CHAPTER VII

PHOTOACOUSTIC STUDY OF LASER INDUCED DAMAGE THRESHOLD AND PLASMA PROCESSES

ABSTRACT

The process of laser induced damage and its detection using the PA technique are described. The threshold energy density for damage of a variety of materials like bulk polymers, metals and thin films have been determined to show the versatility of this technique. In-situ PA monitoring of the laser energy during laser generated plasma processes has also been described.
7.1 Laser Induced Damage Process: General Introduction

When a low power laser beam passes through a transparent material, no irreversible effect is observed, but at sufficiently high power or energy density, transient or permanent effects may be produced in the material. These effects include absorption and refractive index changes, removal of material from the surface, production of internal voids, melting vaporization and even violent shattering. This phenomenon of optical damage has always been a major limiting factor for the operation of high power lasers and their associated optical elements. There is a threshold value for the power density of laser beams for producing such irreversible damage effects in each material and this value is called the Laser damage Threshold (LDT) for the particular material. LDT values have great significance in connection with the studies on interaction of laser beam with materials. Ever since the output of laser systems has reached levels at which these effects are observed, there has been widespread interest in this area of research. The major part of the studies on LDT was done by workers in laboratories pursuing high power laser fusion experiments since it was they who first noticed the adverse effects of this phenomenon. The interest in Laser induced damage (LID) ranges from investigations of the mechanisms involved in this process and its practical applications to the improvement of the quality of laser optic elements by increasing their LDT.
Investigations on newer, more sensitive and dependable methods of determining this quantity are also important [1]. As the mechanism of LID is still not fully understood and moreover, since there are numerous parameters that finally determine the LDT of a material, a technique that can be applied to determine this quantity accurately for different kinds of samples has still not been evolved. Damage can occur either internally or at the surface of the target. The internal damage can occur due to particulate inclusions, small inhomogeneities, absorption or self-focusing in the material. The external damage is a more sensitive quantity and it depends, to a great extent on the surface finish, imperfections, impurities, inclusions or irregularities on the target surface [2]. Of the two, the surface damage is more serious since it occurs at a lower energy density, and it is often the surface of the target material that finds applications in laser reflection optics. The phenomenon of dielectric breakdown in bulk materials due to laser irradiation has not found much importance unlike surface damage mechanism due to the obvious applications of optical surfaces. The study of the bulk processes only helps in understanding the behavior of dielectrics because both the bulk and surface damage are often accompanied by plasma formation and so both of them involve, related, if not identical phenomena. It is seen that the power densities for surface damage is generally 0.3 to 0.5 times the bulk LDT values.

Laser damage threshold can be defined as the laser power or energy density at which physical damage to the surface occurs. Thus the determination of this quantity is a purely destructive testing process, though photoacoustic microscopy can, to an extent determine (non-destructively) the possible sites on the surface that might have a lower damage threshold. It is usually expressed in terms of the energy density or sometimes in terms of
the electric field associated with the laser beam. In general, it is seen that damage occurs to a given target under laser irradiation at a power level which is dependent on both the material parameters and the laser characteristics like wavelength, the temporal and spatial profile of the laser pulse etc. UV lasers have greater ionizing capability by virtue of their shorter wavelength as compared to the greater thermal energy of the IR lasers. Thus, a UV laser can cause greater damage to a surface than an IR laser of identical pulse shape, energy and width characteristics. Most of the mechanisms that result in damage to the target are dependent on the peak energy density though some are dependent on the total energy. In order to explain this phenomenon, various mechanisms have been proposed of which a few important ones are given in this chapter.

The actual measurement of the LDT involves three steps ie, to irradiate the sample at several laser energy densities, to measure the absolute characteristics of the laser pulse and finally to determine which of the laser pulses caused the damage to the target. Though the steps described are quite simple, the process of an absolute measurement of this quantity is beset with various problems. Some of these problems faced are discussed below [3].

7.1.1. Laser Beam Parameters

The questions that arise regarding the laser pulse parameters are the following:

What parameters should be measured to determine the laser flux or intensity? What is the relative or absolute accuracy of the measurements? How large should be the size of the focal spot in order to measure practical laser damage threshold? And, how many sites should be tested?
Since the laser pulse energy varies with the pulse width and the beam profile, these parameters must also be measured accurately. Sophisticated instruments like the streak camera, videocon, recticon [4] or even pyroelectric or photodiode arrays are often required for these measurements. In such cases, the serious problem is that regardless of how the image is recorded, there is a background noise level which greatly complicates the interpretation of the low-intensity wings of the profile. This can be eliminated to an extent by placing an aperture, the diameter of which is approximately equal to the FWHM of the profile. For such a setup, with a laser of pulse width less than 1 nsec, the uncertainties in LDT measurements due to the laser energy, flux and intensity are ±3, ±5-7 and ±10-15% respectively. The absolute accuracy in the energy density measurements, however, depends on the accuracy of the calorimeter used to determine the pulse energy, which, using commercial energy meters, can be measured with good precision within an error margin of ≤ 5%. Since it is the determination of the beam profile that involves serious problems, often, only the results of LDT measurements without shot-to-shot determination of the beam profile are reported. Obviously, the margin of experimental error is definitely enlarged in these cases. Even the ability to determine the laser flux within a 5% error does not imply that the LDT can be measured with the same degree of accuracy since uncertainties can be introduced by the large step-sizes in flux during the sequence of shots used for irradiation, or by indecision as to whether damage has actually occurred or not for a particular laser shot. The laser spot size must be big so as to ensure that the worst-case defects have been encountered. The morphology of laser damage in thin films show that damage occurs at isolated regions in the film, the exact nature of defects responsible for this being still unknown. The test area must be illuminated uniformly to within the desired precision of the LDT
measurement. Typically test areas > 5mm diameter are used. Since damage is a cumulative effect, multiple shots at the same site will lower the LDT. It is better to expose a new site to each shot under the assumption that the surface morphology is uniform within the measurement error. For testing of laser optics, it is needed to know as to how many shots the surface can endure before damage sets in. For such studies, multiple exposure is ideal, so long as the pulse-to-pulse stability of the shots is ensured. The work presented in this chapter has followed the method of "single-shot" laser damage threshold measurements. Moreover, there is no a-priori guarantee that different sites will respond alike to the same flux level.

The total energy $Q$ in terms of energy density $c(r)$ at the focal plane can be expressed as [5],

$$Q = c(r) \int_0^\infty 2\pi r \, dr$$  \hspace{1cm} ......(7.1)

and for a Gaussian beam, $c_0 = \frac{2Q}{\pi r_0^2}$ \hspace{1cm} ......(7.2)

where, $c_0$ is the peak on-axis energy and $r_0$ the radius at which the intensity has fallen to $1/e^2$ of its original value. In terms of the peak on-axis intensity, the damage threshold,

$$I = \frac{2Q}{\pi r_0^2 \tau L}$$  \hspace{1cm} ......(7.3)

The r.m.s. electric field associated with this intensity is,

$$E = 19.41 \left[ \frac{I \text{ (W/cm}^2 \text{)}}{\eta} \right]^{1/2}$$  \hspace{1cm} ......(7.4)
where $T_L$ is the laser pulse width, $n$ is the refractive index of the material. The total energy $Q$ is related to the incident energy on the focusing lens ($Q_{in}$) as,

$$Q = Q_{in} T_L T_S$$

$T_L$ and $T_S$ are the transmissions of the focusing lens and the sample respectively.

### 7.1.2. The Test Sample

The relevant questions regarding the test sample for LDT measurements are:

- What should be the surface finish of the sample?
- How should the sample surface be cleaned before testing?
- Will the use of detection techniques such as 'breath-fogging' during the experiments reduce the damage threshold?
- Can a small 'witness' sample, identical to the actual larger optical element to be tested, be tested for LDT in lieu of testing the original sample?
- And what should be the angle of the test sample with respect to the laser?

Since dust or other minute inclusions at the focal sites reduce the LDT at those sites, careful cleaning of the sample surface with organic solvents helps, but for large diameter beams, this problem is not very critical as compared to focused beams. Scratches and residue on the surface as a result of cleaning can also cause lower LDT, and thus should be done carefully. The surface finish of the sample can be visually inspected using intense white light and, if the sample is not hygroscopic, by breath-fogging technique, which has been a time honored process of
checking surfaces. However, there have been indications of lowering of LDT by repeated breath-fogging and the resulting residue formation on the surface [6]. It is ideal to orient samples like polarizers, reflectors etc., relative to the beam as it would be in actual usage. The LDT of anti-reflection (AR) films have been found to be independent of whether the film is used as an entrance or exit surface. In the case of using a 'witness' sample (for example, a smaller, similar surface coated simultaneously with the actual bigger optical element to be tested) being used instead of the actual element to be tested, there is no guarantee that the witness sample is in every way identical to the actual one, since the damage process is dependent on various parameters. Thus this method cannot be a fool-proof method of testing a sample. Moreover, in AR coatings, the LDT was found to be highly dependent on the substrate material properties [7]. Since there is no guarantee that each point on the sample surface will have identical surface features, multiple irradiation of the sample surface can give an average value of the damage threshold.

7.1.3. Detection Technique

Many methods of detection of the LDT have been reported, none of which can be acclaimed as accurate and fool-proof for all kinds of samples. It is seen that the LDT measurements are influenced by many parameters relating to the experimental conditions like pulse width, repetition rate, beam diameter, beam focusing, temperature, laser frequency, optical pumping conditions etc, and to the sample conditions like material growth or preparation conditions, surface finish, presence of impurities etc. Some of the problems faced in the conventional LDT determination techniques are:

What is the practical definition of laser damage? How does
one determine whether damage has occurred, and how certain is the determination? Is there a single, fool-proof indicator of the damage occurrence that is usable with all types of test samples? And do the LDT measured in the laboratory correlate with the levels at which the optical element actually operates?

The different techniques used for detection of LDT are described below:

(a) Emission of Spark/Light

Detection of sparks and light emission can be made by visual observation of the damage process in a dark room. A spark is defined to be a plasma heated sufficiently that it expands vigorously, sometimes audibly. Often, light emitted by a diffuse plasma appears as a glow rather than a spark. There is also the possibility that fluorescence emission can occur without occurrence of damage. The difficulty in detection may arise from the fact that light emission may not be seen either due to other visual distractions or due to the frequency range of the emission. Also the difficulty exists in distinguishing the actual source of light emission, i.e., if it is from the front or back surface or from the bulk. This technique only aids the detection of LDT rather than the actual determination and is not reliable for multi-layer AR films.

(b) Change in Scattering/Reflection

The visual detection of the variation of small-angle scattering or reflection/transmission of a probe beam from the site of irradiation can give indication regarding the damage process. This simple technique is remarkably successful in thin films if large beams are used so that many scatterers are produced in the near-threshold damage sites.
(c) Particulate Plumes

They are detected by focusing a light beam on to the damage site. The disadvantage in this technique is that very little material is ejected during damages occurring near to the threshold.

(d) Microscopy

Techniques such as scanning electron microscopy (SEM), bright field, dark field microscopy, Normarski microscopy [8] etc. are often used to detect the threshold. SEM technique, though effective in locating damages, is time consuming and destructive in nature. For thin film samples the Normarski microscopy is the most suited technique. This detects the change in optical scattering from the target induced by the microscopic film ruptures caused by the irradiation.

(e) Breath-fogging Technique

It is one of the easiest and time tested techniques to observe the occurrence of laser damage on non-hygroscopic bare surfaces. This technique, as the name indicates, functions so absolutely that other tests are redundant. To be most effective, the test must be performed soon after the irradiation is completed, since the breath-fogging pattern becomes less distinctive after several days. As mentioned earlier, it has been seen that repeated use of this technique leaves a residue which tends to decrease the LDT of the sample.

(f) Surface Potential Mapping Technique

Mapping of the surface potential on the target surface throws light on the post irradiation condition of the surface [9]. It is seen that the surface potential or the work function of the
target material varies as a function of position with respect to the site of laser irradiation. In dielectric materials, an accumulation of negative charges in an area ten times the diameter of the laser spot was observed. Only in the case of copper was the polarity of the surface charges positive. No potential change was observed for ripple formation on silicon surfaces. A Kelvin type non-contact probe, working on the principle of adjusting the d.c. voltage on the test capacitor formed by the sample surface and a reference electrode so as to null out the a.c. variations in the capacitance voltage caused by physically dithering the reference electrode, was raster scanned over the irradiation site with a resolution of ~1mm to obtain the surface potential mapping. Although no pre-damage changes in the surface potential were observed, all larger damage features had a surface potential changes associated with it. Damage types such as the pit formation have been detected successfully using this technique. It is seen that the post-damage surface potential decays over a time scale of hours to a fixed value approximately 1/4th of its initial value which corresponds to permanent damage. The interesting thing to note in this technique is that the absence of pre-damage potential changes indicate that this technique is relatively unaffected by the process of surface cleaning. The relatively large area of the surface potential distribution (4-6mm compared to a laser spot diameter of 0.3mm) with respect to the irradiation site suggests that the adjacent test sites should be sufficiently spaced out during measurement process.

7.2. Mechanisms of Laser Induced Damage

Of the many proposed mechanisms to explain the various aspects of the laser damage process, a few important ones are briefly mentioned below. Since most of these models require complicated parameters such as the material band structure and the electron
effective mass which are often not available for many dielectric materials, it is impossible to calculate the damage threshold due to each of the competing mechanisms. Thus the only practical way to determine the most appropriate model is to examine their predictive ability in describing the various damage thresholds with easily controlled experimental or sample variables such as the laser pulse width, energy, wavelength and sample (bulk and surface) properties.

The optical power levels for catastrophic damage to bulk materials (intrinsic damage level) is related to the thermal and electrical breakdown of an insulating material. Massive insulators have a.c. dielectric breakdown strengths ($E_B$) of 1-5 MV/cm, equivalent to optical power densities ($P_D$) of 50-1000 MW/mm$^2$, obeying the equation,

$$P_D = \frac{E_B^2}{Z'} = \frac{E_B^2 \eta}{Z_0}$$

Where, $Z'$ and $Z_0$ are the impedances of the dielectric and free space respectively, and $\eta$ the refractive index. It is interesting to note that the relation between $P_D$ and $E_B$ is independent of wavelength except through the refractive index $\eta$. Since the interaction can occur between several mechanisms and will modify the apparent power density distribution, these intrinsic quantities are rarely measured. In practice, the laser damage threshold of a material, in a particular set of experimental circumstances may be due to one or more of the many mechanisms involved. Some of these are given below:

7.2.1 Electron Avalanching

Electron avalanching is probabilistic in nature, since it results from the multiplication of an initially produced free electron.
There is always a non-zero probability of the damage, and this is dependent on the optical intensity. If $p_1$ and $p_n$ are the probabilities of damage in the first and the $n$th shot so that $p_1 \propto \exp(-K/E)$ where $K$ is the constant determined by the sample properties and the experimental conditions and $E$ is the electric field associated with the light wave, then [10],

$$p_n = p_1 \left(1 - p_1\right)^{n-1} \quad \cdots \quad(7.7)$$

It is also relevant, to approach practical situations, by considering large areas. In this case, a number of free electrons may be produced instead of one as in the above treatment. If $p = p(E)$ is the probability for breakdown when one initial electron is present, then, $p'(E) = np(E)$ is the probability for breakdown when the area of the beam is increased and $n$ initial electron are sampled. If $np(E) > 1$, then $p'(E)$ is taken as unity. The effect of this is to make the damage probability versus power density curve to have a steep rise, thereby making the LDT well defined. This mechanism does not explain satisfactorily the damage process if,

i. the value of $K$ is high,

ii. a larger volume of material is involved than that which is small enough to reveal the probabilistic properties of damage

iii. an experiment where intermediate power densities were missed or self-focusing always produced an intensity so that intermediate ranges were not studied, or if,

iv. a material in which a non-avalanche process dominates the damage process.

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7.2.2. Multiphoton Ionization

When the incident photon energy is approximately $\frac{1}{3}$rd that of the band-gap energy $E_b$ of the solid, multiphoton absorption can take place and can contribute significantly to the breakdown process. Thus the LDT will decrease as the laser frequency is increased beyond an equivalent photon energy of $\sim \frac{1}{3} E_b$ [11]. The multiphoton ionization process is said to be the prime source of the supply of electrons to start the electron avalanche process [12-14].

The Keldysh model [15] for multiphoton ionization process is widely accepted among the various other models due to its comparatively easier numerical analysis and due to better correlation with experimental results [16,17]. For $n$-photon absorptions ($n > 3$), only this analysis gives comparable correlation between the calculated and experimental values. According to this analysis, the dependence of the optical energy/unit area on the laser pulse width $\tau_L$ reveals that if $E_b \ll \hbar \omega$, the breakdown process is independent of time. For very high order photon processes, $E_b \gg \hbar \omega$, and then the process is linearly time dependent. This also predicts a decrease in the breakdown field with increase in laser frequency. Multiphoton (two and three photon) processes have been shown to be the cause of laser damage in materials like CdTe, CdS and ZnSe under IR laser irradiation. The damage process has been detected using PA technique in conjunction with transmission techniques [18].

7.2.3. Conduction Electron Absorption

It is possible for an electron in the conduction band of a material to be accelerated by the laser field to a greater energy than the band-gap, thus leading to electron avalanche. For this
to occur, the lifetime of the electrons in the conduction band must be long enough and field strong enough to produce sufficient number of electrons with energy greater than the band-gap energy. It has been analyzed that the power density needed for damage to occur by this mechanism changes from being time-independent, for pulses longer than $10^{-7}$ sec to being inversely proportional to the pulse width $\tau_L$ for shorter pulses [19]. The threshold power density has a wavelength dependence ($P_D \propto \lambda^{-2}$) and a temperature dependence through the electron concentration.

### 7.2.4. Stimulated Brillouin Scattering

Stimulated Brillouin scattering results from an internal feedback mechanism which amplifies an acoustic wave and a secondary electromagnetic wave at the expense of the input laser beam [19]. At high power levels, damage occurs from the mechanical stresses associated with the acoustic wave. For long pulse lengths and cw lasers, a steady state scattering is reached and damage occurs at constant power density. For Q-switched lasers, the threshold power density is inversely proportional to $\tau_L$.

### 7.2.5. Absorption by Inclusions

Many samples are likely to contain inclusions and impurities of atoms or clusters of foreign materials. Absorption at the wavelength of the input laser by inclusions, bubbles, sharp scratches etc. can lead to severe local heating and to damage due to the resultant thermal expansion or melting of the surrounding material. The damage threshold in this case may be related to [10],

1. The energy density required to produce a fracture stress in the host at the surface of the inclusion due to expansion of the heated outer shell with little heat being conducted into
the inclusion or the host lattice. This has a \( \tau_L^{1/2} \) dependence and is relevant for very short pulses or for very large inclusions \( (E_D \propto \tau_L^{1/2}) \).

2. The energy density required to produce a fracture stress in the host due to the expansion of the inclusion. This is time independent and relates to the intermediate size of the inclusion for which \( E_D \propto R \), \( R \) being the radius of the inclusion.

3. The energy density required to produce a fracture stress due to the thermal mismatch between the inclusion and the host lattice (both being heated by conduction) and holds good for long pulses or very small inclusions \( (E_D \propto \tau_L/R) \).

### 7.2.6. Bulk Absorption

Bulk absorption can occur due to the presence of impurities, color centers, conduction electrons or by the lattice, and can cause laser damage by the heating and the consequent fracture of the region surrounding the laser beam. This threshold is dependent on both the pulse length and the area heated \( (E_D \propto \tau_L/a^2) \), where \( a_0 \) is the beam radius. The proportionalities are dependent on the thermal properties of the material [19].

### 7.2.7. Self-Focusing

The self-focusing is a reduction of the laser beam diameter below the value predicted from the optical properties of the unirradiated material, and can result from any process which leads to an increase of the index of refraction with increasing light intensity and/or temperature [20]. The actual damage process will still be due to one of the above mentioned mechanisms, but
the damage occurs at a lower damage threshold owing to the substantial increase in energy density due to the additional focusing. Possible causes of self-focusing are, electrostriction, electronic distortion, molecular liberation and absorptive heating.

Electrostriction would occur in a dielectric material under laser irradiation as the net electrostriction force at any point is proportional to the square of the electric field. Thus a radially symmetric beam would lead to a radially symmetrical stress with an associated change in the refractive index leading to self-focusing.

Heating by absorption at the laser frequency will lead to thermal self-focusing if $\frac{d\eta}{dT}$ (\eta is refractive index and T the temperature) is positive. If it is negative, it can contribute to local increase in power density, but not self-focusing. The threshold power density for damage due to self-focusing is inversely proportional to the pulse length provided the latter is small compared to the acoustic interaction time.

The electronic distortions and molecular liberation processes dominate at very short pulse lengths whereas electrostriction dominates for Q-switched pulses and thermal self-focusing for free-lasing pulse trains.

**7.3. Forms of Laser Induced Damage**

As a result of the irradiation of the surface with laser pulse, any one or many of the above mentioned mechanisms can induce different kinds of damage to the test sample. Damage can occur on the front surface, inside the sample or on the rear surface of the test target. Some of the major types of laser induced damage observed are the bulk, surface and the inclusion damages. These
different kinds of damages exhibit different characteristics and occur at a range of threshold energy density for a given material. Scaling laws provide a general guide to the behavior of the damage threshold as the experimental conditions such as the pulse width ($\tau_L$), spot size, surface roughness, etc. are changed. Departures from the expected scaling often indicates the onset of some new phenomena or the introduction of extrinsic factors. Relations such as the $\tau_L^{1/2}$ dependence of the damage threshold, are widely applicable to surface damage occurring due to very short pulses. For longer pulse widths (greater than a few 100 psec), extrinsic factors may enter the scene, which cause a departure from this scaling law. Finally, these scaling laws are empirical and lack full theoretical justification. Nevertheless, they provide a useful guide for exploratory damage studies to new conditions and provide a test of consistency for measured LDT values.

7.3.1. Surface Damage

The measured surface-damage thresholds for samples in air are apparently higher for the front than for the rear surface. At the front surface, the plasma that is formed at the threshold occurs in air and protects the sample by absorption of the incident power. At the rear surface, the plasma occurs inside the material, thus increasing the absorbed power density in the material and causing more catastrophic damage. Sparks are usually visible and these provide some kind of visual indication of the onset of surface damage.

The surface-damage threshold is highly sensitive to the degree of polish, type of polish, surface cleanliness and subsequent treatment. The surface-damage threshold increases with the quality of the surface polishing. The scratches on the surface should be less than $1/100^{th}$ of the wavelength of the laser.
ight for maximum surface-damage threshold [21]. "Soft" materials may have apparently a flawless surface, but still contain a badly disturbed or polycrystalline surface layer. Chemical polishing and ion-beam cleaning of the surfaces does improve the quality and thus the LDT of the surface [22].

In the surface of the damaged layer, another interesting form of damage i.e., the formation of ripple patterns have been observed. Melting of a surface by laser radiation typically leaves its trace in the form of permanent ripples or corrugations. It is seen that the ripple formation occurs due to laser damage, laser annealing, etching etc. They appear close to the melting point or the damage threshold and appear in all materials ranging from metals to semiconductors to dielectrics irradiated with high power lasers of all wavelength (10.6μm to UV) and pulse widths (psec to cw) [9,23]. The patterns are often unrelated to the beam profile and appear even if the incident beam is smooth. Many forms of such patterns like ripples, streaks etc have been reported all of which have not been fully understood as yet. Explaining a particular pattern needs to answer at least two questions, (which may or may not be related) regarding (i) what is the source of the pattern and, (ii) by what physical mechanism is it imprinted on to the sample surface [24].

Of the many possibilities, it is often seen that the source of the pattern generation is light scattering from material imperfections or dust particles. The scattered radiation, being coherent with the incident beam, interferes with the latter to form patterns of modulated irradiance which now acts on the material. A point like scattering centre like a dust particle located in the ambient air at a distance z away from the sample surface makes a system of confocal ellipses (circles in the case of normal incidence) described by,
\[ r_n = \frac{\eta \lambda \left( B_1 + \sqrt{1 + B_2 (1-B_2^2)} \right)}{(1-B_2^2)} \quad \ldots \ldots (7.8) \]

where \( B_1 = \cos \phi \sin \theta \) and \( B_2 = \frac{2z}{\eta \lambda \cos \theta} \), \( \theta \) being the beam incidence angle measured from the surface normal and \( \phi \) the polar angle in the sample surface measured in the plane of incidence. \( \eta \) is the refractive index, \( \lambda \) the wavelength of the laser, and \( r_n \) is the distance from the vertical passing through the scatterer to the \( n^{th} \) fringe. In the case of linear rather than a point-like scatterer, such as scratches on the surface, fringes parallel to the scatterer are produced and usually have a spacing of \( \lambda/(1+\sin \theta) \) [25]. However, these patterns are often more complex than that simple geometric optics would indicate. The efficiency of interference in a particular direction depends on the state of polarization of the incident beam. The formation of fringes with spacings of \( \lambda/\cos \theta \) running parallel to the polarization direction of a p-polarized incident beam was observed on nominally smooth surfaces [26]. It is seen that the spacing of the ripple formed is related to the wavelength of the incident radiation. It is proportional to \( \lambda_0 \) the vacuum wavelength of radiation in the case of metals and small band-gap semiconductors. If the scattered wave propagates inside the material rather than in air, one would expect the fringe spacing to scale with \( \lambda/\eta \), (where \( \eta \) is the refractive index of the sample material for wide band-gap dielectrics) rather than \( \lambda \). Fringes with such spacings were observed in transparent dielectrics [27]. Though these patterns differ in spacing, they all run in a direction normal to the applied optical field [9]. A generalized treatment of interference of scattered waves in terms of nonradiative "radiative remnants" propagating along the surface of the material.
was proposed by Sipe et al [28,29].

Surface deformations are the most common and efficient scatterers but "latent" patterns, such as lateral variations in the lattice temperature or in free-carrier density [30] seem to result in the same scattering even on geometrically smooth surfaces. Stimulated scattering at surface polariton waves [28,31] have been observed in molten Germanium [32] and quartz [33]. Whatever the origin, the scattered fields from different scattering features interact and diffract at the ripples forming secondary ripples. Since the resulting pattern contains Fourier components at several spatial frequencies, once a fringe pattern has been implanted physically on the surface, it can perpetuate itself coherently in subsequent, fully or partially overlapping laser shots [34]. This may explain the gradual build up of periodic damage pattern that is frequently observed during repeated irradiation by pulses too weak to cause any conspicuous damage individually [35]. Once the heavy damage has occurred, these surface patterns tend to deflect or scatter a large part of the incident light, thus enabling the detection of a reduced specular reflectance [36].

How are these modulated irradiance patterns physically transformed into a persistent variation of the surface geometry? The basic sequence is that at laser damage threshold levels, the surface melts, undergoes deformation and finally after irradiation, resolidifies making the deformations permanent. The mechanism of deformation is dependent both on the absorbed fluence and the material properties [37]. The melt pattern actually formed would be random for a mathematically homogeneous beam, but even the slightest modulation of the irradiance by interference or other mechanisms will produce regularities in the pattern.

Also often related to surface rippling are the acoustic
phenomena. Pulsed melting of surface will cause an abrupt local increase in the density which acts as a strong source of acoustic waves [38]. Ripples result from the interference of the incident beam and the surface waves generated on the sample surface though the exact nature of these waves are not clearly known. Surface capillary waves frozen-in after irradiation have been related to surface ripples with wavelengths in the \( \mu m \) range and are unrelated to light scattering [39,40].

Another potential source for ripple formation in the melt regime is surface oxides which can stay solid on top of the melt layer and these tend to become wrinkled like the skin on milk [41]. At even high irradiance, the molten surface is shaped by evaporation [42]. On polished surfaces, strong evaporation results in extreme damage, manifested optically by diffuse rather than specular reflections [43].

A decrease in the surface damage with the ambient gas pressure has been observed in IR optical materials at 10.6\( \mu m \). It has been explained on the basis of the adsorbed water vapour assisted damage process on the surface. The condition for breakdown development in the water vapour region corresponds to the requirement that the rate of increase in of the energy of electrons in the field of laser radiation of intensity \( I \) must exceed the maximum rate of energy loss by electrons due to elastic collisions with neutral molecules [44], so that,

\[
I > \frac{m^2 c \Delta}{2 \pi M e^2} \omega^2 \left(1 + \frac{v_e^2}{\omega^2}\right) \approx 2.65 \times 10^7 \left(1 + \frac{v_e^2}{\omega^2}\right)
\]

......(7.9)

Where, \( m, e \) are the mass and charge of the electron, \( \Delta \) the ionization potential, \( M \) the mass of the molecule, \( \omega \) the laser
frequency and \( c \) the velocity of sound. \( \nu_{\text{e}} = \rho_{\text{v}} v_{\text{e}} \sigma/M \) is the frequency of free electron collision with neutral molecules, \( v_{\text{e}} \) mean electron velocity, \( \sigma \) the cross section of electron collision with molecules and \( \rho_{\text{v}} \) the vapor density. The dependence of the LDT on the vapor density is evident.

### 7.3.2. Impurity/Inclusion Damage

Low threshold levels for internal damage can be associated with identifiable singularities like dielectric inclusions, bubbles (voids), metal or metal oxide particles and misoriented crystallites. All these singularities have their own limited range of damage thresholds and the likely cause of the damage can be determined by repeated analysis of the values and appearance of the damage.

Since the focal point of the lens is unlikely to coincide with an inclusion, some variation in the damage threshold values are to be expected, specially while using focused radiation. Also, it is possible to miss microscopic inclusions when performing single-shot experiments. It is therefore advisable to test the sample with a larger beam diameter or by multiple irradiation of adjacent areas to the test site and obtaining an average value. Voids or bubbles also lead to damage which occurs at higher power levels and this tends to have a greater catastrophic effect. Some materials get damaged more severely when the laser beam is in a certain crystal plane or when it has a certain polarization. The sample is more susceptible to damage by cleavage when the direction of the laser is parallel to the cleavage plane of the crystalline sample [1].

The most noticeable feature unique to the impurity/inclusion model is the prediction of an increase in the damage threshold with decrease in the film thickness due to the fact that
the inclusion size is limited by the thickness of the film \[45\]. Based on this theory, an approximate evaluation of the damage parameters can be made, so that, the radius at which the first damage occurs is given by, \[46\]

\[
r_d = \frac{1}{2} \sqrt{\pi D_h \tau_L}
\]

......(7.10)

where, \(k_m\) is the thermal conductivity of the host material and \(\tau_L\) the laser pulse width. The damage threshold in terms of the electric field associated with the laser is,

\[
E_{\text{dam}} = \sqrt{k_m C_m \rho_m \tau_L}
\]

......(7.11)

Here, \(k_m C_m \rho_m\) are the thermal conductivity, specific heat and the density of the sample (host) material respectively. These relations not only show the square root dependence of the laser damage threshold on the laser pulse width, but also predicts that the LDT is proportional to the temperature at which damage occurs and varies as the square root of the product of the specific heat and thermal conductivity of the host material. By this reasonable approximation, it is seen that the LDT is independent of the impurity properties \[45\].

7.3.3. Bulk Damage

As mentioned earlier, the intrinsic bulk-damage thresholds is related to the dielectric breakdown strengths (Eqn.7.1.). Since the surface damage is a more important factor in laser related optics, bulk damages are only of importance in the study of the damage phenomenon. Generally, the bulk damage is preceded by the surface damage in most cases. One process of bulk damage is due
to the reduction of the damage threshold due to multiple reflections. It is seen that microscopic cracks, grooves, and bubbles account for the apparent lowering of the surface breakdown intensity with respect to the bulk damage threshold [2].

The electric field inside the discontinuity \( E_{in} \) can be represented as,

\[
E_{in} = \frac{E_0}{1 + \left( \frac{1 - \varepsilon}{\varepsilon} \right) L} \quad \ldots..(7.12)
\]

where, \( L \) is the appropriate depolarization factor and \( \varepsilon \) the dielectric constant being equal to \( n^2 \), and \( E_0 \) is the electric field associated with the laser beam.

The effect of the breakdown field for a sharp scratch is,

\[
P = \frac{E^2 \eta}{z} \approx \frac{E^2 \eta}{z_0} \quad \ldots..(7.13)
\]

and is highly dependent on the refractive index. Fig.7.1. shows the effective electric fields at the different types of discontinuities that are encountered by the laser. These arguments are applicable to both internal and surface cracks, grooves or pores, and is the main reason why the laser damage threshold for surfaces are less than their bulk values. It is seen that the LDT decreases with increase in the number of pulses for materials in which electron avalanching effect is temperature dependent. This is due to the fact that since damage is a cumulative process, successive pulses increase the temperature and subsequently due to electron avalanche, the threshold is reduced.
Fig. 7.1. The schematic of the different discontinuities encountered by the laser beam and the effective electric fields associated with the discontinuities.
7.4. Laser Induced Damage in Metals

The laser damage process in metals is not as complex as in the case of dielectric materials. This process is theoretically quite well understood in the case of metals [47,48]. The damage process is mainly due to absorption of the radiation and subsequent melting or cracking of the surface of the target due to thermally induced strain [49]. A small amount of the incident radiation penetrates the target to a distance called the 'skin depth' where this radiation is absorbed by the free carriers, which, under special circumstances, can lead to the above mentioned damage processes [43]. The LDT in the case of metals is found to depend on the absorptivity, surface and thermal properties of the target [50]. The energy density for laser damage in metals can be estimated to be [51],

$$E_0 = \frac{(T_m - T_o)(k \rho C_m)^{1/2}}{\alpha_o}$$

......(7.14)

Where, $T_m$ is the melting temperature, $T_o$ the ambient temperature, $k$ is the coefficient of thermal conductivity, $\rho$ the density, $C_m$ the specific heat and $\alpha_o$ the absorptivity at $T_o$ for the laser wavelength.

7.5. Laser Induced Damage in Polymeric Materials

With the advent of the use of the so-called "organic glasses" i.e., transparent polymeric materials for laser optics, laser damage threshold measurements in various bulk and thin films of polymeric materials such as those in the methacrylate series like polymethylmethacrylate (PMMA) and their co-polymers as well as polymers containing additives in the form of various plastics like
dimethylphthalate have gained great importance. Many of these materials are now being used as laser optical elements and thus the need exists to study the laser induced damage process in these polymeric materials [52]. Thin, protective coatings of Polytetrafluoroethylene (PTFE), commonly known as TEFLON are often used in many applications such as protective coatings in passive components of the excimer laser cavity where highly corrosive halogen environment exists [53]. For the production of thin films of this polymer by laser ablation technique, the damage and ablation measurements in the bulk samples need to be carried out. Again, as mentioned earlier, though many mechanisms have been proposed, none has provided a universal and completely satisfactory explanation of the actual damage processes in polymers. Moreover, the method of increasing the optical strength of polymers is still a developing field. A few relevant cases are presented below.

The effect of high power lasers on transparent polymeric materials is different from that of transparent dielectrics. The former has a lower LDT as compared to the dielectric crystals, a strong dependence of the optical strength on the micro-elastic properties and temperature, a wide range of radiation intensities below damage threshold in which cumulative effects are observed, the occurrence of micro damage of dimensions $\geq 10\mu m$, not accompanied by bright spark, and the absence of formation of highly absorbing products like soot during damage process [54-58]. Another characteristic feature of the polymer materials that distinguishes them from other transparent dielectric materials (glasses and crystals) is the higher optical strength of the surfaces of polymers as compared to their bulk [57,59]. It was seen that this relationship between the two damage thresholds holds good irrespective of the method of surface treatment. This is important from a practical point of view because it is usually
the surface strength that is the limiting factor in its use as laser optical elements.

The damage in polymeric materials has been attributed to various mechanisms depending on the kind of results obtained. Multiphoton photodestruction of the polymer chains is one of the major causes leading to damage in these materials [60]. Another possibility for damage to occur in polymers is due to the mechanisms involving the formation of highly absorbing products and inclusions resulting from chemical changes at high temperatures produced following irradiation by laser beam [57,61,62].

Anomalous micro-elastic properties of polymers can lead to damage in these materials even when the heating of absorbing inclusions is negligible [56]. A mechanism of non-linear absorption of the incident laser radiation associated with triboprocesses in the matrix surrounding the inclusion accompanied by the formation of micro cracks in the matrix has been proposed by Danileiko et al [63]. This mechanism could explain the formation of visible damage of dimensions > 1\(\mu\)m initiated by small inclusions (\(\leq 0.1\mu\)m). This essentially involves surface electronic states being formed during the micro crack formation process, and these are capable of absorbing the incident light energy to cause damage. The existence of such states have been shown by the sub-threshold luminiscences in the VIS-near-UV regions due to radiative de-excitations [64]. In this analysis, the damage mechanism for a spherically symmetric absorbing defect comprising of a small region of dimension (smaller than the wavelength) and having an absorption coefficient appreciably larger than the surroundings, under irradiation for a short pulse is considered. This induced thermo-elastic stresses increase with time in the matrix. At the damage threshold, these stresses reach micro-breaking magnitudes leading to micro cracks. A
further increase in the laser energy causes the increased density of these micro cracks and thus the concentration of electronic states capable of further absorption of the laser energy increases. Assuming the thermo-elastic stress near an inclusion to be proportional to its temperature, the process of non-linear heating in the matrix can be described in terms of a heat conductive equation which describes the absorption of laser energy by the inclusion and possibly by the electronic states formed at the damage sites, the solution of which gives the expression for the temperature at the centre of the defect. The LDT can be estimated from the conditions of loss of stability of the steady state solution of the equation for the temperature with respect to time. This mechanism accounts for damage mechanisms like micro-cracks and micro-damages [65].

7.6. Photoacoustic Detection of Laser Induced Damage

The interaction of high power lasers with matter can be studied by methods that can be grouped into two categories viz, by the properties of the etch products detected in the gas phase above the ablated surface at some time after the ablation process [66-70] and by monitoring the PA response of the sample being ablated [71-77]. Laser induced fluorescence, mass spectroscopy, and optical spectroscopy can be used to characterize the ablated species from the sample. In these methods, it is often not possible to separate these results which relate to the nascent species generated in the ablation process from those which relate to the subsequent collisional expansion. This expansion is supersonic in nature and leads to a re-distribution of the internal energy into translational energy directed normal to the target thereby yielding little direct information about the ablation process itself, or secondary ionization, plasma formation etc. further complicating the interpretation of the results. In
contrast, the PA technique is relatively insensitive to this expansion of gaseous products and can yield direct information relating to the damage and ablation process [78].

High power lasers are becoming increasingly important for controlled removal and etching of organic surfaces in both industrial and medical sectors. In order to obtain the required amount of etching of the sample surface, the laser energy has to be controlled quite accurately, depending on the laser damage threshold of the sample. Removal of polymeric materials under intense laser irradiation can be termed as 'ablative photodecomposition' [72]. Some transparent polymeric materials are also widely used in the fabrication of high power laser optical components like prisms, lenses and beam-splitters and also in nonlinear optics while opaque polymers find applications in areas like photolithography. It would therefore be of considerable significance to investigate the optical strength of polymeric materials. The determination of the optical damage threshold of polymers is thus important for determining the laser energy density required for controlled etching of the material surfaces. Most of the data on laser damage are obtained through microscopic and other methods of visual inspection of the laser damaged surface, which is a tedious and not an in-situ process. Techniques based on phenomena like photothermal deflection and photoacoustic effects have also been proven recently to be very effective in evaluating laser ablation thresholds of both transparent and opaque samples [67,73-77,79-81].

It is well known that the interaction of laser beam with matter produces acoustic pulses in the target material. The absorption of the incident pulsed radiation gives rise to transient thermal variations due to the heat released through non-radiative channels of de-excitations in the sample [82,83]. Since the acoustic signal is linearly-proportional to the energy
absorbed [82] so long as transducer saturation does not set in, the detection of the LDT involves only the monitoring of the acoustic signal pulse resulting from the irradiation of the target by the laser pulse. At lower laser intensities, acoustic waves are generated essentially by thermo-elastic stress. The analysis of the acoustic pulses produced at comparatively lower laser energies can be used for non-destructive testing (NDT) and evaluation of materials [84]. At higher laser energies, where damage of the surface occurs, resulting in plasma formation, the ablation of the material from the surface causes a reactive force which acts as an intense source of acoustic waves [84]. During dielectric breakdown resulting from the optical energy absorbed in the illuminated volume results in local heating, thus producing a thermal expansion. The boundary conditions for a free space stipulate that this expansion be followed by a tension pulse. This shock wave, having a bipolar waveform [78], propagates with a velocity appropriate for a longitudinal wave in a direction opposite to that of the laser [85,86]. The velocity $v$ of this shock wave is [87],

$$v = \sqrt{\frac{E_{\text{eff}}}{\rho}} \quad \ldots \ldots (7.15)$$

where, $E_{\text{eff}}$ is the effective elastic constant for the longitudinal excitation and $\rho$ the material density. The acoustic pulse duration $\tau_a$ is determined by the laser pulse width $\tau_L$ and the acoustic transient time $\tau_t$ of the acoustic signal in the sample, so that [88],

$$\tau_a = \sqrt{\tau_L^2 + \tau_t^2} \quad \ldots \ldots (7.16)$$

For an opaque solid, $\tau_t \approx l/c_o$, where, $l$ is the optical absorption
length and $c_o$ the velocity of sound. In the case of the teflon samples used (7.5mm thick) in the results presented here, the value of $\tau_t$ and $\tau_a$ were determined to be $\sim 940 \text{m/sec}$ and $7.9 \mu\text{sec}$ respectively. The time ($t$) required for this acoustic response to develop is of the order of $10^{-10} \text{ sec}$ [19] after which it begins to propagate through the medium to the transducer. For free lasing and Q-switched pulses, where $\tau_L$ is greater than $t$, the damage threshold power density is independent of the pulse length. For a single mode-locked pulse the power density for damage increases with decreasing pulse length. A mode-locked pulse train, however does give enough response time and damage therefore occurs at similar power density as for longer pulses.

This shock wave can either be detected by an acoustic transducer placed in contact or in the vicinity of the sample or by other techniques like the photothermal deflection (PTD) technique which involves the detection of the deflection of a probe beam grazing the sample surface due to the refractive index gradient developed in the air above the irradiation spot on the sample. These two techniques not only have the advantage of sensitivity over conventional damage detection techniques, but can also be used in-situ for LDT measurements. Among the two, the PA measurements involving the transducer placed in firm contact with the sample is more sensitive than the PTD technique since the latter requires that the layer of air above the irradiation site be sufficiently heated so as to cause detectable deflection in the probe beam. In the former case, since the transducer is in firm contact with the sample, there is good acoustic impedance matching between the sample and the transducer and thus it is sensitive to even sub-threshold levels of laser energy [82]. PA technique also has the added advantage that it can effectively distinguish between bulk and surface sources of heating and thus the respective thresholds. Moreover, the PA transducer output
produced being highly dependent on the amount of energy absorbed, can respond to the anomalous absorption induced by inclusions and impurities in the sample. IR lasers give rise to multiphoton excitation over the vibrational manifolds of the ground electronic states of the polymeric sample which is then followed by thermal decomposition resulting in the ablation or damage of the target surface. Such multiphoton absorptions and subsequent damage studies using PA technique have been studied by Van Stryland et al [85]. It has the added advantage that in the use of PA technique, the amount of energy absorbed is directly measured rather than monitoring the reflected or transmitted energy [85]. For ablation to take place, there exists a threshold laser energy density beyond which irreversible damage of the sample surface occurs. Many of the material parameters influencing the thermal balance of the system are also significantly altered during the ablation process.

The amplitude of the PA signal generated by the heat transfer from the target to air can be estimated as follows [89]. The heating of the air is small due to the comparatively small thermal conductivity of air. The heat flux from the target into the surrounding air can be represented as, \( H(T_m - T_o) \), where \( T_o \) is the ambient temperature and \( T_m \) the target material temperature, and \( H \) is the heat transfer coefficient. For a sample of surface reflection coefficient \( R_s \), the increase in the temperature of the air surface layer of thickness \( l \) next to the target as a result of this heating will be,

\[
T_m = \frac{H (1-R_s) I_o (\tau_L)^{1/2}}{C_v I \left( k_m C_m \rho_m \right)^{1/2}} \quad \ldots \ldots (7.17)
\]

Here, \( I_o \) is the laser intensity, \( \tau_L \), \( k_m \), \( C_m \) and \( \rho_m \) are as defined.
in section 7.3.2. \( C_v \) is the specific heat at constant volume of the air. Consequently, its boundary is shifted by an amount \( \Delta l = \beta_t^{\text{LT}} a \), where, \( \beta_t \) is the thermal coefficient of expansion of air.

The pressure amplitude \( P \) in the far wave field \( \left( r \gg a^2/cT_L \right) \) is

\[
P = P \frac{(1-R_s) \beta_t H W}{r \left( k_m C_m \rho_m \right)^{1/2}} \quad \text{......(7.18)}
\]

\( W \) is the power of the laser irradiation and \( \rho \) the density of air.

In the near field,

\[
P = P \frac{(1-R_s) I_0 (\tau_L)^{1/2} H \beta_t}{r \left( k_m C_m \rho_m \right)^{1/2}} \quad \text{......(7.19)}
\]

The far field detection of the signal using PA or PT techniques is less sensitive and sub-threshold signals cannot be effectively detected. This pressure response cannot be compared to the experimental values due to the bandwidth limitations of the acoustic transducer and the possible dependence of \( H \) on the pulse duration of the laser. For high power IR sources, the problem that could arise is that the target surface gets heated up due to the high peak power of the laser and other sound generation mechanisms like evaporation or desorption of surface impurity layers, microscopic breakdown events or explosion of microscopic inclusions on the surface become important [90, 91]. In the measurements made here, the acoustic transducer is placed in tight contact with the sample and thus the terms \( H \) and \( \beta_t \) do not play an important role in the signal generation. At the same time, for plasma monitoring measurements, the transducer is placed away from the sample and only then does these parameters influence the PA.
The acoustic signals generated in solids due to interaction with pulsed laser beam is used to determine the ablation threshold of bulk polymer samples of teflon and nylon under the irradiation from a Q-switched Nd:YAG laser at 1.06μm wavelength. A suitably designed piezoelectric transducer is employed for the detection of photoacoustic (PA) signals generated in this process. It has been observed that an abrupt increase in the amplitude of the PA signal occurs at the ablation threshold. Also it has been shown that there exist distinct values for the threshold corresponding to different mechanisms operative in producing damages due to surface morphology, bond breaking and melting processes at different laser energy densities.

### 7.6.1. Experimental Technique

The schematic diagram of the experimental setup for evaluation of the damage threshold of bulk polymer samples using PA technique is given in fig.7.2. The sample, in the shape of a disk of diameter 2.5cms and thickness ~ 7mm ( sample surface is polished with 400 grade silicon carbide powder ) is pressure contacted on to the piezoelectric transducer using silicon grease [82]. Since the PZT transducer is mounted inside a steel enclosure (fig.7.3), the 1mm thick steel between sample and the transducer helps in minimizing the acoustic reflection at the interface and gives a delay time limited by the transit time of the longitudinal waves in the transducer casing [84]. Also, care is taken to ensure that the laser beam itself does not fall on the transducer casing. The 1.06μm laser radiation ( pulse width ~ 10 nsec, single shot ) from a Q-switched Nd:YAG laser ( Quanta Ray, DCR-11 ) is focused to a diameter of ~ 1mm using a convex lens on to the surface of the sample kept inside a stainless steel irradiation chamber.
Fig. 7.2. Schematic diagram of the experimental setup for PA-LDT measurements

Fig. 7.3. The schematic diagram of the transducer module used for PA-LDT measurements
provided with quartz windows. The laser spot size was estimated by microscopic measurement of the burn-pattern of the focused laser and the values correlated by the calculation,

\[
\frac{a}{b} = \frac{f}{D - f}
\]

where, \(a\) is the unfocused beam diameter, \(f\) the focal length of the lens and \(b\) the focused diameter of the beam at a distance \(D\), \((D \geq f)\) from the lens.

The laser energy, which was changed from pulse-to-pulse was monitored for each laser pulse using an on-line, pulsed laser energy meter, triggered in synchronization with the laser pulse. Each data point was taken with the laser pulse falling on a fresh surface of the sample by rotating the same about its axis while the distance between the illuminated spot and the centre of the transducer is kept constant.

### 7.6.2. Results and Discussion

The resultant PA signal from the PZT transducer is observed on a 200 MHz digital storage oscilloscope (DSO) using 50 ohm termination. Fig.7.4. shows the typical traces of the oscilloscope outputs of the PA pulse shapes from the PZT acoustic transducer for laser energies below, at and above the laser damage threshold for teflon sample. The PA pulse obtained has a delay with respect to the laser pulse because of the transit time of the acoustic signal through the sample material. The negative peak observed in the pattern is a result of the rarefaction due to cooling of the sample following the compression wave caused by the heating of the same at laser fluence near damage threshold [67,85,86]. The amplitude of these peaks are monitored on the DSO. The variation of the PA signal with the laser energy is studied and the plot of laser energy density versus the PA
Fig. 7.4. The typical PA pulse shapes from the acoustic transducer (PZT) at (a) sub-threshold, (b) damage threshold, and (c) plasma formation for TEFLON sample (5μsec & 5mV/div)
signal for teflon and nylon bulk samples are given in fig.7.5.(a,b). These show a clear and abrupt increase in the PA signal amplitude in the region of the damage threshold in full agreement with the observations of the previous workers [67,72,73,79,84]. Table 7.1. shows the values of the ablation thresholds evaluated for the two polymer samples teflon and nylon at 1.06μm wavelength. At the same wavelength, using multiple beam technique, Milam (1977) [92] determined the damage thresholds for bulk PMMA (acrylic) and polystyrene samples to be of the order of 1.6J/cm² and 0.8J/cm² respectively which is of the same order of magnitude of damage thresholds for the polymeric materials under the present investigation.

The mechanisms of laser induced damage in polymeric materials have not yet been understood clearly. The damage threshold generally depends on visco-elastic properties of polymers as well as on the molecular structure of the monomers. It has been suggested that [93] laser induced damages in low absorbing dielectric materials like polymers are initiated through bond breaking phenomenon which will act as an acoustic source exhibiting the abrupt enhancement of the PA signal near the threshold. A significant fraction of the light energy above the threshold is utilized in the disruption of chemical bonds and also contributes to the thermal and kinetic energy the ablated fragments [71]. The results for bulk nylon and teflon samples as given in fig.7.5a and 7.5b respectively, show that variation in slope occurs at region (A) (at lower laser energy density), as well as at (B) (higher laser energy density). Abrupt increase in the amplitude of the PA signal occurs at both these points. This shows the existence of two separate thresholds for the laser induced surface damage occurring apparently due to different causes [72,84].

The damage threshold will also depend on possible
Fig. 7.5. The plot of laser energy density vs PA signal amplitude for bulk (a) Nylon and (b) Teflon samples in air. Insets: The expanded graph showing region (A) in detail.
Table 7.1. The photoacoustically detected surface and bulk laser damage thresholds in Nylon and Teflon samples at 1.06μm laser wavelength compared to PTD detected values

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>PA TECHNIQUE#</th>
<th>PTD TECHNIQUE@</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>REGION (A) J/cm²</td>
<td>REGION (B) J/cm²</td>
</tr>
<tr>
<td>TEFLO N#</td>
<td>1.78</td>
<td>2.85</td>
</tr>
<tr>
<td>NYLON#</td>
<td>1.53</td>
<td>2.25</td>
</tr>
<tr>
<td>PMMA*</td>
<td>1.60</td>
<td>----</td>
</tr>
<tr>
<td>POLYSTYRENE*</td>
<td>0.80</td>
<td>----</td>
</tr>
</tbody>
</table>

*Ref.[81],  **Ref.[74],  ***Ref.[92]

Estimated error ~ 20 %
absorptive inclusions [93] and surface polishing of the sample as mentioned in the earlier parts of this chapter. The laser threshold at (A) is very sensitive to the sample surface conditions unlike the threshold at (B). This observation leads to the conclusion that the threshold at (A) is determined by the surface morphology of the sample. The threshold (A) will characterize damage due to inclusions, impurities and surface inhomogeneity, while that at (B) should correspond to the initiation of bond breaking processes resulting in plasma formation and melting of the sample surface. This observation has been confirmed by recording the PA signal from various points at random on the sample surface at laser energy densities corresponding to the surface (A) and bulk damage (B) thresholds for nylon (ie, near 1.53 and 2.25 J/cm² respectively). Fig.7.6 shows that the magnitude of the PA signal corresponding to threshold A varies from point to point whereas that corresponding to threshold B is practically constant. This implies that the threshold A is sensitive to surface conditions while that at B is virtually independent of the nature of the surface. The endothermic phase change occurring at the region of melting can cause a change in the response of the PA signal amplitude (note the change in slope near B). There is a significant absorption of photons by the sample at the damage site or within the plasma produced at the damage, and this added energy being transferred to the sample via electrons. Thus, where laser damage is accompanied by mechanical damage, but with no significant increase in the optical absorption, the PA signal will not increase dramatically [73]. At laser fluences much higher than that at (B), the PA signal tends to saturate due to possible re-absorption of the laser beam by the plasma plume [84]. Visually, there is little or no plasma formation below (A), and as the laser energy crosses the damage threshold, the plasma plume begins to appear and it grows with further increase in laser energy density.
Fig. 7.6. The plot of the variation of the PA signal at various points on the sample (nylon) at the two thresholds corresponding to A (~ 1.53 J/cm\(^2\)) and B (~ 2.25 J/cm\(^2\)).
Fig. 7.10. shows the plasma plume from a bulk sample of teflon at laser energy density $\sim 3\text{J/cm}^2$. Both in the case of nylon and teflon, the profile of the variation of the PA signal with laser energy density is identical. The relatively larger uncertainty in the slopes above region (A) could be due to the presence of spatial hot spots in the beam profile which gives rise to scatter in the data points above (A). This is a consequence of the strongly non-linear behavior of the PA signal above threshold (A) [73]. The lack of efficient beam diagnostic equipment for accurate monitoring of the laser beam shape and pulse width for each pulse, and methods to accurately determine the surface characteristics (like surface finish etc.) of the sample all add to increasing the error margin in these experimental data.

The PA detection of laser damage has also been used to study the LID of a few different samples like stainless steel (fig. 7.7), TiO$_2$ thin film on quartz substrate (fig. 7.8.), SiO$_2$ thin film, aluminium and commercially available transparent acrylic. The obtained values measured using the present technique are listed in Table 7.2. The fig. 7.8. shows clearly two abrupt variations in the PA signal, the first one due to the film damage and the second one, possibly due to the quartz substrate damage. The value of the damage threshold for quartz ($\sim 9\text{J/cm}^2$) corresponds to previously reported bulk damage value ($\sim 10-15\text{J/cm}^2$) for the same [49].

Figure 7.9. shows the damaged site on the surface of bulk nylon clearly showing the pitting that has occurred due to ablation of the surface. From the micrographs of the damaged surfaces in transparent samples, some of the different damage patterns that occur on laser irradiation are evident. Fig. 7.11. shows the damage sites on the surface of a transparent acrylic. Two forms of damage, i.e., ripple formation and microcrack formation are clearly seen in the above micrographs. These tend to occur away
Table 7.2. The photoacoustically estimated laser damage threshold for a few bulk and thin film samples at 1.06μm laser wavelength.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>SAMPLE THICKNESS</th>
<th>SURFACE DAMAGE THRESHOLD (J/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stainless steel</td>
<td>~ 1mm</td>
<td>0.27</td>
</tr>
<tr>
<td>TiO₂ thin film</td>
<td>~ 4000 A</td>
<td>0.58</td>
</tr>
<tr>
<td>SiO₂ thin film</td>
<td>~ 4000 A</td>
<td>4.8</td>
</tr>
<tr>
<td>Aluminium</td>
<td>~ 3mm</td>
<td>0.32</td>
</tr>
<tr>
<td>Quartz flat</td>
<td>~ 3mm</td>
<td>9.03</td>
</tr>
<tr>
<td>Transparent*</td>
<td>~ 3mm</td>
<td>3.25</td>
</tr>
<tr>
<td>Acrylic</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All other samples are polished with 400 grade silicon carbide abrasive. Estimated error ~ 20%.
Fig. 7.7. The Plot of the PA signal vs the laser energy density for a 1mm thick stainless steel target.

Fig. 7.8. The Plot of the PA signal vs the laser energy density for a 400nm A thick TiO$_2$ thin film sample on quartz substrate.
Fig. 7.9. The photograph of the damaged surface of nylon at a laser energy density of \( \sim 3 \text{J/cm}^2 \) (Photographed in the reflection mode of the microscope).

Fig. 7.10. The photograph of the plasma plume from bulk teflon sample in air at a laser energy density of \( \sim 3 \text{J/cm}^2 \) in air.
Fig. 7.11. The transmission micrographs of the damage site in transparent acrylic showing (a) the ripple formation (66x), and (b) Microcracks (132x)
Fig. 7.12. The transmission micrograph of the damage on transparent acrylic sample initiated by a sharp scratch on the surface (66x). The dark line across the micrograph is the scratch on the surface. (The microcracks are also visible here)
Fig. 7.13. The transmission micrographs of the damage sites in (a) TiO$_2$ (66x) and (b) SiO$_2$ (66x) thin film samples.
from the irradiation site and is possibly due to the propagation of the intense shock waves that originate from the irradiation site. The damage at a scratch on the surface of the transparent acrylic material is seen in fig.7.12. Similar observations were made by Wood et al on scratch-initiated damage on germanium surface using 10.6μm laser beam radiation [94]. The melt pattern on the surface of the TiO₂ and SiO₂ thin film in the vicinity of the laser damage threshold are shown in fig 7.13. The melt profiles are made prominent using Normaski prism facility in the metallurgical microscope (Versamet-2) used to obtain the micrographs.

7.7. Photoacoustic Monitoring of Laser Ablation Process

One of the widely used applications of laser induced plasma is the synthesis of thin films. Laser ablation provides an ideal method to vaporize materials like ceramics, high temperature superconductors [95], metals [96] for deposition on suitable substrates and for selective photoablation of polymers [67], and applications to microelectronics and medicine. This technique offers a better control of the parameters that determine the nature of ablation unlike conventional vaporization techniques. The PA technique can be applied for in-situ monitoring of the laser ablation process and its related parameters such as the laser energy and emission intensity in laser plasma experiments like those mentioned above [97,98]. To correct the pulse-to-pulse variations in the laser generated plumes, one has to know the total amount of the material vapourized during each pulse. It was shown by Chen and Yeung, that the magnitude of the PA pulse associated with the plasma generation was linearly associated to the emission intensity of the plasma constituent elements and it was also shown that the acoustic signal could track the emission signal over four orders of magnitude [99].
laser ablation experiments, sub-threshold signals are not relevant since the incident energy density is much above the damage threshold. The experimental setup for the detection of emission intensity and the acoustic pulse is shown in fig. 7.14. A miniature electret microphone (Knowles BT 1759) placed in the vicinity of the target monitors the PA signal pulse and a monochromator-PMT combination (0.2m McPherson monochromator with Hamamatsu R928 PMT) detects the emission intensity of a particular species (C\textsubscript{2} molecules, 561.2nm extended region of the plasma) in the plasma plume [69]. The typical CRO traces of the output signal from the microphone and the PMT output for the plasma emission are given in fig. 7.15. for a laser energy density of \( \sim 1.8 \text{ J/cm}^2 \) for teflon sample. By calibrating the PA signal amplitude and the emission intensity against the laser energy density, (fig. 7.16.) an in-situ monitoring of the latter is possible. From Fig. 6. it can be seen that the PA signal and the emission intensity vary linearly with the laser energy densities up to \( \sim 5 \text{ J/cm}^2 \) after which saturation of the microphone signal occurs. The PA signal increases when the pressure in the chamber is increased, but at the same time, the plasma plume intensity decreases.

One disadvantage of this method of laser energy monitoring is that the microphone needs to be placed either in contact or in the vicinity of the target sample. Moreover, the PA signal intensity decreases as the pressure in the plasma chamber is decreased. The limited frequency response of the microphone is another limiting factor. An alternative is to use the PTD method of detection [79-81] which reduces these drawbacks, but then, the alignment of the probe beam is critical and the signal is sensitive to the air temperature in the region between the sample and the probe beam, and this temperature is strongly affected by the ablation process. It was seen that by using a focused PZT
**g.7.14.** The experimental setup for monitoring the PA signal and the emission intensity of the plasma plume during ablation process.

**g.7.15.** CRO traces of the (a) PA signal (50mV & 2μsec/div.) (b) PMT response (10mV & 1μsec/div.) of the emission from C₂ species (λ = 561.2nm) in the extended region of the laser induced plasma from TEFLON. Laser energy density ~ 1.8J/cm².
**Figure 7.16.** Plot of the PA signal pulse and the emission intensity for the C$_2$ species in the extended region of the laser plasma plume of Teflon.
The various aspects of laser induced damage process have been discussed in detail. The PA effect has been applied to the estimation of the laser damage threshold in various materials. There exists abrupt changes in the PA signal in the region of laser damage threshold energy density for both surface and bulk damages. Different kinds of damage processes were also observed using microscopic techniques. The PA effect was also utilized to
monitor successfully the laser induced plasma process.

7.9. References

[53] Hect J, Laser Focus, 28, no.6, 63, (1992)
[63] Danileiko Y K et al, Proceedings of the "4th All Union Conference on Non-linear Interaction of Optical Radiation"
Symbols and Notations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$a_0$</td>
<td>Laser beam radius</td>
</tr>
<tr>
<td>$a$</td>
<td>Laser beam diameter at sample surface</td>
</tr>
<tr>
<td>$\alpha_0$</td>
<td>Absorptivity at $T_0$ for the laser wavelength</td>
</tr>
<tr>
<td>$b$</td>
<td>Beam diameter at a distance $D$ from lens ($D&gt;f$)</td>
</tr>
<tr>
<td>$\beta_t$</td>
<td>Thermal coefficient of expansion of air</td>
</tr>
<tr>
<td>$c_0$</td>
<td>Velocity of sound</td>
</tr>
<tr>
<td>$C_m$</td>
<td>Specific heat of sample</td>
</tr>
<tr>
<td>$C_v$</td>
<td>Specific heat at constant volume</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>Ionization potential</td>
</tr>
<tr>
<td>$D_h$</td>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field associated with the laser</td>
</tr>
<tr>
<td>$E_B$</td>
<td>Electric breakdown strength</td>
</tr>
<tr>
<td>$E_b$</td>
<td>Bandgap energy</td>
</tr>
<tr>
<td>$E_D$</td>
<td>Threshold energy density</td>
</tr>
<tr>
<td>$E_{\text{in}}$</td>
<td>Electric field inside the discontinuity</td>
</tr>
<tr>
<td>$E_o$</td>
<td>Electric field associated with the laser</td>
</tr>
<tr>
<td>$E_{\text{eff}}$</td>
<td>Effective elastic constant</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Dielectric constant</td>
</tr>
<tr>
<td>$f$</td>
<td>Focal length of lens</td>
</tr>
<tr>
<td>$\hbar\omega$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>$H$</td>
<td>Heat flux from target surface to surrounding air</td>
</tr>
<tr>
<td>$I$</td>
<td>On-axis intensity of damage threshold</td>
</tr>
<tr>
<td>$k,k_m$</td>
<td>Coefficient of thermal conductivity of sample</td>
</tr>
<tr>
<td>$K$</td>
<td>Constant determined by sample properties</td>
</tr>
<tr>
<td>$l$</td>
<td>Optical absorption length</td>
</tr>
<tr>
<td>$L$</td>
<td>Depolarization factor</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Laser wavelength</td>
</tr>
</tbody>
</table>
\( \lambda_0 \)  Vacuum wavelength
\( \rho_m \)  Density of sample
\( M \)  Mass of molecule
\( m,e \)  Mass and charge of electron
\( \eta \)  Refractive index
\( p \)  Pressure amplitude
\( P_1,P_n \)  Probability of damage in the 1st and nth pulse
\( p(E) \)  Probability of breakdown when 1 initial electron is present
\( p'(E) \)  Probability of breakdown when n initial electrons are sampled
\( P_D \)  Optical power density
\( Q \)  Total energy
\( Q_{in} \)  Incident energy on the focusing lens
\( R \)  Radius of inclusion
\( R_s \)  Surface reflection coefficient
\( r_0 \)  Radius at which laser intensity falls by \( 1/e^2 \)
\( r_d \)  Radius at which first damage occurs
\( \rho_v \)  Vapour density
\( \rho \)  Density
\( \sigma \)  Cross section of collision of electrons with molecules
\( t \)  Time for the acoustic response to develop
\( \tau_L \)  Laser pulse width
\( T_L, T_s \)  Transmission of the focal lens and sample
\( T_m, T_o \)  Melting and ambient temperature
\( \tau_T \)  Acoustic signal transit time
\( \tau_a \)  Acoustic pulse duration
\( T \)  Temperature of the sample
\( u_e \)  Mean electron velocity
\( v_e \)  Frequency of free electron with neutral molecules
\( v \)  Velocity of shear wave
\( \omega \)  Laser frequency
\( z', z_o \)  Impedances of dielectric and free space