CHAPTER VII

LASER DAMAGE STUDIES

7.1 Introduction

Ever increasing demand for high quality power laser systems in research, industrial and defence applications are rapidly increasing. Optically induced damages to laser materials and to components generally determine the limit of the useful performance of high power solid state lasers. Therefore an understanding of the mechanism that cause radiation damage to optical components and a knowledge of the damage threshold of the materials employed in building laser are of great importance in designing a laser system. In the present investigation, solution casted polyaniline-EB, lightly doped polyaniline and polypyrrole, and polypyrrole/polyaniline-EB blend films have been subjected to laser induced damage and the threshold energy densities estimated.

7.2 Damage mechanisms

7.2.1 General concepts

The damage threshold is defined as the physical appearance of permanently induced defect on the surface of the film of a material or as the onset of a degradation by a laser beam. This reduces 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 center and the degradation in laser performance. Hence it is possible 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 damage threshold is also specified in terms of the electrical field associated with the laser pulse.

Laser induced damage may occur either internally or at the surface of the optical component. Internal damage is caused by particulate inclusions, small inhomogeneties, absorption or self-focusing in the material and surface damage is caused by impurities, imperfections, inclusions or irregularities on the surface of dielectrics [1]. Of the two, the effect of 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 that serve as reflecting or anti-reflecting coatings to reduce transfer losses. This is because, due to surface imperfections and contamination, it is the surface which generally fails first [2].

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 [3]. Raising the damage threshold of hosts, windows and coatings reduces the probability of failure of the laser system.

To develop quality coatings, one needs to understand the fundamental damage processes and their dependence on frequency and pulse width [4]. The three most frequently proposed processes of laser induced damage mechanism in thin film materials are, avalanche ionization, multi-photon ionization and absorption by impurities within the film. A brief description of the above processes is given in the following sections.

7.2.2 Avalanche ionization

This model states that avalanche ionization occurs when an electron in the conduction band of the material absorbs sufficient energy from the electromagnetic field to impact ionise a valence electron. The two 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 field and catastrophic damage of the material occurs from the locally deposited electrons [5]. It has been well established [6] that when the conduction electron density reaches a value of the order of $10^{18}/cm^3$, the absorption of the residual laser becomes appreciable, leading to localized heating and subsequent irreversible damage to the optical material. Hence the appearance of 10^{18} conduction electrons/cm^3 is taken as the criterion for laser induced damage.

7.2.3 Multiphoton ionization

Multiphoton ionization occurs when the electrons are promoted from the valence to the conduction band by direct absorption of two or more photons resulting in a plasma. The number of photons required for each ionization depends on the band gap of 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 breakdown 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 [7], which gives meaningful results for 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 $E_g < \hbar\omega$, the breakdown process is independent of time, where E_g is the band gap energy of the solids and ω the photon frequency. For very high order photon process, $E_g >> \hbar\omega$, and the process depends linearly on time.

7.2.4 Impurity dominated breakdown

The main causes 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 [8,9]. 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 film formation process or infiltrate into the film during exposure to the environment.

The unique feature of the impurity 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.

7.2.5 Choice of the mechanism

Extensive research has been carried out on laser induced damage as a function of film thickness [10,11], wavelength [12-14] and pulse width [15]. Avalanche and multiphoton ionization theories predict conflicting laser wavelength dependence, while the impurity dominated theory predicts little or no wavelength dependence. However if the Mie absorption coefficient [5] is included in the impurity model, there is no distinction between the wavelength predictions 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. Furthermore, both theories predict an inverse dependence of damage threshold on laser frequency.

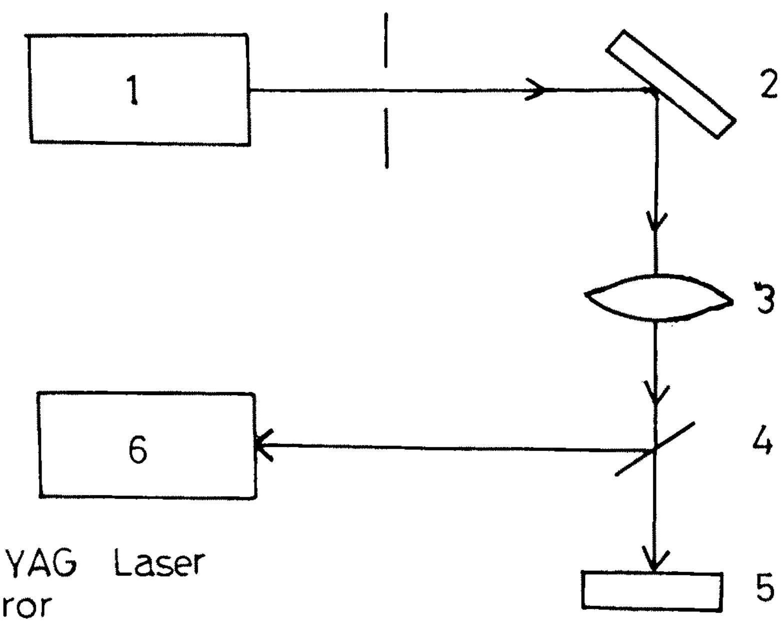
In general, studies of damage as a function of only one parameter cannot be expected to reveal the dominant damage mechanism and often lead to controversial results [16,17]. Also it is not possible to correlate the results of the past research efforts on a multi-parameter study of the breakdown process. This is because 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 ionization require complicated parameters such as the material band structure and electron effective mass 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 ionization 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 ionization in the avalanche ionization brings the theoretical prediction closer to the experimental results [18]. However, contradictions are observed when the data is dealt with as a whole. Also, neither the avalanche nor the ionization model can account for the observed thickness dependence [5]. 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.

7.3 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 damage. Next the absolute characteristics of the pulse are measured and finally, the shot in the sequence which causes damage is determined.

The schematic diagram of the experimental setup for damage studies is shown in Fig. 7.1 DCR-11 quanta ray (Q- switched mode) emitted by a Nd :YAG laser was employed. The laser output at 1.06 μm 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



1. Nd:YAG Laser
2. Mirror
3. Lens
4. Beam Splitter
5. Polymer Thin Film
6 Energymeter

Fig. 7. 1 Schematic diagram of laser damage measurement set up

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 is 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.

7.4 Results and Discussion

7.4.1 Threshold energy density

Polyaniline-EB, acid doped polyaniline, polypyrrole and polypyrrole / polyaniline blend films of various thicknesses prepared by casting technique have been subjected to laser induced damage studies. Once the shot which caused the threshold damage was identified, the threshold energy density and the power density could be calculated, knowing the area of the damage site from geometrical considerations. Table 7.1 shows the threshold energy densities determined for these films. It is observed that the threshold energy of polymer films involved in the present study decreases with the increase of film thickness and with the increase of the acid doping concentration. It is interesting to note that the laser damage threshold is very high for acid doped pani film. This may be due to protonation of pani film by methylsulfonic acid.

Surface damage in thin films arises mainly from impurities, imperfections or irregularities in the surface [19]. Even though the parent and dopant materials are pure, impurities and imperfections are included in thin films during the growth process or by infiltration during the exposure to the environment. Hence, in addition to the infiltration of oxygen, the absorption of other impurities from the atmospheric air into the film cannot be avoided or ruled out, since the laser damage study is being carried out in normal atmospheric air. The maximum size of the impurity is limited by the film thickness. i.e., as the film thickness increases so does the impurity size.

The above mentioned factors indicate that the breakdown mechanism followed in the polymer films of the present study is an impurity dominated one. Eventhough no report is available on the laser damage threshold density studies on polymer films, other reports on semiconducting and insulator films [10-11] are clearly supporting this argument.

7.4.2 Laser breakdown patterns

When the laser beam passes through the film, according to the energy of the pulses, different damage patterns were observed in the films. Damage spots having different shapes and sizes indicate the total damage at those sites. Figs. 7.2 to 7.5 show the typical photographs of the damage sites observed in Polyaniline-EB, acid doped polyaniline, polypyrrole and polypyrrole/polyaniline-EB blend films respectively. The micrographs show initial cracking in the films followed by total destruction at the laser focused sites. The agglomeration of damage craters is clearly seen in the figure.

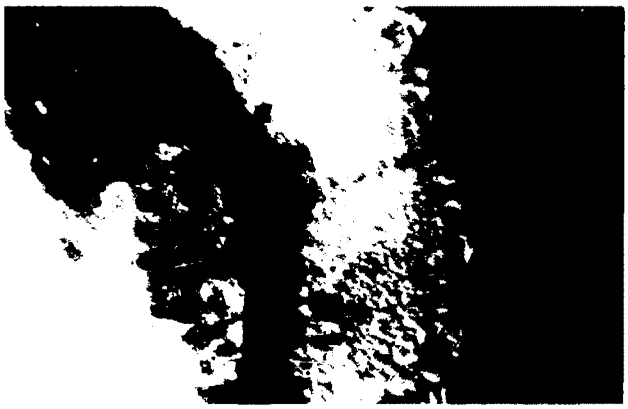


Fig. 7.2

Fig. 7.3

Fig. 7.2 & 7.3 Laser damage sites in Pani-EB and acid doped Pani films

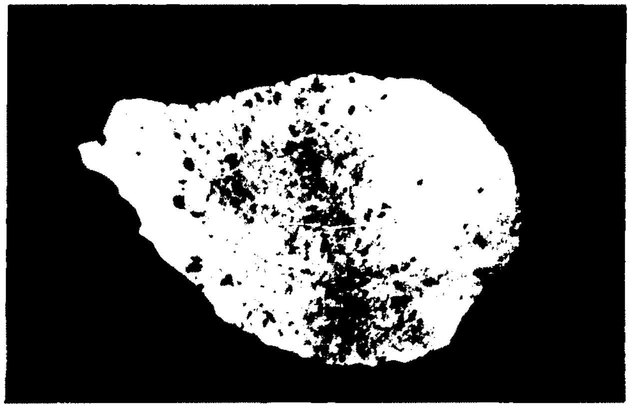


Fig. 7.4

Fig.7.5

Fig. 7.4 & 7.5 Laser damage sites in PPY and PPY/Pani-EB films

Table 7.1 Threshold energy density for different film thicknesses

Conducting polymer films	Film thickness (μm)	Threshold energy density (mJ cm^{-2})
Pani-EB	5	150
	30	135
	50	100
Acid Pani	3	220
	20	150
	30	120
PPY	8	98
	20	60
	35	24
PPY/Pani-EB	3	45
	15	30
	45	20

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