A brief overview of some of the previous work in the field of laser induced plasma is presented in this chapter. The emphasis is given to the characterization of laser induced plasma rather than to its applications.
In recent years lasers have been attracting increasing interest in surface science. Properties such as brightness (high photon flux), narrow band width (high monochromaticity) and short pulse length (picosecond pulse width or shorter) allow novel approaches to be made for the studies on the complicated processes occurring at the gas-solid interfaces.

Important applications of lasers in surface science include the static-selective investigation of the dynamics of the molecule-surface interactions, the study of surface properties using lasers as probes and the laser induced variation of the state of the surface. The latter category of the applications includes melting, desorption, ablation leading to the plasma formation, etching and deposition.

This chapter summarises recent developments in the investigations of laser induced plasma studies from different solid samples by high power IR and UV laser pulses. The information obtained by the optical emission studies and the characteristics features of the laser induced plasma processes are discussed in detail. The laser induced plasma processes in the UV and IR region are compared to gain insight into wavelength specific behaviour. Finally thin film deposition of the material by using LIP under various laser parameter conditions are also discussed.

The availability of the short pulse allows the realization of rapid heating rates not achievable by conventional methods. Using microseconds to nanoseconds laser pulses, heating rates of \(10^8 - 10^{12}\) K/s have been achieved whereas heating rates as high as \(10^{15}\) K/s have been reported in the case of femtosecond pulses [1]. These high heating rates should be compared with the traditional heating rates of about 10 K/s or less in thermal programmed desorption in order to appreciate new opportunities offered by the lasers in the study of the surface processes. The experimental findings that even large molecules can be desorbed intact with a
pulsed laser, whereas slower heating rates leads to effective fragmentation, are interpreted as the competition between the the rate of desorption and the rate of reaction [2-4]. This is based on the efficient energy exchange that occur between the surface bonds and the chemical bonds of physisorbed molecules when a laser beam is incident on an optically transparent or weakly absorbing substrate covered by the adsorbed species in a suitable wavelength region. With pulsed IR lasers, an efficient excitation of internal vibrational modes of molecules in the submonolayer, monolayer and multilayer coverage region is possible. Studies involving electronic excitation of the molecular adsorbate and films as well as molecular solids using UV and visible lasers have been made. For electronic excitation, excimer lasers are of increasing importance. The molecular systems which possess different binding energies (as in polymers), that the use of photons with varying energy (IR, UV) provides insight into the mechanism of laser induced desorption and ablation.

The development of pulsed lasers has stimulated research in the interaction of the laser light with matter. Most of the experiments which have been reported however, have used lasers in the visible and IR range. It is only recently that pulsed UV lasers have found use in the field of plasma production.

2.1. LANGMUIR PROBE TECHNIQUE

The langmuir probe theory was used to describe high density plasmas generated by excimer laser photoablation [5]. Both ion velocities and ion densities have been determined in addition to electron temperatures. High ion velocities indicate that substantial optical absorption must be occurring in the plasma directly. It is also possible that direct excitation of the electron may occur at 248 nm due to several close by electronic transitions [6]. So this diagnostic technique will provide valuable information about the laser produced metal vapours in
terms of their plasma characteristics.

There is a considerable interest in the processing of surfaces by laser pulses like, in the surface etching of semiconductor and in the laser etching of metals and ceramics which are used for the processing of electronic microcircuitalry in integrated circuits [7].

2.2. LIP FROM METALS

When a metallic surface is illuminated by a laser beam several effects may operate and lead to electron extraction. These include (a) the surface photoelectric effect, (b) Volume photoelectric effect (c) thermionic emission (d) the field emission effects and (e) the plasma formation [8].

When a laser induced plasma is formed near a metallic surface irradiated by a powerful laser radiation, the mechanism of laser target interaction is dramatically changed. This enhanced action was obtained in experiments with pulsed CO2 lasers, the near surface plasma being a non-linear transformer of laser energy to the metal target.

When a dense gas plasma is formed near the irradiated surface, its properties and subsequent evolution are fully determined by the laser intensity \( I \) and geometry of the irradiation and do not depend on the surface properties. When the target surface is involved as an initiator of the gas breakdown, it influences the threshold intensity which is required for the plasma formation. It was shown that [9] in the initial stage of the gas breakdown near the metallic surface, the material is overheated by the laser radiation, evaporates and serves as the initial micro-plasma sites.

The interactions of near infrared and mid infrared pulsed laser beams with metals have been studied extensively [10] because of its importance in micromachining, thin film deposition and lithography. The UV lasers are much more useful for such applications because of low UV reflectivity for most of the metals
and more energy coupling efficiency and high optical resolution offered by the short wavelength lasers [11-13]. It is also seen that neutral vapour removal regime could be maintained at a high irradiance level than for IR lasers because of the increased threshold for plasma generation.

The spatially and temporally resolved optical emission spectra of plasmas produced by the flash lamp pumped dye laser focussed on an aluminium target have been recorded and analyzed by Knudson et.al [14]. These spectra provide a map of electron density and temperature distribution in the plasma. Relative ion emission intensities provide electron temperature and stark broadened line widths provide electron densities. These quantities are reported as a function of the distance from the target surface and the laser intensity.

The results of the study of the delay in the production of plasma from the surface of metals and insulators were studied by Panchenko et.al [15]. They have determined how the plasma expansion velocity depends on the particular material and the composition and the pressure of the surrounding gas during the illumination of the metals with the laser beam at the wavelength of 308 nm.

2.3. LIP FROM POLYMERS

Laser induced ablation of polymers due to resonant absorption of laser radiation in the UV spectral range was pioneered by a Japanese research group [16,17] and an American research group [18,19]. The clean and efficient photoablation of molecular materials provide potential applications in processing microelectronic devices and this accounts for the widespread use it has received. The various mechanistic aspects such as direct photochemical bond breaking and photothermal degradation have been discussed by several workers [20-22]. With respect to the mechanism involved, polymer ablation with pulsed CO₂ lasers is of great interest [23].

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It is reported that excimer photoablation provides an efficient and technologically viable means for structuring organic polymer surfaces [24-27]. From this, it is concluded that there should be strong absorption in the wavelength of excimer laser and significant ablation occurs if the light intensity exceeds a threshold value (laser fluence of the order of $10^{-10}$ J/cm$^2$ for pulses of 15-20 nsec durations). In the case of weakly absorbing polymers like Teflon, highly intense short UV pulses can induce strong absorption [28,29]. There has been much research directed towards the preparation and characterization of plasma polymerized Teflon films. They are used as protective films on optics and other passive components used in corrosive environments like that in the cavity of an excimer laser, where the halogen gas environment tends to corrode the laser optics [30] inside the laser cavity. Over the years, it has been shown by many groups that interaction of pulsed UV laser radiation with polymer surface can lead to a precise removal of material in a geometry that is defined by the light beam [31]. The interaction of UV laser pulses with polymer molecules will lead to a multiphoton excitation to the upper electronic states resulting in ionization and decomposition by a variety of paths [32,33]. When the pulsed UV laser radiation falls on the surface of an organic polymer, the material at the surface is spontaneously etched away to a depth of 0.1 to several microns and the depth of etching can be controlled by controlling the number of pulses and fluence of the laser [34,35]. This was later confirmed by other groups working with different lasers and other polymer samples [36-39]. Optical emission spectroscopy has been used by several groups for the detection of transient species such as atoms and diatomic molecules (which are the source of light emission) formed by the secondary photolysis of the initially formed product [25]. This technique can be used as a fundamental method to probe the transient species such as C$_2$ and CN molecules in the laser ablation of several polymeric samples [24].

The spatially resolved spectroscopy and time resolved analysis
of the laser produced plasma from polyethylene was studied by Boland et al [40]. The spectroscopic analysis of the spatial resolution estimated the electron temperature as a function of distance from the target surface. The time resolved analysis, through the Saha-Boltzmann equation gives an estimate of the plasma electron temperature, electron density and velocity of carbon ions having charge I to VI. Srinivasan and co-workers have suggested that at 193 nm excimer laser wavelength, in the case of polymers, the mechanism of ablation is necessarily due to photochemical and bond breaking processes, whereas at longer wavelengths, thermal contributions may arise [35,41].

The spectroscopic study of the laser ablation from PMMA was made by Davis et al [42]. Their results are consistent with previous suggestions [34,43,35] that the ablation occurs as a result of direct bond scission by the energetic laser pulses.

2.4. LIP FROM GRAPHITE

Recently there has been growing interest in the plasma assisted techniques for diamond like carbon-film deposition [44]. Large areas of film of high optical quality and uniformity were grown in vacuum [45-48], and in gas mixtures containing hydrogen [49,50]. Optical diagnostics of excimer laser induced graphite plasma in ambient gas mixture of argon and hydrogen using direct emission spectra were made by Chen et al [51]. They found the occurrence of $C_2$ and CN bands in addition to the atomic and ionic lines in the plasma emission spectra. They obtained the vibration temperatures of the $C_2$ and CN radical as $\approx (1.22 \pm 4.8) \times 10^4 K$ and $(1.48 \pm 4.9) \times 10^4 K$ respectively, which are found to be in good agreement with each other but much higher than the graphite melting point. The laser interaction with the plasma plume is considered to be responsible for this.

Diamond has many physical properties which makes it attractive as an electrical material [52]. Diamond like film was produced from graphite target by using pulsed frequency doubled Nd:YAG
laser on a silicon substrate [53]. It was found that crystalline hexagonal, diamond-like films of sub-nanometer thickness grew epitaxially on the silicon surface. The mechanism for electron creation and acceleration in a laser produced plasma from a graphite surface was studied by Cronberg et al [54]. Graphite is an appropriate choice for such studies, because laser induced emission of clusters is believed to be a thermal process [55]. Electronic excitation and ionization should therefore be due to process in the plasma and not in the bulk. They showed that electrons in a laser induced plasma can be accelerated to energies in excess of 15 eV. The energy distribution of the electrons, which depends on the laser pulse energy was found to have a strong dependence on the chemical state of the emitted species.

2.5. LIP FROM HIGH T\textsubscript{c} SUPERCONDUCTORS

Laser ablation is well suited for implementation into automated fabrication schemes for producing superconducting thin film devices [56]. Spectroscopic study of the laser ablation technique is useful because information can be obtained about deposition parameters such as laser power, plasma chamber pressure, substrate temperature etc. By controlling the above parameters high quality thin film will be obtained. Wayne A Weimer [57] studied emission spectra generated during the excimer laser ablation of high T\textsubscript{c} superconductor YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7}. Evaporation techniques using thermal sources produce only neutral metals in the gas phase and result in the oxygen deficient thin films [58]. It may be possible to enhance the formation of metal oxides within the plasma by producing ionic forms of the material during ablation.

The plasma emission spectra obtained by the Nd:YAG laser and by the excimer laser show that more excited atoms than ions were produced by the excimer lasers [59]. The ion/atom ratio should affect the chemistry of reaction between the various species and correspondingly the quality of the deposited films.
The ablation process is used for fundamental understanding of the processes and they relate the quality of the films. Analysis of the optical spectrum emitted from the plume has been used to identify the emitting species vapourized and ejected from the target [60-62]. Identification of these species is important in understanding the complicated ablation, transport and deposition processes.

An analysis of optical emission produced by laser ablation of YBaCuO target using wide range of laser wavelengths showed that 193 nm radiation produced mostly excited atomic species [60]. The production of mostly ionic species reported using the longer wavelength lasers may simply be the result of a smaller energy overshoot existing between the energy of several Nd:YAG photons and ionization potential of Y, Ba and Cu as compared to sum of smaller multiple of the higher energy excimer laser photons.

The formation of oxides in the plume is shown to be essential for the production of high quality superconducting thin films, indicating the value of optical spectroscopy as a diagnostic tool [63]. The time resolved measurements of optical emission shows that a strong prompt emission and other a slow delayed emissions peaking after a few microseconds. It is also observed that the overall optical emission begins after a 7 nsec delay after the start of the laser pulse indicating the time required for significant evaporation of the species from the surface. The prompt emission result from the laser excitation of the evaporated species. On the other hand the slow emission is most likely due to the electronic collisional excitation and is sensitive to oxygen pressure particularly in the case of oxide species.

It is reported that in comparative study of the high $T_c$ thin films obtained using various lasers, the emphasis is on the optimization of the laser processes, the parameters which include wavelength, intensity and pulse duration [60]. From their studies it is observed that (1) The CW Nd:YAG laser is better than the excimer laser and is much better than the pulsed Nd:YAG laser
Of the same Nd:YAG laser the second harmonic is better than fundamental, which is due to the higher absorption coefficient. Film deposited at lower temperatures will be better (100°C - 450°C). It was also found that in general, short wavelength lasers and short pulses and high repetition rate were advantageous for the formation of stochiometric films.

Among the different successful techniques already developed for the superconducting thin film deposition, including electron beam evaporation, sputtering and molecular beam evaporation, the pulsed laser ablation of superconducting targets appears to be one of the most promising because of its relative simplicity, high deposition rates and ability to control the deposition in terms of film thickness and composition. Moreover it has been shown that the characteristics of high Tc films are strongly dependent on the oxygen partial pressures within the pulsed laser induced thin film deposition vessel.

From the time and spatially resolved spectroscopic studies of plasma emission from high Tc samples by using excimer laser ablation under different oxygen pressures it is seen that the emission intensities of almost all the detected lines and bands are significantly enhanced under oxygen atmosphere compared to vacuum conditions. It has also been concluded that the ejection velocities of ablated products are very sensitive to oxygen pressures in the plasma chamber and that the velocities of the atomic species (neutral and ionic) remain constant from vacuum up to an oxygen pressure of \( \approx 10^{-2} \) mbar and decreases rapidly beyond this, whereas the velocities of diatomic species seem to decrease regularly with the oxygen pressure.

The application of high Tc superconductors in microelectronics depends on to a large extent on the availability of the high quality for the superconducting thin films. Films with high transition temperatures have mostly been fabricated by the post annealing of deposited thin films. This processes have several drawbacks like high annealing temperature causing the reaction with the substrate, coarsening of the surface, contamination from
environment during the transfer to the furnace and distributed interface in further processing [64]. During the high $T_c$ thin film growth, sufficient oxygenation has got several advantages like (1) lower substrate temperature and less interdiffusion, (2) smooth surface by a direct epitaxial growth of the final structure on a single crystal substrate and (3) suitable growth of an interface.

Girault et al [65] studied the KrF laser-induced plasma plume located above the target by time and spatially resolve spectroscopic measurements, under vacuum and oxygen pressure. A high resolution plasma emission spectrum from high $T_c$ target were obtained and ejection velocities and decay constants of the ablated species were deduced from their temporal evolution. These parameters are of interest as they influence the deposition process and the hence the properties of the deposited film. From the time resolved studies, they concluded that the expansion velocity varies with species and its evolution processes with oxygen pressure, which is similar for all atomic (neutral and ionic) and molecular products. The velocities remain constant from vacuum up to a pressure of $10^{-2}$ to $10^{-1}$ mbar and decrease rapidly beyond this.

The pulsed laser ablation of laser materials is relatively simple to implement and can transfer fairly large amounts of materials to a collector substrates at large rates. The energy of the ejected species tend to appear in the translational rather than internal (electronic, vibrational and rotational) degrees of freedom [68-70]. For many materials, large molecules can be transferred to the substrate without decomposition so that the stochiometry of the target can be preserved in the deposited film [71]. Thin film of YBaCuO by 1.06 $\mu$m laser radiation from Nd:YAG laser from a non superconducting target in an oxygen atmosphere in room temperature substrate was studied by Lynds et al [72]. The approach of using 1.06 $\mu$m radiation instead of excimer radiation was suggested by past success in Nd:YAG laser ablation of oxides which produced stochiometric, large domain crystalline films.
Thus laser ablation of high $T_c$ material may be important because the low energy photons is less likely to initiate the photochemistry leading to damage and decomposition. Further, all gaseous environments will be transparent to 1.06 μm radiation so that the target ablation in the presence of an oxidizing atmosphere is to incorporate the necessary oxygen in the deposited film.

Thin films of high $T_c$ YBaCuO superconducting sample were prepared using Nd:YAG laser ablation by Misra et al [73]. They showed that when the repetition rate of the laser increases, the superconducting transition of the film obtained will be more sharp and also when the film is cooled faster after deposition.

2.6. PRESENT STATUS OF THE WORK

Most of the earlier workers in this field have used excimer lasers rather than IR lasers. Here with present work, 1060 nm radiation from Nd:YAG laser spatial and temporal analysis of the plasma characteristics were studied and several interesting results were obtained. Using polymer (PTFE) and graphite samples, spatial variation of vibrational temperature of C$_2$ and CN molecules with laser energy were calculated. In the case of high $T_c$ materials, most of the earlier workers haven't identified the presence of oxide species whereas in this work the oxide species were detected along with the lines of neutral and ionic species. The time resolved analysis of all species were done and some important results regarding temporal dependence of the plasma evolution processes were obtained.

Eventhough the main application of laser ablation processes is in producing thin films, this work is mainly concerned with the studies on spectral as well as temporal/spatial analysis of plasma characteristics which will help to optimize different deposition parameters like laser energy, number of pulses, substrate temperature and the pressure of the ambient gas which affect the deposition conditions (plasma density and temperature). Since
all the above parameters affect the property of the thin film obtained using laser ablation technique, the information about the plasma conditions are extremely important and this has motivated the present series of investigations given in the succeeding chapters of this thesis.
REFERENCES


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