films were determined by knowing the area of the damage sites from geometrical considerations. From LIDTED values, the TOF were calculated using the formula suggested by Bettis et al [40]. These values are given in Table 9.1. Fig. 9.2 depicts the variation in LIDTED with the immersion time. The thicknesses corresponding to the various immersion times of these films are discussed in the table. The undoped CA films show a sudden decrease in the LIDTED value with the increase in thickness or immersion time. The same trend has been observed for 0.05%, 0.1% and 0.15% nickel doped CA films, but the magnitude of their decrement is less. This is due to the thickness variation with the dipping, i.e., in the case of pure CA films, thickness varies appreciably with the dipping time, whereas in doped films this was not so.

The decrease of LIDTED value is observed on doping. That is in the pure CA film of thickness about 7,300 Å, the observed value of LIDTED is 69.1 J/m². Where as, in the 0.05% nickel doped film (of 7,600 Å thick), this value is 54.80 J/m². On comparing the change LIDTED value among the doped samples, a increase in this value with in creasing the dopant percentage was noticed. That is in 0.1% nickel doped samples. Film with thickness of 16,500 Å shows the LIDTED of 30.10 J/m², whereas on further doping of 0.15% results with the 37.87 J/m² for 16,800 Å thickness.
**TABLE 9.1 LIDTED AND TOF Values evaluated from experimental studies**

<table>
<thead>
<tr>
<th>Material (Film code)</th>
<th>Immersion time (Mins.)</th>
<th>Thickness (Å)</th>
<th>Laser Induced Damage Threshold Energy Density (LIDTED) J/m²</th>
<th>Threshold Optical Field (TOF) V/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure 4% CA (I)</td>
<td>15</td>
<td>2,800</td>
<td>110.34</td>
<td>90.50</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>7,300</td>
<td>69.10</td>
<td>71.56</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>9,200</td>
<td>56.07</td>
<td>64.49</td>
</tr>
<tr>
<td>0.05% Ni-doped CA (II)</td>
<td>15</td>
<td>7,600</td>
<td>54.80</td>
<td>63.80</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>11,000</td>
<td>40.93</td>
<td>55.09</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>12,100</td>
<td>40.10</td>
<td>54.58</td>
</tr>
<tr>
<td>0.1% Ni-doped CA (III)</td>
<td>15</td>
<td>14,800</td>
<td>33.62</td>
<td>49.92</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>16,500</td>
<td>30.10</td>
<td>47.20</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>17,100</td>
<td>29.49</td>
<td>46.81</td>
</tr>
<tr>
<td>0.15% Ni-doped CA (IV)</td>
<td>15</td>
<td>16,800</td>
<td>37.87</td>
<td>53.00</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>19,600</td>
<td>27.90</td>
<td>45.50</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>20,200</td>
<td>25.12</td>
<td>44.14</td>
</tr>
</tbody>
</table>
Fig. 9.2 Variation of LIDTED with immersion time.
The surface damage in thin film arises mainly due to impurities, imperfections or irregularities in the surface [41]. Even though the parent and dopant materials are pure, impurities and imperfections are included in thin films during the growth because of the technique used (solution growth technique) and infiltration during the exposure to the environment. The observed thickness dependence of threshold energy density shows that the breakdown mechanism followed in these films is an impurity dominated one. The impurity embedded in the film absorbs the incident radiation and causes a rise in temperature. This damages the film around the impurity. The size and number of impurity is directly proportional to the film thickness, hence the threshold energy decreases with the increase in film thickness. Similar inverse dependence of damage threshold on film thickness has been reported by earlier workers on rare earth compounds [6-7] and dielectric materials [11-42]. On adding dopant with CA, it is expected that it would increase the impurity concentration in the film resulting with the sudden decrease in the LIDTED. But, in the present case, only a slight decrease in LIDTED was observed. It may be due to the formation of charge transfer complexes [43] or molecular aggregates of the dopant material in the polymer, which may require more energy than that for the undoped material.

9.4.2 laser damage patterns

When the laser beam passes through the film according to the energy of the pulse and the target material, different damage patterns were observed in the films. Figs. 9.3 (a-d) and 9.4 (a-d) show the typical photographs of the damage sites observed in pure and nickel doped CA films respectively. The micrographs show the different stages of damaged patterns associated with these films. They are

a. Initial cracking and peeling of film
b. Circular confinement of damage site
c. Melting of the material and
d. Evaporation of film material resulting with the complete damage.
Fig. 9.3 Laser damage patterns of pure CA films.
(A) Initial stage (B) Circular confinement of damage site (C) Melting of the material (D) Complete damage after the removal of material by evaporation.
Fig. 9.4 Laser damage patterns of nickel doped CA films.
(A) Circular confinement of damage site
(B) Melting of the material
(C) Complete damage after the removal of material by evaporation.
References