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

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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 10 mm to 50 mm from the target surface along the direction normal to the 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 accelerated and thermal ions, while two categories of thermal electrons were detected in electron TOF spectra. The behaviour of these ions and electrons is studied as a function of laser fluence, ambient gas pressure and distance from the target surface.

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1. Introduction
Laser ablation is being widely used in various applications of material processing, such as thin-film deposition, chemical reactions, surface modifications and synthesis of nano-clusters. The interaction of laser beam with solid matter and the consequent plasma generation has actively been studied for the last decade [1-7]. Despite the great efforts to exploit the laser matter interaction for material processing and diagnostic purposes, many aspects still need to be elucidated and clarified. In particular, the plasma induced by ultraviolet and visible nanosecond laser is successfully employed for thin film deposition of a wide range of classical and novel materials [8-10] and for in situ qualitative elemental analysis [11-13]. However, to improve the quality of the deposited films for desired application, a sound understanding of the plume dynamics, and physical and chemical properties of the ablated species are required. The properties of thin films deposited by pulsed laser ablation (PLA) are closely related to the dynamics and to the composition of the laser generated plasma. Generally, there is a correlation between the plume dynamics and the structural properties of the films deposited. Thus the study of the characteristics of the plume contributes to a better understanding and control of the deposition process itself [14, 15]. As the plume expands in an ambient medium the ablated species from the target undergo collisions with the atoms and molecules of the ambient gas resulting in scattering and slowing down of the plume [16, 17]. The plume boundary constitutes predominantly
particles of high kinetic energy; the collision processes get enhanced by high reactivity of the charged species [18]. The hydrodynamic expansion of the plume, the composition, and size distribution of clusters depend not only on initial conditions, but also on the laser intensity, pulse width, and ambient gas pressure.

Plasma emanating from the PLA of zinc oxide (ZnO) has attracted wide attention among researchers owing to its importance in the fabrication of thin film optoelectronic devices [19-22]. Zinc oxide has been of much interest to researchers due to its wide band gap (3.3 eV), abundance and non-toxicity. Due to high melting point, ZnO can withstand high temperature annealing and processing associated with doping and contact formation. There are several reports of lasing action at room temperature due to excitonic transitions [23, 24]. Zinc oxide generally exhibit n-type conductivity which can further be enhanced by doping with aluminium or gallium. There are reports of ZnO thin films with p-type conductivity when doped with gallium and ablated in N₂ or NH₃ ambience [25]. In this article we report the kinematics of ions and electrons in the laser induced plasma of gallium doped ZnO, under the ablation conditions used typically for the deposition of thin films. Cylindrical Langmuir probe is employed for mapping the plasma plume. The TOF spectra of electrons and ions were recorded at (i) various positions of charge collector along the surface normal to the target, (ii) varying the background gas pressure and (iii) various incident laser fluences. The phenomenon of ion acceleration and subsequent electron deceleration are discussed in the light of double layer (DL) formation caused by ambipolar diffusion of charges within the plume.

2. Experiment
The experimental set up used for the investigation has been reported previously [19] and features relevant to the present study are summarized here. Third harmonic of Q switched Nd:YAG laser (Quanta Ray, Spectra Physics) operating at 355 nm, 10 Hz repetition frequency, pulse width 6 nm was used for ablation. Target was prepared by doping ZnO (99.9 % Aldrich) with 5 wt.% Ga₂O₃ (99.99 % Alfa Aesar) made into 1 inch pellet at a pressure of 7 tons and sintered at 1000°C for 8 hours. The base pressure of the ablation chamber was 10⁻⁶ mbar. The laser beam was focused on to the target to a spot size of 1.0 mm and laser pulse energies varied from 20 mJ to 140 mJ. This corresponds to laser fluence variations of 2.55 J cm⁻² to 17.85 J cm⁻². The ablations were carried out in high vacuum (10⁻⁶ mbar) and at four different ambient gas (nitrous oxide) pressures in the range 0.0001 mbar to 0.1mbar. The TOF spectra were collected using suitably biased probe (Tungsten fiber, 5 mm length and 125 µm diameters) placed along the normal to target surface and normal to the propagation direction of the plume. The spatial variations of TOF spectra were investigated over a distance of 5 cm from the target surface. The probe was biased using a stabilized power supply having voltage sensitivity of +/−5 mV per division. The current signals were collected using a digital storage oscilloscope (Tektronix, 100 MHz, and 1 Gs/sec) which was externally triggered using a fast photo diode to coincide the interaction of laser pulse with the target. The TOF signals were averaged over five laser shots. The wavelength dispersed spectra of the plume was recorded using monochromator – CCD assembly the specifications of which are given elsewhere [19].

3. Results and Discussion
3.1 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 J cm⁻² to 17.85 J cm⁻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 bias is in the ion saturation region. Figure 1 shows the TOF spectra recorded for various laser fluences at 10 mm 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. 1 (a)] while at high laser fluences the slow ion peak got suppressed due to the intensity of fast ion peak [Fig. 1 (b)]. Bulgakova et al [26] 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 double layer (DL) has been attributed for this effect. In the process of laser ablation of metals and semiconductors there is always a generation of fast electrons due to the phenomenon of inverse bremsstrahlung or three-body recombination involving ions and electrons in the plasma. In three-body recombination, an electron is captured by an ion to some excited state through radiationless transition and the excess energy is transferred to another electron, making it faster in the process. These electrons move to the periphery of the plume leaving behind net positive charge. This creates a net electric potential and there by an electric field which accelerates the ions diffusing in to the field. This causes some ions to acquire additional energy and reach the probe faster. As the ions gain energy due to the DL, the electrons in the quasi-neutral region of the plume subsequently suffer deceleration and hence show extended TOF spectra compared to those of ion. This is discussed in detail in the later sections.

Figure 2. Spatial variations of ion TOF recorded in vacuum and its dependence on laser fluences, (a) 3.825 Jcm⁻², and (b) 17.85 Jcm⁻²
The figure 2 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 energies. This substantiates the fact that the DL is very prominent in the early stage of plume expansion. At probe positions away from the target the fast ion peak intensities are weak and since thermal ion peaks are weaker they become hardly distinguishable at low laser energies and gain prominence only at very high laser pulse energies. Thermal ion peak of 50 mm is marked [Fig. 2 (b)]. The peaks of both species of ions shift to shorter time regime as laser fluence is increased.

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 caused by the ambipolar diffusion increases due to the difference in the velocities of ions and electrons causing the field due to DL to diminish as the plume advances.

(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 ion velocity varied from 34.50 km/s to 80 km/s corresponding to the laser fluence variations from 2.55 Jcm$^{-2}$ to 17.85 Jcm$^{-2}$, for the probe at 10 mm 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 [21], oxygen ambiances [19] and in the present study, the only ion detected in the plume is singly ionized zinc (Zn II). Hence the ion kinetic energies referred here are assigned solely to singly ionized zinc. The ion velocities at 40 mm distance from the target were 13 km/s and 33 km/s for the above range of laser fluences and corresponding energies are 59 eV and 386 eV. The order of zinc ion energy at this distance agrees with the observations of Claeyssens et al [21]. They have also reported that zinc ions in the plume have greater velocities compared to neutral zinc and neutral oxygen present in the plume, justifying the observation of 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 several hundreds of eV have been reported for laser produced plasma of metals ablated even at lower laser fluence range [27]. The thermal ion energies are very low compared to fast ions. At 10 mm distance from the target thermal ion energies varied from 74 eV at 17.85 Jcm$^{-2}$ to 13.5 eV at 2.55 Jcm$^{-2}$ laser fluences.

3.1.1 Effect of pressure. The ion TOF spectra in the N$_2$O 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 [24]. 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.
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 figure 3 represents influence of various N\textsubscript{2}O ambiences on TOF spectra 20 mm away from the target and laser fluence of 12.75 Jcm\textsuperscript{-2}. The fast ions reaching the probe are delayed with increase in the N\textsubscript{2}O ambient pressure. The fast ion peak of the TOF in vacuum is very sharp as compared to those in N\textsubscript{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 [19, 28-31] to the forward propagation velocity of the plume.

3.2 Electron time of flight
The TOF spectra of electrons accompanying pulsed laser ablation in vacuum and also in the N\textsubscript{2}O 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 TOF’s became independent of the probe bias. As described earlier, DL is formed due to fast (hot) electrons generated in the early stages of ablation. These electrons escape from the main body of the plume. The TOF spectra of electrons exhibit the presence of slow or thermal electrons of two different energies. The velocities of hot electrons are in the same order as that of fast (accelerated) ions. Decay of electron current pulses is slow at low laser fluences and at points away from target, compared to ion current pulses.
Figure 4. Ion and electron TOF spectra recorded at 10 mm distance in vacuum when ablation was carried out at laser fluences of (a) 5.1 J cm\(^{-2}\) and (b) 17.85 J cm\(^{-2}\).

Figure 4 is a comparison of ion and electron TOF spectra in vacuum at 10 mm distance from the target for laser fluences of (a) 5.1 J cm\(^{-2}\) and (b) 17.85 J cm\(^{-2}\). The two types of thermal electron peaks are prominent only at reduced laser fluences. At 10 mm 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 follow thermal ions in the process of plume expansion. 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(b)].

Figure 5. Electron TOF spectra recorded in vacuum at laser fluences of (a) 17.85 J cm\(^{-2}\) and (b) 5.1 J cm\(^{-2}\). (Arrows indicate the faster component of thermal ions)

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. The Figure 5 depicts the electron time of flight at various spatial positions ablated in vacuum at two different laser fluences, (a) 5.1 J cm\(^{-2}\) and (b) 17.85 J cm\(^{-2}\). TOF spectra indicate that majority of the electrons fall on the low energy side of thermal electrons. All species of electrons are 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. In the event of laser ablation the energy carried by the particles is very low at low laser
fluences. Therefore the majority of electrons fall in the low energy category as visualized from the
broad slow thermal energy electron peak. The faster component of the thermal electrons, which is
relatively small, continuously loses energy along with other particles, due to collision and
Bremstrahlung as the plume advances in space. They appear to be shifted in to the slower thermal
electrons category and hence leave only faint signature at large distances. The presence of hot
electrons, even though small, is detected in the TOF spectra recorded at all spatial positions and laser
fluences. Hot electron peak appears very sharp at 10 mm distance from the target. As the probe is
moved away from the target, this peak gets slightly temporally elongated, but remains as a permanent
feature in all the electron TOF spectra.

The figure 5 also indicates that at very high laser fluence the electrons are not much delayed
over spatial variations of the probe. As the laser fluence is decreased, the thermal electrons get delayed
with thermal electron peak arrival time approaching 7.5\(\mu\)s. 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 still continued to move forward due to
the energy acquired during the ablation process. The increase in the ambient gas pressure has caused
suppression of the thermal electrons and slowing down of the fast electrons.

4. Conclusion
The presence of fast ion peak and the temporally elongated electron TOF strongly suggest the
occurrence of DL in laser ablated ZnO plasma. 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 pulse energies. Thermal electrons reach the probe few microseconds 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. 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.

5. References
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