CHAPTER IV

Spatial investigations of ion and electron time of flight in laser ablated ZnO plasma
Abstract

The time of flight (TOF) spectra of ions and electrons of laser ablated ZnO:Ga plasma plume were recorded. The laser fluence was varied from 2.55 Jcm$^{-2}$ to 17.85 Jcm$^{-2}$ and the ablation was carried out in vacuum and N$_2$O ambient pressure ranging from 0.0001 mbar to 0.1 mbar. The TOF spectra were recorded at positions along the direction normal to the surface from 10 mm to 50 mm distance from the target surface. Ion acceleration and corresponding electron deceleration were detected in the plasma due to the formation of electric double layer during plasma expansion. Twin peaks were recorded in the ion TOF spectra, corresponding to the accelerated and thermal ions, while two categories of thermal electrons were detected in electron TOF spectra. The behavior of these ions and electrons were studied as a function of laser fluence, ambient gas pressure and distance from the target surface.
4.1 Introduction

The kinematics of charged particles (electrons or ions) in laser ablated plasma is an important aspect in the purview of structural composition, surface morphology, thermal and electrical properties of thin films, deposited by laser ablation. The phenomenon of ion acceleration/electron deceleration taking place in laser induced plasma plume of ZnO:Ga target, ablated at conditions used typically for deposition of thin films, is the subject of this chapter. This behavior of charged particles is attributed to the occurrence of a self consistent ambi-polar electric field arising in the expanding plasma. Hairapetian and Stenzel [1] have given a comprehensive study of double layer (DL) formation with a detailed picture of the ion dynamics and electric field evolution during plasma expansion. The potential, electric field and space charge density vary qualitatively within the layer. This happens as a consequence of breaking the quasi-neutrality of the plasma. The ions, those enter the region of potential drop, experience acceleration. In effect the DL divides the expanding plasma into regions with thermal and accelerated ions.

Early works on LIP with Langmuir probe measurements have yielded double peak [3-5] or multi-peak structure of ion signals [6], indicating that ion acceleration is an integral part of laser ablated plasma. The multi-peak structure of ion signals is reported to be due to the presence of differently charged ions in the plasma. These experiments were performed at very high laser power in which emission of soft x-rays [3] is also reported. In the event of plasma production by pulsed laser ablation splitting of ion flux in to two or several components have been reported [7-10]. As in high fluence experiments, the reports [11,12] on ion acceleration are related to the ambi-polar electric field, which invokes the concept of DL. Recently Sunil et al [13], reported multiple
peak structure in ion current transients and temporally elongated multiple peak electron current transients in the plasma produced by high fluence (40 Jcm$^{-2}$) irradiation of lithium fluoride target. In the present work the LIP of ZnO:Ga is studied by recording the TOF of ions and electrons and are discussed in conjunction with ion acceleration and corresponding electron deceleration initiated by DL effect in the plasma.

4.2 Mechanism of DL formation

The plasma is in general quasi-neutral and hence field free. Localized strong electric field arises due to the formation of so called double layer (DL) which is consisting of two equal but oppositely charged, essentially parallel but not necessarily plane space charge layers having separation of the order of Debye length. The production of a double layer requires regions with a significant excess of positive or negative charge, where quasi-neutrality is violated. In general, quasi-neutrality can only be violated on scales of the order of the Debye length. The charge distribution in a double layer is such that the charge density is located in two very thin layers, and inside the double layer the density is constant and very low compared to the rest of the plasma. In this respect, the double layer is similar to the charge distribution in a capacitor. The ions entering at the high potential side of the double layer are accelerated while; the electrons entering at this region are decelerated and successively reflected. Although electric double layers have been studied for many decades, the understanding of the occurrence and the effect produced by this in laser ablated plasma are still far from complete.
The double layer is actually called "double layer" because it is composed of a layer of positive charge, "bending" the plasma potential like a normal sheath, and a layer of negative charge, "bending" the plasma potential back in the other direction, in order to join to the null-electric-field plasma. On each side of the double layer, the plasma may be perturbed by extended pre-sheaths, matching the conditions at the edges of the double layer to those of the undisturbed plasma, in the same fashion as a normal sheath. A typical double-layer potential profile and the associated electric field and charge density profiles are shown schematically in figure 4.1.

The figure 4.1 also illustrates how the thermal (slow) electrons are getting pushed back or severely decelerated in the main body plume on the basis of formation of DL in expanding plasma. Space charge neutral plasma in region C is expanding against vacuum A. From the plasma surface area B, the electrons of the same temperature as the ions are leaving faster due to their small mass letting behind a positive ion cloud such that the charge density due to the Gauss law produces a potential $\Phi(x)$ depending on the depth $x$ and the derivative of $\Phi$ results in an electric field $E(x)$ within B. It is assumed that the thickness ($l$) of the double layer B is equal to the Debye length $[\lambda_D]$ [14],

$$l = \lambda_D = \left( \frac{kT_e}{4\pi e^2 N_e} \right)^{\frac{1}{2}}$$

(4.1)

where, $k$ is the Boltzmann constant, $T_e$ is the plasma temperature, $e$ is the charge of the electron, and $N_e$ is the electron density.
Fig. 4.1 Expansion of quasi-neutral plasma (region C) of temperature $T_e$ into vacuum (region A). An Interface is created by the faster electrons leaving the surface area of region B letting behind positive charges in a double layer of thickness of the order of $\lambda_D$.

The positive charge in B causes that after the fast electrons have left, that the following electrons from the plasma interior are either driven back or severely decelerated (see the bent arrows in the figure). The electric double layer of B is acting like a work function for the electrons of which the fast ones of the Maxwellian distribution have to overcome the potential step $\Phi$ to reach the vacuum resulting in the well known thermionic Richardson equation as known for the electron emission of hot surfaces.

It is generally accepted that double layers must fulfill the three conditions below.
(i) The double-layer potential drop $\Phi$ must obey $|\Phi| > kT_e/e$, where $k$ is the Boltzmann constant, $T_e$ is the downstream electron temperature and $e$ is the elementary charge.

(ii) The electric field must be much stronger inside the double layer than outside, so the integrated positive and negative charges nearly cancel each other.

(iii) Quasi-neutrality is locally violated at the position of the double layer. The formation of the well-developed DL in LIP is associated with the generation of energetic (hot) electrons which advance ahead of the main body of the plasma plume. They gain additional energy from within the expanding plume. For the low energy electrons the terms "thermal" and "cold" are commonly used. Two mechanisms that can be assigned for the formation of hot electrons in laser-ablation plasmas are, (a) three-body recombination [refer section 1.3.1] when an electron is captured by an ion to some level (not to the ground state) with transfer of the excess energy to another electron [15] and (b) absorption of incident laser radiation due to inverse bremsstrahlung [4,16,17] [refer section 1.3.3]. The cold and hot electrons undergo energy changes during the plume expansion which may be explained as follows. The rate of photo-recombination depends on the electron temperature as $T_e^{-1/2}$, whereas the rate of three-body recombination follows a $T_e^{-\nu/2}$ dependence [15]. Thus, a cold electron has a large chance to recombine in collision with an ion, while a hot electron can take part in three-body recombination as a third particle, so that it gets additional energy becoming all the more energetic. The total cross section of the electron degradation in the gas phase tends to decrease with $E_e$ at $E_e > 10$ eV [18]. Hence, the electrons that received an additional energy are more capable of surviving compared to cold ones. These electrons move ahead faster leaving
behind the dense plasma and reach the region A (refer figure 4.1) creating situation conducive for DL formation in LIP.

A number of theoretical models [19-21] are available to understand the DL formation in expanding plasmas. These theoretical and numerical models are designed for collisionless and one dimensional expansion of plasma. In the laser ablated plasma from solid target, the degree of ionization decreases during expansion due to recombination process and hence cannot be treated collisionless. Here, the ambi-polar electric field responsible for ion acceleration/electron deceleration apparently varies in a much greater range than it can be described in the framework of a collisionless model.

In this chapter, Langmuir probe measurement of ion/electron TOF transients are recorded in laser ablated ZnO plasma over a range of fluence typical for thin film deposition [22-26]. The spatial dependence of TOF signals in vacuum and various N\textsubscript{2}O ambiances have been studied to elucidate the kinematic behavior of charged particles in the plume.

4.3 Experimental set-up

Using cylindrical Langmuir probe TOF experiments were carried out in a vacuum chamber evacuated to a base pressure of 10\textsuperscript{-6} mbar. The ion and electron TOF transients averaged over 5 laser shots were recorded on a fast digital storage oscilloscope and stored in a PC for further processing. In order to examine the effect of ambient gas on the plasma expansion, the nitrous oxide (N\textsubscript{2}O) gas at various pressures was introduced in to the chamber. The target preparation, Langmuir probe specifications and other circuit details for signal acquisition and processing are discussed in the section 2.2.2. The laser beam was focused on to the target to a spot size of 1.0 mm radius and laser pulse energies
varied from 20 mJ to 140 mJ. This corresponds to laser fluence variations of 2.55 Jcm$^{-2}$ to 17.85 Jcm$^{-2}$. The laser ablations of ZnO:Ga target were carried out in high vacuum (10$^{-6}$ mbar) and at four different ambient gas (N$_2$O) pressures in the range from 0.0001 mbar to 0.1 mbar. Experiments were performed for target-to-probe distances varying from 1 cm to 5 cm. The Langmuir probe was placed along the target normal and oriented parallel to the target surface. The probe bias voltage was suitably varied to record the ion and electron TOF transients.

4.4 Results and discussion

4.4.1 Ion time of flight

Ion current signals were recorded in high vacuum at various distances from the target surface for laser fluence varying from 2.55 Jcm$^{-2}$ to 17.85 Jcm$^{-2}$. The probe bias voltage was fixed at -20 V for recording the ion current signals as at this voltage the TOF signals became independent of the probe bias. Now the probe will be biased in the ion saturation region. Figure 4.2 shows the TOF spectra recorded for various laser fluences at 1 cm distance from the target surface. The two distinct peaks in the spectra correspond to those of fast (accelerated) ions and slow (thermal) ions respectively. Both peaks of the ion current pulse gained intensity and both categories of ions became faster with increasing laser fluence. The twin peaks were more distinct and possessed large temporal separation at low laser fluences [Fig. 4.2 (a)] while at high laser fluences the slow ion peak got suppressed due to the intensity of fast ion peak [Fig. 4.2 (b)].
Fig. 4.2 Ion TOF spectra recorded when ablated in vacuum with probe placed at 1 cm from target. (a) Twin peaks are distinct at low laser fluences. (b) At high laser fluences both peaks tend to merge.
The area enclosed by the time of flight spectrum is proportional to the charge collected by the probe. The sharp fast ion peaks suggest that only relatively few ions from the plasma bulk undergo acceleration due to DL. The peak position corresponds to the average arrival time of the ions from which the average velocity was derived. With increase in laser fluence, large number of ions is ejected from the target with increased energies which in turn increased the forward propagation velocity of the plume. The TOF behaved as if the ions transfer gradually from slow to fast peak with increase in the laser fluences.

Bulgakova et al [27] have reported the occurrence of twin peaks in the TOF spectra of ions recorded using ion probe in the laser ablated plasma plume of graphite. The phenomenon of ion acceleration initiated by the electric field of DL has been attributed for this effect. The DL causes some ions to acquire additional energy and reach the probe faster. As the ions gain energy due to the DL, they exhibit fast decaying TOF spectrum at points closer to the target at all laser fluences. The electrons in the quasi-neutral region of the plume on the other hand subsequently suffer deceleration and hence show extended TOF spectra compared to those of ion. This is discussed in detail in the later sections.

Mannion et al [28] have reported the occurrence of twin peaks in the ion TOF spectra of plasma plume in the ablation of silver target. They have observed the fast peak diminishing in intensity with successive laser shots and altogether disappearing after a certain number of laser shots. Contamination of the target surface has been quoted as the reason for this phenomenon. Ultra fast peaks (along with slower ones) are reported in the ion TOF some LIP [6] due to the presence of ions of higher degree of ionization states in the plume. In the present
investigation no variations in the intensity of hot ion peak was observed with more number of laser shots impinging on the target. Moreover the wavelength dispersed optical emission spectra of the plume taken using the monochromator - CCD assembly neither showed any spectral emission line other than those corresponding to the target material nor emissions corresponding to any doubly ionized species. Thus the possibility of contamination of the target surface or simply the presence of species of second or higher ionization states as the reasons for the occurrence of fast peak is ruled out in the present study.

The figure 4.3 shows the ion TOF spectra recorded at various laser fluences and probe positions when ablation was carried out in vacuum. Close to the target the fast and slow peaks in the TOF spectra were very sharp and distinct for all laser fluences. This substantiates the fact that the DL is very prominent in the early stages of plume expansion. At probe positions away from the target the fast ion peak intensities are weak and since thermal ion peaks are still weaker they become hardly distinguishable at low laser energies but gain prominence only at very high laser pulse energies [thermal ion peak shown with arrow mark Fig.4.2 (b)]. Both slow and fast ion peaks shift to shorter time regime as laser fluence is increased.
Fig. 4.3 Spatial variations of ion TOF recorded in vacuum and its dependence on laser pulse energy, (a) 3.825 Jcm\(^{-2}\), and (b) 17.85 Jcm\(^{-2}\). Twin peaks at large distances are visible only at very high laser fluence. [Thermal ion peak is shown with arrow mark in (b).]
The fast and slow ion current peaks show wide temporal separation and both kinds of peaks are suppressed very much when Langmuir probe was positioned at large distances from the target surface. The absence of clear twin peaks at larger distance is due to the following reasons.

(i) The DL gets degraded as the plume advances. This is because the charge separation becomes wider due to the difference in the velocities of ions and electrons causing the field due to DL to diminish as the plume advances in space. The ambi-polar electric field thus apparently varies in a much greater range.

(ii) The thermal ions suffer more scattering due to collision with particles in the plume compared with fast ions and hence only a very few thermal ions reach the probe.

(iii) There exists a greater electron – ion recombination probability for thermal ions which further reduces its number reaching the probe.

The figure 4.4 shows the variations of fast ion peak position with laser fluence in vacuum. The spatial variations of velocities of fast ions were deduced from the respective TOF transients. The ion velocity varied from 34.50 km/s to 80 km/s for laser fluence variations from 2.55 Jcm\(^{-2}\) to 17.85 Jcm\(^{-2}\), the probe being placed at 1 cm distance from the target. This corresponds to zinc ion energy variations in the range of 400 eV to 2220 eV. In the event of laser ablation of pure ZnO in vacuum [29], oxygen ambiences [30,31] and in the present study, the only ion species detected in the plume is singly ionized zinc (Zn I). Hence the ion kinetic energies referred here are assigned solely to singly ionized zinc.

The ion velocity obtained here is one order higher compared to the velocity of neutrals found in laser ablated ZnO by optical emission spectroscopy (refer Fig. 138.
3.5 where the velocity is plotted for laser fluence of 3.81 Jcm\(^{-2}\)). Thus the hot ions even though fewer in number, as deciphered from the narrow peak are accelerated to a large extent compared to the neutrals or thermal ions due to the electric field of DL. The velocities of these hot ions have been drastically brought down due to collisions (a predominant feature of LTE) with other particles in the plume, as they propagate.

![Graph](image)

**Fig. 4.4** Variation of arrival time of fast ion peaks with laser fluence

The hot ion velocities at 4 cm distance from the target are respectively 13 km/s and 33 km/s for the above laser pulse energies and corresponding ion energies are 59 eV and 386 eV. The order of zinc ion energy at this distance agrees with the observations of Claeyssens et al [29]. They also have reported that zinc ions in the plume have greater velocities compared to neutral zinc and neutral oxygen.
present in the plume, justifying the contention that ions gain additional velocity over neutral particles due to the phenomenon of DL occurring in laser ablated plasma. Ions with energies in the range of 900 eV [32] have been reported for laser produced plasma. TABLE 4.1 illustrates a comparison of the energies of fast and thermal ions in vacuum at various laser fluencies and distances.

TABLE 4.1 Fast ion kinetic energies \(E_f\) and thermal ion kinetic energies \(E_t\) at 1 and 4 cm distance for various laser energy.

<table>
<thead>
<tr>
<th>Laser Fluence (Jcm(^{-2}))</th>
<th>1 cm</th>
<th>4 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_t) (eV)</td>
<td>(E_f) (eV)</td>
<td>(E_t) (eV)</td>
</tr>
<tr>
<td>7.65</td>
<td>19.6</td>
<td>1160</td>
</tr>
<tr>
<td>10.2</td>
<td>23.8</td>
<td>1410</td>
</tr>
<tr>
<td>12.75</td>
<td>47.5</td>
<td>1750</td>
</tr>
<tr>
<td>15.3</td>
<td>59.2</td>
<td>1960</td>
</tr>
<tr>
<td>17.85</td>
<td>74</td>
<td>2220</td>
</tr>
</tbody>
</table>

The thermal ions on the other hand exhibited very low energies compared to fast ions but in reference to the energy (or velocity) of the neutrals, the energies of the thermal ions are nearly double (refer Fig. 3.5). At 1 cm distance from the target thermal ion energies varied from 13.5 eV (~6.33 kms\(^{-1}\)) at 2.55 J cm\(^{-2}\) to 74 eV (~14.6 kms\(^{-1}\)) at 17.85 J cm\(^{-2}\) laser fluence. This means that ions are in general accelerated due to the ambi-polar electric field with very few of them acquiring very high velocities (hot ions). The forgoing discussions suggest that the leading edge of the expanding LIP plume is predominantly populated with
ions of both kind, following behind are neutrals of varying propagation velocities and at the rear with thermal electrons.

ZnO thin films grown by PLD in vacuum were highly amorphous and non-uniform when substrate was placed closer to the target and also when high laser power was used for ablation. The film gained crystallinity, stoichiometry, and transparency when substrate placed at 6 cm distance and ablated at low laser powers [33]. At points near to the target and at high laser powers the ion energy is of the order of keV. The high energy ions bombard the substrate and may cause re-sputtering from the substrate, defect formation etc. The substrate placed beyond 5 cm from the target surface and the ablation at low laser powers favors the film growth.

(a) Effect of pressure

The ion TOF spectra in the N₂O ambience do not show twin peaks as distinct as those obtained in vacuum. The increase in ambient gas pressure decreases the flux of thermal ions reaching the probe. The cross-section for scattering of ions due to collision with particles in the plume follows inverse relationship with ion energy [34]. Hence the fast ions having very high energy are scattered less and they literally plough through the plume and reach the collector. When the pressure is increased the thermal ions are scattered more and hence the thermal ion current become too small, along the target normal, to be detected along with that of fast ions.
Fig. 4.5 Variations of ion TOF with ambient gas pressure at 2 cm distance from the target and laser fluence of 12.75 Jcm$^{-2}$.

The peak positions are shifted to the longer time regime and pulse heights diminished with increase in ambient gas pressures. That is the average velocity and fast ion flux decreased with ambient gas pressure. The Fig. 4.5 represents influence of various N$_2$O ambiences on TOF spectra at 2 cm away from the target and laser fluence of 12.75 Jcm$^{-2}$. The fast ions reaching the probe are delayed with increase in the N$_2$O ambient pressure. The fast ion peak of the TOF in vacuum is very sharp as compared to those in N$_2$O atmosphere. Thus the ambient gas pressure produces large spread in the kinetic energies of ions in the plume. The delay in the arrival of ions to the probe can be attributed to the impedance offered by the presence of gas [30, 35-37] to the forward propagation
velocity of the plume. The absence of thermal ion peak with increase in ambient pressures may also be due to the reasons listed below.

(i) As the pressure is increased the mean free path of electrons and ions in the plume is reduced due to shrinking of the plume thereby causing greater probability for electron-ions recombination.

(ii) There occurs change in the shape of the plume with increase in gas pressure. In vacuum the plume is highly forward directional so that the ions are all confined to small solid angle, while as the pressure is increased the plume shrinks and assumes hemi-spherical shape [37,38], thereby increasing the angular distribution of ions. Therefore in the later case ion flux reaching the probe, positioned along the target normal collects lesser number of ions compared to that in vacuum or at low ambient pressures.

The Fig. 4.6 represents the arrival time of hot ion peak at various probe positions for TOF spectra recorded when ablated at 0.001 mbar N$_2$O pressure. Comparison of this with Fig. 4.4, where TOFs were taken in vacuum and similar laser fluences, shows the delay in the arrival of fast ion to the probe. This can be attributed to the impedance offered by the N$_2$O ambience on the plume propagation. This delay increased with increase in ambient pressures. At very high ambient pressure (~0.1 mbar) the ion current pulses were very weak and hence comparison of peak arrival time with those in vacuum was difficult beyond 2 cm distance from the target. This substantiates the phenomenon of increase in the electron-ion recombination processes leading to suppression of twin peaks in the ion TOF spectra recorded in the background gas.
Fig. 4.6 Variations of average arrival time of fast ions with laser fluence at various spatial positions of the probe from the target and TOF spectra recorded under the N₂O ambient pressure of 0.001mbar.

### 4.4.2 Electron time of flight

The TOF spectra of electrons accompanying pulsed laser ablation in vacuum and also in the N₂O ambiences, its behavior with variations in laser fluence and Langmuir probe positions merit elaborate considerations. All TOF spectra of electrons were recorded with the probe bias voltage of ± 30 V as at this voltage the electron TOF’s became independent of the probe bias (electron saturation regime). As described earlier, DL is formed due to fast (hot) electrons generated in the early stages of plume expansion. These electrons escape from the main body of the plume.
Fig. 4.7 Ion and electron TOF spectra recorded at 1cm distance in vacuum when ablation was carried out at laser fluencies (a) 5.1 Jcm$^{-2}$ and (b) 17.85 Jcm$^{-2}$. 
The TOF spectra of electrons exhibit the presence of slow or thermal electrons of two different energies along with the tail (slower component) of hot electrons. The velocities of hot electrons are in the same order as that of fast (accelerated) ions (Refer Fig. 4.4 and Fig. 4.10). Decay of electron current pulses is slow at low laser fluences and at points away from target, compared to ion current pulses.

A comparison of ion and electron TOF spectra recorded in vacuum at 1 cm distance from the target for laser fluences of (a) 5.1 J cm$^{-2}$ and (b) 17.85 J cm$^{-2}$ is given in figure 4.7. The two types of thermal electron peaks are prominent only at reduced laser fluences. At 1 cm distance from the target, the two species of thermal electrons have velocities 5 km/s and 2 km/s for the laser fluence of 5.1 J cm$^{-2}$. These velocities are very small compared to those of thermal ions indicating that electrons are severely decelerated and move behind thermal ions during plume propagation. When ablation was carried out with higher laser fluences the temporal separation of the two kinds of thermal electrons gradually decreased. At the highest laser fluence (17.85 J cm$^{-2}$), both species of thermal electrons merged into a single broad peak with an average velocity of 6 km/s [Fig. 4.7 (b)]. The hot electron peak is very narrow indicating that hot electrons are ultra fast and short lived and only the tail (slower component) of the hot electrons generated in the ablation process is recorded by our instrument as the rest escapes from the main body of the plume at a very rapid pace.
Fig. 4.8 Spatial behavior of electron TOF spectra recorded in vacuum at laser fluences (a) 17.85 Jcm$^{-2}$ and (b) 5.1 Jcm$^{-2}$. (Arrows indicate the faster component of thermal ions)
The Figure 4.8 depicts the electron time of flight at various spatial positions of the plume when target was ablated in vacuum at two widely different laser fluences, (a) 17.85 Jcm\(^{-2}\) and (b) 5.1 Jcm\(^{-2}\). TOF spectra indicate that majority of the electrons fall on the low energy side of thermal electrons. The arrival of all species of electrons is delayed with increase in probe distance from the target. The faster components of the thermal electron pulses are indicated with arrow marks. The two types of thermal electrons showed large temporal separation at low laser pulse energies and the faster component of thermal electrons becoming less prominent at large distance from the target. The presence of hot electrons, even though small, is detected in the TOF spectra recorded at all spatial positions and laser fluences. The hot electron peak is not well resolved at 1 cm distance from the target, but is better resolved as plume advances in space.

The figures 4.8 (a), where, the TOF's were recorded at high laser fluence the thermal electrons are centered around 2 \(\mu\)s in time scale. As the laser fluence is decreased, the thermal electrons get severely delayed with thermal electron peak arrival time approaching 8 \(\mu\)s [Fig. 4.8 (b)]. Various TOF spectra suggest that electrons reach the probe several microseconds after the termination of ion current pulse. This means that the electrons were trailing behind the main body of the plume and continue to move forward due to the energy acquired during the ablation process. The reason for the thermal electrons getting pushed back from the plume or severely decelerated can be well substantiated due to the effect of DL in LIP, illustrated in Figure 4.1.
Fig. 4.9 The spatial variations of average arrival time of (a) fast electrons and (b) thermal electrons with laser fluences in vacuum.
The TOF of electrons recorded at high laser fluences [Fig. 4.7(b)] do not show thermal electrons of two different energies because at this laser fluence the average Maxwellian kinetic energies of all electrons diffusing from region C must be sufficiently high to overcome the potential step $\Phi$ of region B [refer Fig. 4.1] and hence form a broader thermal electron peak. As the laser fluence was reduced the temporal separation of the two kinds of thermal electrons increased steadily. Figure 4.7 (a) shows the electron TOF in vacuum for laser pulse energy of 5.1 Jcm$^{-2}$, the electron current persisted up to 8 $\mu$s, very much delayed, even after the termination of ion current pulse. For larger distance of the probe from the target, the electrons were delayed up to 10 $\mu$s [Fig. 4.8 (b)].

The reduction in the laser fluence results in the reduction of fast electrons and majority of the electrons fall in the thermal electron category. The figures 4.9 (a) and (b) are the plots of peak arrival time of hot and thermal electrons. Both kinds of thermal electrons showed similar spatial behavior. The hot electron peak velocity in vacuum is in agreement with those of fast ions, justifying earlier reports that ions are very much accelerated due to DL and attain velocities comparable with those of fast electrons.

(a) Effect of pressure

The increase in the ambient gas pressure has caused suppression of the thermal electrons and slowing down of the fast electrons. Signature of the presence of thermal electrons is found in the TOF spectra taken at points closer to the target [Arrow marks in Fig. 4.10 (b)]. This kind of thermal electrons were found only at low laser fluence. As the laser fluence was increased the electron TOF spectra exhibited only fast electrons [Fig. 4.10 (a)].
Fig. 4.10 Spatial behavior of electron TOF recorded in the ambient gas pressure of 0.001 mbar and ablated with (a) 17.85 Jcm\(^{-2}\) and (b) 5.1 Jcm\(^{-2}\) laser fluences.
Even at low laser fluence as the probe is moved away from the target only fast electrons with delayed TOF were observed. It has been mentioned earlier that the plume expands isothermally from the moment the leading edge of the laser pulse hits the target, to the termination of the pulse. Thereafter the plume expansion is adiabatic and it will have very high pressure gradient directed perpendicular to the target surface. This pressure gradient pushes the front portion of the plume against the impedance of the background gas while the rear portion of the plume which mainly consists of thermal ions, slow neutrals and thermal electrons, owing to less velocity, will receive greater impedance and might get detached from the front portion of the plume. This kind of phenomena, known as plume splitting exists in LIP where high fluence and ambient gas pressure are employed [39-43]. The rear portion of the plume fail to reach the collector placed at large distances from the target, accounting for the absence or suppression of thermal electrons or thermal ions in the respective TOF spectra recorded in ambient gas pressures. The effects of DL formation in the plume add to the probability of occurrence of plume splitting.

The plume density gets reduced as it propagates in space and the pressure gradient of the plume diminishes rapidly. This causes delay in the arrival of electrons and spread in the electron energy distribution as revealed from the elongated temporal profiles of electron TOF spectra at points away from the target surface. Another reason for the suppression of thermal electron in the electron TOF spectrum taken in the presence of high ambient gas is that unlike ions and neutrals present in the expanding plume the electrons in it exhibit greater angular distribution and the angular distribution increases with ambient gas pressure. Most of the thermal electrons move radially outward after the event of ablation and only fast electrons move closer to the target normal. The
fast electrons are less scattered and hence move ahead of the fast ions from the target surface making a small solid angle with propagation direction of the plume.

**4.5 Conclusion**

The occurrence of ambi-polar electric field due to DL formation in LIP is responsible for the observation of different energies of charged particles within the plume. The ion acceleration has caused some ions to attain energies comparable with that of electrons. The fast ion energy is of the order of keV in the vicinity of the target while at far away from target reduces energy to hundreds of eV when ablated in vacuum at high laser fluences. Thermal electrons continue to reach the probe for few microseconds more after the termination of ion current pulse when ablated in vacuum. They trail behind the main body of the plume and hence are not lost either by scattering due to collision with particles of the plume or by electron-ion recombination, for plume analyzed in vacuum. The presence of ambient gas results in slowing down of the ions and electrons and severe reduction in the number of thermal ions and electrons. In the context of ZnO thin film growth, low laser fluences for ablating the target is advisable. At high laser fluences the ions liberated having energies in the order of keV will hamper the uniformity and stoichiometry as these energetic particles hitting the substrate are capable of causing re-sputtering from the film. High ambient gas pressure is not desirable as the propagation length of the plume decreases with pressure particularly when the target is ablated at low laser fluences. The ambient gas pressure suppresses DL in ZnO plasma.
Reference


