5.1 Introduction

Material ablation by short laser pulses is the basic process in many laser technologies such as pulsed laser deposition or laser sputtering. For a sufficient understanding of these processes and for an effective technology optimization, especially for increasing efficiency and productivity, experimental determination of the nature, quantity and properties of ablated particles and their transformation into high-energetic plasma jet is necessary. The transformation from hot vapour to high energetic plasma jet is directly coupled with the expansion of laser induced plasma in the vacuum. Laser energy is primarily absorbed by the electron gas. The electrons with their high thermal velocity try to expand in free space dragging behind the sluggish ions [1]. Ion fluxes produced by high-power lasers from solid targets are the subject of continuing interest in regard to basic research of laser-plasma interaction with profound applications in various fields. They can be potentially useful in large heavy ion accelerators [2] as well as in modifying material properties through ion implantation [3]. The development of laser-ion sources also creates prospect for the construction of compact tabletop particle accelerators, with applications in nuclear physics and medicine [4]. Despite the extensive experimental work that has been performed, various effects of laser beam interaction with metallic surfaces are still not
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satisfactorily explored. Most of the published works are done with IR lasers, and only a few experiments employed lasers in the visible and UV region [5].

In laser ablation of metal targets, the plume is significantly ionized and the ions present have high kinetic energy (up to ~ 100 eV) [6,7]. The kinetic energy distribution of the ejected particles results from the interactions occurring in the plume and is affected primarily by the high density vapour which is formed very close to the ablated target surface. A study of laser plasma at the advanced stage of its expansion gives information about the kinetic energy distribution of the emitted particles, and makes it possible to follow the changes occurring during the variation of experimental parameters.

Pulsed laser deposition offers several attractive features such as the relatively easy preservation of stoichiometry and good structural quality of the deposited film, even when the film is grown at a relatively low temperature. This is attributed to the large kinetic energy of the ablated atoms and molecules upon arrival at the substrate surface. This kinetic energy is obtained in the actual laser ablation process as a result of the laser-matter interaction. However, the precise shapes of the velocity, or kinetic energy, distributions of the depositing particles are the result of various interactions occurring after desorption. Due to the high vaporization rate, there will be a region near the surface where the gas density is sufficiently high for collisions to occur between the desorbed particles. There has been considerable effort, both theoretically and experimentally, on the problem of a gas cloud created by transient desorption from a solid surface [8]. The kinetic energy distributions of ions produced by ablating Si, Ge and Cu targets by high-fluence excimer laser pulses have been demonstrated [9]. Average kinetic energies of Cu$^+$ ions of the order of 1-30 eV have been observed in the excimer laser produced plasma from copper targets[10]. The ablation depth per pulse and the flux and energy distributions of the ions in the plume of laser ablated copper has also been studied with special emphasis on the growth of thin films [11].
The expansion of a laser-ablated plume in different ambient gases has been investigated theoretically using a two-fluid gas-dynamic model and experimentally with time-of-flight mass spectrometry by Bulgakov and Bulgakova [12]. Simple gas-dynamic considerations based on the analogy between an ablation plume and a supersonic underexpanded gaseous jet was found to explain a number of effects of the interaction between the plume and background gas. Dynamics of a dense, laser-produced vapour plume has been analytically studied by Anisimov et al.[13] and the analysis is based on the special solution of gas dynamic equations that describes the expansion of an ellipsoidal gas cloud into vacuum. The ‘flip-over effect’ suggested in this model has been used for the interpretation of the time-of-flight spectra of atoms in laser ablation, and for the desorption of the shape of vapour cloud expanding into an ambient gas. In the theoretical model suggested by Singh and Narayan [14] for simulation of laser-plasma-solid interaction, the laser-generated plasma is treated as an ideal gas at high pressure and temperature, which is initially confined in small dimensions and is suddenly allowed to expand in vacuum. The three dimensional expansion of this plasma gives rise to the characteristic spatial thickness and compositional variations observed in laser-deposited thin films of multicomponent systems.

The successful deposition of stoichiometric thin films by the method of pulsed laser deposition demands the characterization of the ablation plume with temporal, spatial and angular resolutions. When laser plasma is considered under the context of thin film deposition, there exits two different angular distributions which are (i) the source angular distribution and (ii) the film thickness distribution. The highest energies of ablated particles occur in directions close to the target normal and with increasing angle of emission the average energy as well as the total ion flux decreases strongly [15,16].
Geohegan and Purezky [17] describe the broadening of the time-of-flight profile in Yttrium plasma at high pressure levels due to collision with the background gas molecules. In vacuum, they found narrow velocity profile for ionic species. At high ambient pressure, the plasma plume has a large angular spread due to scattering, which is negligible in vacuum. Gas phase collisions inside the plasma play a major role in determining the spatial, temporal and angular distribution of ablated species. When the particle densities are high enough, collisions induce the formation of thermalization layer called Knudsen layer with a few mean free paths from the target surface where negative velocities develop among the particles[18-20]. In order to have momentum conservation, a positive flow velocity also develops for the species. In the presence of collisions in the plasma and KL formation the half-range Maxwellian velocity distribution for various species in collisionless plasma gets modified into a full-range Maxwellian in a centre of mass system. A Knudsen layer can also be defined as the layer at which the change in velocity distribution occurs. The backward moving particles are either re-condensed or reflected from the target surface [21]. The Knudsen layer formation is followed by a more forward peaked particle flux with an unsteady adiabatic expansion of the plasma.

Recently, there has been a report on the characterization of collinear double pulse laser-induced plasma from copper and zinc at several ambient gas pressures by spectrally and temporally resolved imaging technique [22]. This double pulse configuration leads to a significant increase of the plume volume and to a different spatial distribution of the emitters, compared to the case of a single pulse of the same total energy.

The characterization of laser-induced plasmas (LIPs) has been recognized as essential for the understanding and use of these complex and interesting sources of radiation and materials. Amongst the various techniques which are convenient tools to detect various transient species with optical transition in visible spectral region, the
optical emission spectroscopy has definite advantages pertaining to high spatial and temporal resolution without perturbation of the plasma. Multari et al. [23] has studied the variation of neutral atom and ion emission distributions for different laser focusing conditions by using an acousto-optic tunable filter placed in front of an intensified CCD detector. Castle et al.[24] used a similar detector to obtain wavelength-integrated and spectrally-resolved images of LIP where as neutral atom and ion emissions were selected by Aragon et al. [25] using interference filters.

4.2 Experimental

The experimental set up used for this study is the same as that described in previous chapters. The plasma is produced in a chamber by irradiating a copper target with the fundamental output of the Q-switched Nd: YAG laser with pulse width 9 ns and repetition rate 10 Hz. During the experiment, pressure inside the chamber could be varied. The optical emission spectrum is recorded by a monochromator-PMT assembly using a computer interfaced Boxcar averager in the wavelength range 350-650 nm. From the recorded spectrum, different emission lines are identified by comparing the spectrum with standard emission data. The emission spectrum contain signature of Cu I, Cu II and Cu III when the pressure inside the chamber is 2 x 10^{-5} mbar. Emission lines from the ionized species of nitrogen have also been recorded, when the ambient pressure in the chamber is increased to 1 x 10^{-3} mbar. Since the intensities corresponding to various transitions are very low, we selected only those emission lines which showed a considerable intensity. The main emission lines chosen for detailed investigations are 521.8 nm emission corresponding to Cu I and 490.7 nm corresponding to Cu II.
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4.3 Results and Discussion

4.3.1 Spatial variation of Cu I

The temporal profile of the emission corresponding to Cu I species is analyzed with spatial resolution. Monochromator is fixed at the wavelength of 490.7 nm corresponding to Cu I species and the PMT output is given to a digital storage oscilloscope. The intensity of emission and the time delay are recorded by imaging different sections of the plasma into the entrance slit of the monochromator. These experiments are performed at rotary vacuum at a pressure of about 150 x 10^{-3} mbar. The temporal profile of the signal for different distances from the target surface is recorded for different energies of the laser pulse. Figures 4.1, 4.2, 4.3 and 4.4 show the variations in intensity and time delay of the temporal profiles with distance for 100 mJ, 150 mJ, 200 mJ and 250 mJ of laser energy, respectively. The intensity distributions of the emission lines are found to be sensitive to laser fluence:

Spectral emission intensity is observed to decrease with increasing distance from the target surface for all laser energies probed. The intensity decreases up to a distance of 2 mm, beyond which it remains a constant. However, for laser energies of 200 mJ and 250 mJ, it is observed that the intensity of the Cu I species increase suddenly at close proximity to the target. Due to the high electron densities of plasma nearer to the target, the ions and other species in the plasma collide. Maximum intensity is found at a distance of 1 mm from the target for a laser pulse energy of nearly 250 mJ. The increase in intensity of Cu I is mainly due to the collisional recombination of Cu II species with the free electrons.
Figure 4.1: Variation of intensity and time delay of Cu I emission with distance for 100 mJ laser pulse

Figure 4.2: Variation of intensity and time delay of Cu I emission with distance for 150 mJ laser pulse
Figure 4.3: Variation of intensity and time delay Cu I emission with distance for 200 mJ laser pulse

Figure 4.4: Variation of intensity and time delay of Cu I emission with distance for 250 mJ laser pulse
Figure 4.5: Variation of velocity of Cu I species with distance for different energies of the laser pulse

As is evident from the figures, time-delay of the emitted neutral copper species shows a monotonic increase close to the target, which then remains constant up to a certain distance, beyond which there is an increase with distance. This sudden change in the time-delay, shows that there is a considerable change in the expansion velocities of the plasma front for the neutral species of copper around these distances from the target. The velocity of the species is determined by observing the time when the plasma emission is strongest at a particular distance from the target. The emission of Cu I is chosen for this purpose, as this line is long-living and not appreciably self-absorbed. Since distances from the target are small and plasma signal is not sharp peak but a broad noisy maximum, judging the exact time of maximum plasma emission is tricky, especially at larger distances from the target. As a result, the derived velocity can be taken only as a rough estimate of the real plasma expansion velocity. However, it is difficult to expect a sharply defined expansion velocity for
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the plasma plume. Rather, a distribution of velocities is more plausible, and our result
give a rough measure of the averaged plasma expansion velocity. An initial expansion
velocity of the order of several kilometers per second is indicated by the experimental
data plotted in the figure. Figure 4.5 shows the variation in velocity of the neutral
copper species with distance for different fluences of the laser. Measuring the time of
radiation onset yields directly the plasma front axial velocity, which is defined as the
expansion velocity of ablation surface perpendicular to the target. The velocity of the
neutral copper species is found to increase with distance from the target. But in the
region between 5-9 mm from the target surface, the variation in velocity deviates
from this regular trend. Detailed experimentation is necessary to confirm the
observed deviation in velocity.

4.3.2 Spatial variation of Cu II

The production of metal ions during ablation is important since the chemistry of these
species differs markedly from the neutral forms. Evaporation techniques using
thermal sources produce primarily neutral metals in the gas phase and result in the
deposition of oxygen deficient films. It may be possible to enhance the formation of
metal oxides within the plasma by producing ionic forms of these metals during
ablation. The ionization potential for Cu$^+$ (7.726 eV) is greater than the laser photon
energy [26]. But, production of Cu$^+$ is mainly due to multi-photon ionization, as the
laser beam is tightly focussed. The presence of significant emission from neutral
atoms indicates the plasma produced is not fully ionized. The copper plasma is
developed during nanosecond laser pulse on the basis of these atom/ion collisions and
multiphoton absorption[27].

Figure 4.6 gives the typical temporal profile of Cu II line corresponding to a
wavelength of 490.7 nm, at different distances from the target. The temporal profile
of the emission line has three different peaks, of which the first and second peaks are
Figure 4.6: Typical temporal profiles of Cu II species at 1mm, 2 mm, 2.5 mm and 3mm distance from the target
Figure 4.7: Intensity variation with distance for Cu II species

Figure 4.8: Spatial distribution of time-delay for the different peaks of Cu II species
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seen at all distances investigated during the course of this study, but the third peak is observed only at a distance of 2.5 mm and 3 mm from the target surface. The detailed investigation of this region is explained in the next section. Figure 4.7 gives the variation in the intensity of emission of Cu II species with distance. The intensity is found to decrease considerably with distance from the target.

The emission line corresponding to the first ionized species of Cu is recorded with the pressure in the chamber at 0.01 mbar and a laser energy of 150 mJ per pulse. Variation in the time-delay of the peak emission is plotted in figure 4.8 for the various distances from the target surface. The time-scales at which the three peaks appear is seen clearly from the figure. The first and the second peaks remain for the entire distance considered for the study, whereas the third peak remains only for a specific distance from the target. The time delay for the first peak remains the same for different distances, but the second peak shows noticeable variation. During the appearance of the third peak, the time delay for the second peak reduces to a very low value, and after the disappearance of the third peak, the time delay for peak 2 remains the same for the different distances considered.

The expansion velocities, as calculated by the method described in the previous section, for Cu II reveals a different behaviour. The velocity is found to increase with distance for the first two peaks of the temporal profile. The increase in the velocity has a linear relation with distance. Figure 4.9 shows the variation in velocity distribution of the slow and fast components of Cu II species in the plasma with distance from the target. The velocity of the ionic species of copper atom is found to be higher than the neutral species considered in the previous section. The origin of such high velocities could be explained as follows. Firstly it should be
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Figure 4.9: Plot between the distance from the target and the velocity of ions

mentioned that the absorption of laser radiation by the dense plasma such as is produced when a solid target is irradiated may have a strong effect on the velocities attained. It is possible that a significant part of the incoming energy is transferred to the plasma and only a lesser amount dissipated in the solid. This occurs by coupling the light frequency with the plasma frequencies before significant expansion has occurred, i.e., when the plume is at a short distance from the target. The pulse duration is relatively long and this follows an efficient coupling with the plasma, before the pulse terminates. The partial absorption of laser energy by the ejected plasma, through an inverse bremsstrahlung process, above the target surface gives rise to an increase in the velocities and energies [28].

The expansion dynamics of laser-generated plasma has been described by semiquantitative models. The behaviour of the gas cloud moving away from the target could be treated theoretically by means of hydrodynamic equations. The
analytical models describe time- and space-dependent gas density and angular velocity distribution of the ejected particles [29]. The particle motion in the perpendicular direction \( x \) and the two lateral directions \( y, z \) with respect to the target plane can be separated into three: (i) interaction of the laser with the target leading to plasma formation, (ii) isothermal expansion, and finally (iii) adiabatic expansion of the gas cloud. The first two regimes occur during the laser pulse while the latter applies in the absence of laser pulse. In the isothermal expansion, gas-dynamic equations of mass and momentum conservation are applied.

The linear increase in velocity is in agreement with the widely accepted theory of adiabatic plasma expansion [30]. During adiabatic expansion, the \( x \)-component of velocity \( v_x \) is given by the relation,

\[
v_x = \frac{x}{X(t)} \frac{dX(t)}{dt}
\]

Here \( X(t) \) is the dimension of expanding plasma along \( x \)-direction and corresponds to the distance at which the plasma density decreases to 60.65\%.

In the case of adiabatic expansion, velocities of all the constituent species increase linearly with distance from the target. Here the thermal energy of the particles is converted to kinetic energy.

### 4.3.3 Pressure dependence of Cu II

Since the temporal profiles of the emission corresponding to Cu II species shows multiple peaks at certain distances from the target surface, its dependence on the pressure inside the chamber was investigated for these distances. Figures 4.10(a), 4.11 (a) and 4.12 (a) give the variation in intensity of emission corresponding to the different peaks for various pressures of the chamber at distances 2mm, 2.5mm and...
3mm from the target surface, respectively. Figures 4.10(b), 4.11(b) and 4.12(b) give the corresponding variation of time delay for these peaks for various pressures at distances 2 mm, 2.5 mm and 3 mm, respectively.

The intensity of the first peak, which is the fastest peak, formed at a distance of 2 mm from the target surface, increases with increase in pressure of the chamber. However, the first peak at distances 2.5 mm and 3 mm remain at the same intensity with increase in pressure. The intensity of the second peak increases with pressure to a maximum value and then decreases at a distance of 2 mm. At 2.5 mm away from the target surface, there is an additional component originating, which shows a complimentary variation in intensity with the second peak observed. The intensity of the second peak increases to a maximum value at a pressure around 0.2 mbar and then decrease with pressure, while the intensity of the third peak (slowest peak) decreases to a minimum value around 0.2 mbar and then increases with increase in pressure. At 3 mm from the target surface, the intensity of the second peak remains a constant, where as the third peak increases sharply with pressure and then decreases. This behaviour is similar to the second peak at a distance of 2 mm from the target. The maximum value of the intensity for the distance of 2 mm is at a pressure of about 40-50 mbar, where as that for 3 mm it is around 15-20 mbar. The second peak could not be detected, when the pressure was increased more than 1 m Bar at distances 2.5 mm and 3 mm.

The time-delay for the emitter at these distances and pressure also show similar variations. Time delay is the same for the first peak in the temporal profile, at different pressures considered, for the three distances from the target surface. It is also seen that time delay of the second peak at a distance of 2 mm is same as that for third peak at distances 2.5 mm and 3 mm from the target. The time delay for peak 2(pk 2) at 2mm and peak 3(pk 3) at 2.5 mm and 3 mm, is found to remain a constant
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Figure 4.10 (a) : Variation of the intensities for different pressures for the two peaks (pk1 and pk2)

Figure 4.10 (b) : Variation of the time delay for different pressures for the two peaks (pk1 and pk2)
Figure 4.11 (a) : Variation of the intensities for different pressures for the three peaks (pk 1, pk 2 and pk 3)

Figure 4.11 (b) : Variation of the time delay for different pressures for the three peaks (pk 1, pk 2 and pk 3)
Figure 4.12 (a): Variation of the intensity for different pressures for the three peaks (pk 1, pk 2 and pk 3)

Figure 4.12 (b): Variation of the time delay for different pressures for the three peaks (pk 1, pk 2 and pk 3)
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The various complex processes in the laser plasma such as plasma instabilities, chemical reactions, gas phase collisions and formation of Knudsen layer, make the temporal profiles difficult to analyse. A twin peak distribution in the temporal profile of silver atoms in vacuum has been investigated [31]. There are also reports on the twin peak distribution in the temporal profiles of ions which exist only at a particular distance from the target. The appearance of the double peak depends critically on ambient pressure and it has been reported due to the onset of Rayleigh-Taylor instability at the plasma boundary [32]. These peaks were observed in the case of singly ionized species and were absent for highly ionized species. A simple ballistic behaviour of particles cannot explain such observations which indicate the complex nature of the behaviour of constituents in the laser generated plasma.

During the expansion, plasma acts like a piston and it expands into the ambient with supersonic velocities and a shock front is generated. The pressure of the expanding plasma and the ambient pressure, equalizes at certain distances forming a well defined boundary. At this boundary, there exists a turbulent mixing of the ablation plume with the ambient gas and triggers the onset of Rayleigh-Taylor instabilities and other nonlinear processes at the boundary. The partial ionization of the vapour due to temperature increase near the shock wave front can also result in an acceleration of the flow [33]. The addition of kinetic energy to the laser-induced flow through absorption of incident laser energy will result in a moderate deceleration of the shock wave velocity than the predicted blast wave theory. Simultaneously, the part of the ablated species that collide with background gas will lose their kinetic energy. Thus, the plume itself might be split as observed by Harilal et.al[34 ].

4.3.4 Ionization of the ambient molecule

The recorded spectrum of the emissions from copper plasma also contained signature of ambient ionization at high pressure in the chamber. The spatial variation of these
Figure 4.13 (a): Variation of the intensity of emission of 391.7 nm line corresponding to N$_2^+$ with distance for various laser energies.

Figure 4.13 (b): Variation of the time-delay of emission of 391.7 nm line corresponding to N$_2^+$ with distance for various laser energies.
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emissions corresponding to the $\text{N}_2^+$ transition at 391.2 nm has been investigated for different fluences of the laser pulse. Figures 4.13(a) and (b) represent the variations in intensity and time-delay for various energies of the laser pulse for different distances from the target surface. The intensities of emission are found to decrease with increase in distance from the target surface. The intensity of emission is high for higher fluences and the time delay decreases for higher fluences and remains the same for various distances from the target. These emissions corresponding to the ionization of the ambient molecule has been investigated in detail. They are found to be originating as a result of the prompt electrons produced in the plasma and by the subsequent ionization of the ambient gas molecules. Ambient ionization of various gases present in the chamber has been reported earlier by Riju et.al.[35].

There are different mechanisms by which the ambient molecules may be excited and ionized. One of the possible ways is by the absorption of ultra violet radiation arising in the plasma core. For these ionizations energies of the photons should be very high, as the ionization potentials of the ambient gases are high. Another possibility for the ionization of ambient molecules is through the direct multiphoton absorption of laser light resulting in gas breakdown. But for the case of nitrogen, for multiphoton ionization to occur, atleast 12 photons are required and hence this option could be ruled out. Another probability, which has gained lot of interest in recent years, is the ambient excitation and ionization by collisions between the ambient species and the electrons produced during the laser ablation. The energy of the prompt electron pulse is much higher than the first ionization energy of the ambient species and it is very likely that the species become ionized due to collisions [36]. Hence the observation of the ionized species could be confirmed due to presence of prompt electrons.
4.4 Summary

In this chapter, the evolution of the neutral and first ionized atoms of Cu has been investigated. Space-resolved studies of these species for different energy fluences reveal that intensities of the neutral species is found to increase and then decrease. This increase is mainly attributed to collisional recombination among the ions with electrons in plasma. Space resolved studies of the ionic species show a decrease in the intensity distant from the target. Temporal profiles show signatures of different velocity components for the plasma species. Ambient gas molecules present in the chamber is also found to be ionized and this is due to the interaction with the prompt electrons generated in the plasma.
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