Chapter 6

Laser Induced Plasma from Solid and Thin Films: Comparative Study

Abstract

The evolution features of lithium plasma generated by two different schemes viz. the laser-blow-off (LBO) of multicomponent LiF-C thin film and conventional laser ablation referred to here as laser produced plasma (LPP) from solid lithium have been studied using fast imaging and optical emission spectroscopic techniques. Modifications of the plume structure in different experimental conditions are monitored as a function of ambient gas pressure and distance from the target. Apart from their similarities, some interesting differences are noticed in temporal profiles of the plumes generated by LPP and LBO both in vacuum as well as in the presence of the ambient gas.
6.1 Introduction

In previous chapters, we have discussed the expansion dynamics of lithium ions and neutrals produced by laser-blow-off (LBO) of LiFC thin film in different experimental conditions. We found certain striking differences in comparison with the conventional solid ablation i.e., laser produced plasma (LPP). Therefore, we were motivated to perform investigation specifically to study the lithium plasma generated from solid lithium target. Also, it is of interest to study the differences in the dynamics of plasma plumes generated by the LBO and LPP.

In conventional laser ablation of solid targets i.e., in LPP, laser of few nanosecond pulse width with energy above the ablation threshold is incident on a solid target, the formation of plasma plume involves the following stages. The leading edge of the laser pulse ejects an envelope of material from the front surface. At an early stage, the ejected material mostly consists of atoms and a small fraction of ions and electrons. As the temperature increases, boiling and explosive boiling/phase explosion occur which then changes the composition and dynamics of ejected species \{1, 2\}. Even for density well below the critical density for absorption of laser light, some portion of incident radiation is absorbed by plume resulting in strong heating of the plume. During the initial phase of expansion, particle density is high, and the particles move with strong collisions between them. A layer called Knudsen layer, in contact with the target in which reflections and collisions occur which will tend to thermally equilibrate the plasma \{3-5\}.

In contrast, the mechanism for the formation of LBO is impulsive heating of the film. This heating process continues until the vapor pressure at the film support interface becomes large enough to expel the film material \{6-9\}. The expansion dynamics in LBO strongly depends on the thickness of the thin film. If the thickness is less than the skin depth -defined as the penetration depth of the laser in solid target, then it would result in explosive expansion of plume with less
number of collisions. It has been found that neutral species are the main constituents of the LBO plumes {10, 11}.

We have already discussed the important applications of LPP and LBO plasmas {Sec.1.5}. One of the most important applications of LPP is the thin film deposition with pulsed laser (PLD) {12-14}. LBO technique is one of the most commonly used tools for production of neutral atomic beams in Tokamak plasma diagnostics {15-18}. Lithium is particularly important because of the low mass and high penetration speeds and its simple structure of emission spectra. Therefore, the Li beam is extensively used to determine the parameters of edge plasma in Tokamak. Several experimental investigations related to laser induced lithium plasma formed by thin film as well as solid targets have been reported in the past {18-25}.

We present here a direct comparison between the conventional solid ablation (LPP) and laser blow off (LBO) of thin films using fast imaging and OES. The image analysis of the plume has been largely employed as a diagnostic technique of laser ablation plume {26-32} and is capable of revealing different changes occurring during the propagation of the ablated species. Since the plasma formation mechanism in these two schemes, i.e., LBO and LPP are entirely different, a direct comparison in the plume geometry is not much relevant. Keeping this in view, more emphasis has been given to emission spectroscopy. The evolution features of the spectral lines of Li I and Li II generated by LPP and LBO are compared on a one-to-one basis in high vacuum and in different ambient gas pressures.

6.2 Experimental details

A detailed description of experimental setup has been explained in chapter 2. Plasma was created inside a vacuum chamber, which was evacuated to a base pressure of $10^{-6}$ Torr. In order to study the effect of ambient gas, argon gas was
introduced into the chamber and the pressure was controlled by a fine controlled needle valve. For LPP studies, solid Li rod with purity of 99.999% purity and for LBO studies, LiF thin film target was used. Nanosecond pulses from Nd:YAG (λ = 1064 Å) laser having 8 ns pulse width with maximum pulse energy 1.6 J was used to ablate target. Same fluence was used for the LBO and LPP experiments. Time resolved images were recorded using an intensified CCD (ICCD) camera having variable gain, gate time and spectral response in 350-750 nm region. In the present experiment, the gate time was set to 4 ns. To measure the spatio-temporal evolution of emitting plume species, the plasma plume was viewed normal to the direction of expansion and imaged at the entrance slit of a monochromator (Δλ = 12.5 Å). The temporal profile of emission signal was detected by a photomultiplier tube (PMT) {33}.

6.3 Expansion dynamics in vacuum

A detailed picture of plume formation and dynamics has been given in Sec.1.2 of this thesis. As the laser hit on the target, the laser energy is absorbed by the electrons in the target (solid/ thin film) and leads to strong heating of the irradiated volume. This causes the ablation of the irradiated area and the evaporated material continuous to absorb the incoming laser radiation. After the termination of the laser pulse, the initial gas layer expands in all directions. In the case of LBO, plume propagation is in the laser direction and is opposite in the case LPP. In both cases, plume expansion is driven by the energy, which is accumulated as thermal energy and energy which is stored as excitation and ionization in the initial layer. This energy is converted to kinetic energy of the atoms in the plume, and eventually all atoms will move with an asymptotic, constant velocity distribution. In this part of the thesis, a comparative study has been discussed between plume generated by LBO and LPP schemes in a low-pressure region (10⁻⁶ Torr).
6.3.1 Fast imaging of LPP and LBO plasma in vacuum

After the formation, plume dynamics is highly depends on the medium through which it expands. This part of the thesis present the results obtained using the imaging studies of plume expansion formed by solid and thin film targets in vacuum.

![Plume images of Li plasma recorded using ICCD at a pressure of 10^5 Torr, at different time delays after the onset of plasma formation. Colorbar shows the normalized intensity in arbitrary units.](image)

Figure 6.1 Plume images of Li plasma recorded using ICCD at a pressure of 10^5 Torr, at different time delays after the onset of plasma formation. Colorbar shows the normalized intensity in arbitrary units.

Since the formation mechanism of these two schemes (LBO and LPP) is completely different, a direct comparison of the plume geometry cannot be appropriate. However, it gives rough idea about the differences in geometry of the plume generated from LPP and LBO schemes in vacuum. For this, plume images
are recorded at various time delays (0-1000 ns) after the plume initiation. Figure 6.1 shows the recorded plume images generated from LiF-C thin film and Li solid targets. All these images are representative of the geometrical shape of plume in a time domain, which was normalised to their maximum intensity for better representation and comparison. Analysis of the images revealed many interesting features regarding the plasma generated under two different schemes.

We have already seen in chapter 3 that, LBO plume expands adiabatically and has an ellipsoidal shape \cite{19, 20}. During the expansion, electron density reduces rapidly and hence the probability of electron impact excitation is reduced. This leads to reduction in the emission intensity of the plume and for a time delay $t > 1000$ ns, emission intensity is beyond the detection limit of the ICCD due to lower dynamic range of the camera. On the other hand, plasma generated in LPP scheme exhibits an entirely different shape in vacuum. During initial period, the plume expansion shows an elongated shape and as time progresses, intensity at the leading edge of the plume decreased drastically. This dissimilarity in plume geometry may be attributed by the difference in formation mechanism of plasma in the two cases LBO and LPP. We have already discussed earlier that plume formation in LBO is by impulsive hearing of the film and complete irradiated area is converted to plasma in each ablation \cite{Chapter 4}. In contrast to LBO where the plume is detached from the target surface after a time delay, LPP plume found to be attached to the solid target (Fig.6.1). At later time intervals ($t > 400$ ns), LPP plume acquires a spherical shape with maximum intensity at the center portion. Size of the LBO plume is found to be much smaller compared to that of LPP plume.

In vacuum, intensity of LBO plume is much lower compared to the emission intensity of LPP and hence the lifetime also. This is because of the limitation of ablated material in the case of LBO scheme. From the recorded images and also from earlier analysis (Sec.3.4), it has been observed that there exist a linear behaviour between the plume front position and time delay in the case of LBO.
plume. On the other hand, in LPP expansion, part of plume is found to be static with respect to the target. The scattered structure of the LPP plume boundary, limit the possibility of measuring the exact plume front position. An approximate estimated of the LPP plume length in comparison with the length of LBO plume at the same time delay, shows that LPP plume front propagates larger distance. For a fixed delay 600 ns, plume length is found to be 10 mm in LBO whereas it is 22.5 mm in the case of LPP.

6.3.2 Emission spectroscopy of LBO and LPP in vacuum

In the previous section, we have been discussing a comparative analysis between plume geometry of plasma generated by LBO and LPP scheme. Though it gives information about the plume geometry, there exist few limitations for ICCD imaging for explaining the exact plume dynamics as it acquire the resultant emission of all the wavelengths present in the plume. To get a better understanding, we compared the time and space resolved emission spectroscopy of the evolution features of the two ionic lines 478.8 nm \((3p^1P_1 \leftrightarrow 4d^1D_2)\) and 548.4 nm \((2s^3S_1 \leftrightarrow 2p^3P_{2,1,0})\) and two neutral lines 610.3 nm \((2p^2P_{1/2,3/2} \leftrightarrow 3d^2D_{3/2,5/2})\) and 670.8 nm \((2s^2S_{1/2} \leftrightarrow 2p^2P_{3/2,1/2})\) respectively. Due to similarities in the expansion features of the ionic spectral lines (478.8 versus 548.4 nm) and neutral lines (610.3 versus 670.8 nm) and for the sake of simplicity, all the discussions are based on the observations for only one ionic line Li II (548.4 nm) and one neutral line Li I (670.8 nm).

On comparing the recorded spectral lines (Fig. 6.2), it can be seen that during the initial phase of LBO plume expansion \((z=2 \text{ mm})\), the temporal profile of ionic and neutral species exhibits double peak structure, designated as ‘fast’ (first peak) and ‘slow’ (delayed peak) components (Fig. 6.2). Away from the target \((z \geq 6 \text{ mm})\), slow component disappears and only the fast component with reduced intensity was present in the ionic profile. On the other hand the neutrals in LBO maintained their
double peak structure throughout the distance of observation i.e. upto \( z = 12 \) mm (Fig. 6.2).

**Figure 6.2** Spatially resolved OES spectra of the LBO and LPP plume at high vacuum measured at distances (\( z \)) 2 mm, 6 mm and 12 mm.

Entirely different results are observed in the case of LPP. No splitting of the profiles is observed for any of the emission lines (both ionic and neutral species), and a single peak structured profiles are maintained throughout the distance \( z = 2–12 \) mm. During the initial phase of evolution (\( z = 2 \) mm), ion and neutral species move with approximately same velocity (\( 1.9 \times 10^6 \) cm/sec). With increasing distance, i.e., \( z > 2 \) mm, ions were moving with much higher velocity as compared to neutral species. At larger distance (at \( z = 12 \) mm) the ion velocity was almost double that of neutrals. Another remarkable difference between the LBO and LPP
scheme is that the arrival time distributions of ejected species observed by LBO is much broader than those of profiles observed in LPP.

In order to investigate further we attempted to compare the plasma temperatures of LBO and LPP. The spectral line intensity ratio of Li II 478.8 nm and Li II 548.4 nm lines are used to estimate the electron temperature of LBO as well as LPP plumes. It is found that the peak electron temperature of LBO (11 eV) corresponding to fast component is greater than that of LPP (2 eV).

The above observations can be interpreted as follows. In LBO, the observed splitting of LBO profile in vacuum is basically due to the formation of species by two different mechanisms that can produce two different velocity distributions \{5, 6\}. When the laser heats the thin film, the front surface of the film (towards the substrate) is superheated and produces the energetic ion species. These energetic ions form the leading edge of the plume \{Sec.6.3.1\}. On the other hand, majority of the materials propel from the substrate in the form of neutral vapor, moving with much low translational energy as compared to its faster counterpart. The slow components of both neutrals and ionic profiles are formed by collision processes mainly, electron impact processes of the neutral species \{38\}. As the time evolves, the plume expands in vacuum causing a rapid reduction in electron density. As a result, probability of ionization/excitation reduces and for sufficiently large distances from the target (z > 6 mm), slow component disappears from the ionic profile.

Situation is quite different in LPP. Here the laser pulse heats the bulk of material and the ablated material consists of electrons, ions and neutrals. These particles escape from the target and undergo multiple collisions between themselves. During the early stage of plasma, both ions and neutral move with same velocity. In general, for transient plasma plumes, the larger mobility of electrons induces a self-generated and localized electric field \{34, 35\}. This electric field
accelerates the ions in addition to the pressure gradient. Therefore, at the latter stage, ionic species move with higher velocity as compared to neutrals.

### 6.4 Effect of ambient gas on the plume expansion dynamics

The presence of ambient gas significantly affects temporal and spatial distribution of ejected species. In order to compare the influence of ambient gas on the dynamics plasma formed by LBO and LPP scheme, we have analysed various aspects of the plume generated from both solid and thin film target as a function of ambient pressure and is presented in the coming sections.

#### 6.4.1 Fast imaging of LPP and LBO plasma in an ambient medium

Figure 6.3 shows the plume images recorded at various delay times with LBO and LPP scheme as a function of ambient gas pressures. These images are representative of the plume expansion for argon pressure levels $10^{-2}$ and 1 Torr. We have seen in earlier discussions that plume follows linear expansion in vacuum. Upon increasing the pressure, plume is found to experience resistive force from the ambient gas.

As we have seen in chapter 3, plume geometry is completely modified upon introducing the ambient gas (Sec.3.2). Though there are some similarities, the way in which ambient medium influenced the plume expansion is entirely different in the case of plume formed by LBO and LPP. Some observations are common for plume formed by LBO and LPP in ambient gas. At $10^{-2}$ Torr of argon pressure, plasma plume becomes wider and intense in comparison to that observed in vacuum (Fig.6.1). A bright luminescence on the plume boundary (wake like) is formed at the leading edge of the plume (Fig.6.3).

Overall intensity of the plume is increased and lifetime of the plume persists upto $t > 2500$ ns after the plume initiation. Plume penetrates into the ambient gas and this caused an increase in collision between the plume species and ambient gas.
With further increase in pressure, $P > 1$ Torr, plume became more confined. Intensity of the plume also increased with increase in pressure. Increase in ambient pressure results in the confinement of the plume and in turn increase in collisions. This leads to more and more emission from the expanding plume (increase in the lifetime of the excited species in the plasma) and hence plume is sustained for a longer time at high pressures.

Figure 6.3 Plume images of Li plasma recorded using ICCD at an argon pressure of $10^{-2}$ Torr and 1 Torr, at different time delays after the onset of plasma formation. Colorbar shows the normalized intensity in arbitrary units.

At $10^{-2}$ Torr, LBO plume showed more focusing in the forward direction compared to LPP. Intensity enhancement is also found to be more in the case of LBO plume. At higher-pressure levels, the shape is again modified. Lateral
confinement has resulted in the case of LBO, on the other hand LPP plume has acquired a spherical shape and which was unchanged over time (Fig.6.3). At higher time delays, the lateral confinement becomes more pronounced in the case of LBO plume unlike in the case of LPP plume. Some of the above mentioned results and its interpretations are already discussed in chapter 3. For further understanding, the emission spectra of Li lines are analysed and results are presented below.

6.4.2 Emission spectroscopy of LBO and LPP in ambient medium

In order to explore the effect of background pressures of ambient gas on the dynamics of the LBO and LPP plasma plume, the study has been extended by monitoring the temporal and spatial evolution of its spectral line emission.

![Figure 6.4 Effect of ambient gas pressure on the temporal profiles of the Li I and Li II observed in the case of LBO and LPP schemes](image-url)
For OES studies, the ionic and neutral emission lines are monitored as a function of ambient pressure. Figure 6.4 shows the emission profile recorded at a distance 6 mm from the target.

In the case of LPP, both ions and neutrals show a splitting (fast and slow components) in their profiles under the influence of gas pressure. As already mentioned, no splitting is observed in vacuum environment (Fig. 6.2). Therefore, argon gas appears to be responsible for the observed splitting. The physical reason for this behavior is discussed below. When the ambient pressure was $10^{-2}$ Torr pressure, the profiles split into two components. The comparison of the observed profiles in vacuum and in the presence of ambient gas suggests that a fraction of ions/ neutrals loses its momentum in the presence of ambient gas, whereas the rest of them penetrate into the ambient gas with little interaction.

The ions/neutrals that penetrate into the ambient gas have similar velocities as in vacuum and those that get affected by the ambient gas have lower velocities. The ionic species that have larger velocities form the fast component and the rest of the ions having lower velocities form the slow component. These results can be explained on the basis of a momentum transfer between the plume species and background atoms {38}. In this process, the Li atoms that collide with argon atoms can lose $\sim 27\%$ of their kinetic energy {36}. As the pressure increases, the species may suffer more collisions with argon atoms before reaching the point of observation and hence arrival time is further delayed. This effect is reflected in our results where the time delay of the slow components for both ions and neutrals increased with gas pressure. Further, the intensities of slow components of both ions and neutrals increased with pressure; the effect being more pronounced in the case of neutrals. The increase in electron density due to ionization of ambient gas should be responsible for the observed enhancement of intensity at high pressures {37}. Fast neutrals can also be produced by electron recombination of fast ions. The fast component in neutrals that appeared after the introduction of ambient gas was
unaffected by the increase in pressure, whereas for ions it vanished at 1 Torr pressure. This behavior indicates that most of the fast ions undergo electron recombination at higher pressures.

Another interesting feature that is observed is in the relative broadening of temporal profiles of slow neutrals and slow ions. The temporal profiles became much broader in the case of slow neutrals, whereas there was relatively no broadening in the case of slow ions. It can be understood by the fact that ions having higher energy have less scope for thermalization and hence cannot exhibit broadening, whereas the neutrals may get thermalized resulting in broadened profiles.

In the case of LBO, the profile of fast ions observed at z = 6 mm did not show any change as compared to vacuum when ambient gas was introduced. As the fast ions have larger kinetic energies, the probability of collision with ambient gas molecules is very small for such higher energies. Therefore, these ions transmit through the argon gas without getting affected in any manner. As expected, with increase in gas pressure a small increase in intensity of slow ions has been observed because of collisional ionization. The fast neutrals are also unaffected by the variation in gas pressure, which can also be understood on the basis of their higher energies.

When the pressure is increased from $10^{-5}$ to $10^{-2}$ Torr the slow neutrals of LBO also show the same behavior as that of LPP (Fig.6.4). With further increase in argon gas pressure (1 Torr), the profiles became sharper associated with an increase in the peak intensity but with no change in the integrated intensity. As shown in Fig.6.4, with increase in the background pressure, the peak amplitude of the profile increases with a reduction in width. Interestingly, the integrated intensity area under the curve remains constant throughout the chosen pressure range. This observation support the imaging results {Sec.6.4.1} and indicates that in the presence of ambient gas, plume is localized in small volume in space without reduction in total
number density. It is known that the slow ions are produced by electron impact ionization of slow neutrals \cite{39, 40}. The localization of slow neutrals causes an increase in the rate of electron impact ionization and hence results in an increase in the intensity of Li II.

### 6.5 Conclusions

The evolution dynamics of lithium plasma generated by the LBO of multicomponent LiF–C thin film and LPP from solid lithium have been studied using fast imaging and optical emission spectroscopic technique. The differences between the expansion dynamics with regard to plume splitting, plume confinement and plume expansion were discussed in this chapter. Plume generated in low pressure ($10^{-2}$ Torr) and different argon gas pressure levels were studied. Apart from their similarities, some interesting differences were also noticed in temporal profiles of the plumes generated by LPP and LBO both in vacuum as well as in the presence of the ambient gas.

Imaging studies showed that plume geometry (size, shape etc.) for the plasma generated by LBO and LPP scheme were entirely different. Lifetime of the plume was more for the LPP plume generated in vacuum in comparison with LBO. On the other hand, LBO plume was visible for longer duration in an ambient medium. Nearly, linear expansion of the plume was observed in LBO plasma whereas LPP plume is found to be localized in space with increasing the time delay. A comparative analysis of experimental results indicated that the ablation mechanism and subsequent laser-plume interaction were responsible for the observed differences in LPP and LBO plumes. OES studies of LPP plume in vacuum showed single peak structures for both ions and neutrals, whereas in the case of LBO we observed double peaked structures up to $z = 6$ mm for ions. In the presence of the ambient gas, both ions and neutrals of LBO and LPP showed an increase in intensity and splitting of plumes.
6.6 References


