High spatial resolution in laser-induced breakdown spectroscopy of expanding plasmas

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Abstract

We report a technique that is able to achieve high spatial resolution in the measurement of the temporal and spectral emission characteristics of laser-induced expanding plasmas. The plasma is imaged directly onto the slit of an imaging spectrograph coupled to a time-gated intensified camera, with the plasma expansion direction being parallel to the slit extension. In this way, a single hybrid detection system is used to acquire the spatial, spectral and temporal characteristics of the laser induced plasma. The parallel acquisition approach of this technique ensures a much better spatial resolution in the expansion direction, reproducibility and data acquisition speed than commonly obtained by sequential measurements at different distances from the target. We have applied this technique to study the laser-induced plasma in LiNbO₃ and Bi₁₂Ge₁₀O₂₀, revealing phenomena not seen in such detail with standard instruments. These include extreme line broadening up to a few nanometers accompanied by self-absorption near the target surface, as well as different ablation and expansion dynamics for the different species ejected. Overall, the high precision and wealth of quantitative information accessible with this technique open up new possibilities for the study of fundamental plasma expansion processes during pulsed laser ablation.

Keywords: Plasma; Spectroscopy; Imaging; Stark effect; Self-absorption; Lithium niobate

1. Introduction

Laser-Induced Breakdown Spectroscopy (LIBS) is an optical technique for non-contact, remote material analysis and is receiving growing interest in a wide range of research areas and disciplines [1]. In LIBS, a specimen is irradiated with a high-energy laser pulse and the emission spectrum of the laser-induced plasma formed near the material surface is measured to determine the elemental composition of the material. The most common experimental approach is based on the use of a spectrometer, and time resolution can be added by use of a fast photomultiplier. A drawback of this approach is the restriction to single-point measurements, providing spectral information of only a single spatial point of the plasma or a space-averaged emission spectrum of the entire plasma. However, for expanding plasmas in low pressure atmosphere or vacuum environment, space resolution is required because the emission spectrum becomes a function of space and time. By use of an imaging detector, such as a time-gated Intensified Charge-Coupled Device (ICCD), images of the plasma at different stages of the expansion process can be obtained, but spectral information is lost [2]. Spectral information for each pixel of the plasma image can be obtained by using an imaging approach based on Fourier transformation, but this technique is time-consuming since it requires the sequential collection of many images (typically 100) [3]. Alternatively, spatial resolution can be obtained by scanning the plasma image over the entrance aperture of a spectrograph-ICCD [4]. This appears to be the most common approach but it also requires sequential image acquisitions for different positions of the plasma. Besides, this technique is restricted to discrete spatial positions and the precision of the measurements is...
were achieved in vacuum (10⁻⁶ mbar). The laser-induced light-emitting plasma that expands along the normal to the target surface (z-direction) is imaged onto the entrance slit of a Czerny–Turner imaging spectrograph (f/4 aperture ratio, 25 cm focal length, 0.15 nm nominal resolution, 2.5 nm/mm dispersion) via two quartz lenses (f₁ = 160 mm, f₂ = 100 mm). The intermediate image of the plasma formed at the entrance slit of the spectrograph is rotated by 90° using a periscope, thus ensuring that the expansion direction (z) lies along the orientation of the slit. A long-pass filter is installed in front of the spectrograph to prevent second order diffraction of short wavelength light. At the image plane that is conjugate to the entrance slit, the spectrograph produces a 1D-spatial and spectral hybrid image of the expanding plasma. In this hybrid image the vertical axis corresponds to the expansion direction and the horizontal axis to the emission wavelength of the species, as seen in the image included in Fig. 1. Alternatively, if the spectrograph grating is operated in reflection rather than in diffraction and the entrance slit is fully open, a 2D-spatial image of the plasma can be formed, which eases the alignment procedure and enables the recording of the spectrally integrated plasma dynamics in two dimensions. The hybrid/2D-spatial images are recorded with a time-gated ICCD camera that has a spectral range from 180 to 870 nm, a resolution of 512 × 512 pixels with an effective pixel size of 24 μm, an A/D resolution of 16 bit and a minimum gate width of 2 ns. The time gate of the ICCD can be delayed by a user-defined value with respect to the laser pulse, using a computer-controlled delay generator.

2. Experimental setup

The experimental setup is shown in Fig. 1. An ArF excimer laser (λ = 193 nm, pulse duration 20 ns) is focused on a target that can be placed in air or inside a chamber in a controlled atmosphere. The experimental results presented here were achieved in vacuum (10⁻⁶ mbar). The laser-induced light-emitting plasma that expands along the normal to the target surface (z-direction) is imaged onto the entrance slit of a Czerny–Turner imaging spectrograph and incubation effects. It is therefore of prime importance to record spatial and spectral information in parallel to eliminate these error sources. An important step into this direction has been done by Pérez-Tijerina et al., [5] who used an imaging fiber bundle to record simultaneously the spectral and 2D-spatial information of the plasma. However, using this approach, the spatial resolution obtained is limited by the number of fibers that can be employed. An elegant alternative has been developed already in 1999 by Monge et al., providing much higher spatial resolution along the transversal direction of the plasma [6]. Their approach is essentially based upon imaging of a transversal section of the plasma onto the entrance slit of the spectrograph, the output of which is detected by an ICCD camera. In this way, a composite image containing radial and spectral information is acquired in parallel. In a recent paper, the same group was able to provide 2D maps of the plasma parameters such as temperature and number densities of neutrals and ions by recording radial-spectral images at several, fixed distances from the target [7]. While this technique provides continuous resolution in the radial direction it is confined to discrete resolution and separate acquisitions along the axial direction.

In our approach, we aim to achieve a high and continuous spatial resolution in the axial direction of the expanding plasma with the benefits of parallel acquisition. Our technique is similar to that described in Ref. [6] but introduces additional optics to rotate the plasma image in such a way that the expansion direction is parallel to the slit direction. This approach has proven capable of recording simultaneously the 1D-spatial and spectral information of the expanding plasma induced by a single laser pulse [8]. The single hybrid imaging detector, based on an imaging spectrograph and a time-gated ICCD camera, will be applied to the study of laser-induced expanding plasmas in LiNbO₃ and Bi₁₂Ge₁₀O₂₀ targets under vacuum conditions. The capability of the system to perform a precise measurement of all three plasma emission parameters (spectral, spatial and temporal) and their interdependence enables us to quantify important plasma properties, including electron density and the dynamics of the ejected neutral and charged species.

Fig. 1. Experimental set-up for 1D-spatial and spectral hybrid imaging of laser induced plasmas with temporal resolution. The spatial and spectral profiles shown at the sides of the transient hybrid image correspond to cross sections taken along the arrows of the white cursor in the upper part of the image.
3. Results and discussion

We have applied this technique to the study of different samples to demonstrate the variety of physical phenomena that can be visualized and whose investigation benefits strongly from the high spatial resolution and enhanced precision available with the parallel acquisition approach used. LiNbO₃ is a material of great interest for optical applications, for which pulsed laser deposition appears to be one of the best synthesis approaches to achieve good quality films [9]. In this case we have acquired one time-gated image of the expanding plasma for each imaging mode under the same experimental conditions. Each image was obtained by irradiation with a single laser pulse (fluence = 1.2 J/cm²) and using the same gate width (Δt = 30 ns) and delay time (t₁ = 140 ns) with respect to the laser pulse. Fig. 2a shows the spectrally integrated image obtained in the 2D-spatial imaging mode (grating operates in reflection) whereas Fig. 2b shows the spectrally resolved image obtained in the 1D-spatial and spectral hybrid imaging mode (grating operates in diffraction). In both configurations, the brightness of each image pixel corresponds to the local/spectral emission intensity at the given delay and constitutes the third image dimension. The two-dimensional plasma expansion process from the target surface (z = 0 mm) can be appreciated in Fig. 2a, showing a forward expansion into the z-direction with a relatively low angular spread.

The apparent blur around the target surface is caused by chromatic aberrations of the lens imaging system. In the 1D-spatial and spectral hybrid imaging mode (Fig. 2b), using an entrance slit width of 50 μm and a grating with 150 grooves/mm and blaze of 500 nm, the horizontal image axis now represents the wavelength of the emitted light, whereas the vertical axis still represents the expansion direction. The presence of chromatic aberrations of the imaging system can be appreciated also here by the slight tilt of the near-target surface emission with respect to the horizontal plane. The delay used to record this image was sufficiently long (140 ns) to reduce the contribution of the short-lived continuum emission ("bremsstrahlung") near the target surface [10]. Several individual emission lines can be clearly identified in Fig. 2b. The lines at 610.3 nm (3p²2P3/2,5/2 → 2p⁷3P1/2,3/2) and at 670.7 nm (2p⁷3P2,5/2 → 2s²5S1/2,3/2) correspond to radiative transitions of excited Li neutrals (Li*), whereas the emission at 777 nm (3p²2P3/2,1 → 3s²S1) corresponds to transitions of excited oxygen neutrals (O*). Besides, a multitude of emission lines mainly due to excited Nb neutrals (Nb*) are present. The large differences in intensity between the Nb* lines and the Li* lines, together with the wide spectral range used to cover the O* line, makes the simultaneous detection of all species involved a challenge. Yet, as can be seen in Fig. 2b, our system is capable of recording the spatial distributions of Li*, O* and Nb* lines simultaneously. The beauty of parallel acquisition is that it is very robust to laser fluctuations and sample inhomogeneities that might be present, since the measurement of all emitting species covered by the spectral window will be performed under exactly the same experimental conditions. Based on a single acquisition following a single laser pulse we are able to discern two entirely different behaviors in the expansion dynamics of the different species. O* is ejected from the target only at the early stages of the ablation process, which can be appreciated by the distinct gap to the target surface 140 ns after the laser pulse. In contrast, Li* and Nb* are still being ejected from the target surface at this delay, which indicates a continuous release of excited neutrals of these species.

Higher spectral resolution has been achieved by use of a grating with 600 grooves/mm and a blaze at 750 nm. Fig 3a shows a time integrated (Δt = 5 μs, t₁ = 0 ns) 1D-spatial and spectral hybrid image recorded upon irradiation with a single laser pulse of the same fluence as before. The Li* line at 610.3 nm extends along more than 10 mm in target distance and strong Stark broadening of the line can be observed near the sample surface [11]. As Stark broadening under these conditions is dominated by electron impact, the electron density Nₑ can be calculated directly from the linewidth Δλ, using the relation Δλ = 2W (Nₑ/10¹⁶) Å [12]. W is an electron impact parameter, which is known for this line and only weakly dependent on temperature [11]. Using this relation and extracting Δλ from Fig. 3a, we obtain Nₑ(z), i.e. the electron density as a continuous function of the target distance (Fig. 3b). For z<2 mm a dramatic increase in electron density can be observed, yielding a maximum value.

Fig. 2. Time-gated (Δt = 30 ns, t₁ = 140 ns) images of the plasma expanding from the surface of a LiNbO₃ target (z = 0 mm), each obtained by irradiating the target with a single laser pulse and using the (a) spectrally integrated 2D-spatial imaging mode and the (b) spectrally resolved 1D-spatial and spectral hybrid imaging mode. The images are represented in a logarithmic intensity scale to compensate for the large differences in emission intensities between the different species (Li*, O* and Nb*). The characteristic emission lines of Li* and O* are labeled in image (b), whereas most of the other emission lines correspond to Nb* and constitute the quasi-continuous background.
of \( N_e = 7.6 \times 10^{17} \text{ cm}^{-3} \) at \( z = 0.5 \text{ mm} \). A recent study on LiNbO\(_3\), employing a single-point scanning technique, reported a value of \( N_e = 0.29 \times 10^{17} \text{ cm}^{-3} \) at a distance of \( z = 2 \text{ mm} \) [12]. As \( N_e \) is expected to decrease with \( 1/z \), our much higher value is consistent with the much shorter target distance. For distances \( \geq 2 \text{ mm} \), the line width measured with our system is currently limited by the resolution of the spectrograph-ICCD system to \( D_k = 0.5 \text{ nm} \).

Very close to the surface, self-absorption effects may occur when the density of a given species is high enough for light emitted by this species to be partly reabsorbed by the same species [13]. Moreover, the probability for self-absorption to occur in transitions between the ground state and an excited state is higher than for transitions between two excited levels, because the population of the ground state is always higher than that of an excited state. We have been able to observe this prediction experimentally by comparing the self-absorption of the 610.3 nm Li\(^*\) line, which decays to an excited level, and the 670.7 nm Li\(^*\) line, which decays to the ground state. Fig. 4 shows enlargements of two 1D-spatial and spectral hybrid images recorded under the same conditions upon irradiation with a single laser pulse per image for the 610.3 nm line (Fig. 4a) and the 670.7 nm line (Fig. 4b). A smaller darker triangle very close to the target surface, indicating self-absorption, can be observed in both cases. This dark triangle is significantly more pronounced in the case of the 670.7 nm Li\(^*\) line, which confirms the prediction of enhanced self-absorption in ground-state transitions. The observation of almost negligible self-absorption for the 610.3 nm line is consistent with the low absorption coefficient \( k \) of this line, 0.5 mm from the target (where self-absorption is more probable). We have calculated \( k \) to be \( \approx 0.5 \), using the expression given in Ref. [10] and following the approach described in Ref. [14] to evaluate the total concentration of Li atoms in the plasma, assuming an electron temperature of approximately 1.5 eV via extrapolation from measurements at longer distances [12]. Assuming a plasma depth of approximately 1 mm, we obtain an optical depth \( \tau \approx 0.05 \), which is \( \ll 1 \) so that the plasma is optically thin for this line. The triangular shape of the spectral region of self-absorption reminds of the shape of the Stark broadened lines and indicates that the process of self-absorption does not only affect the center wavelength but also the broadened wings of the line in situations where the plasma density is sufficiently high, as it is the case very close to the target surface.

We have also applied this technique to the study of Bi\(_{12}\)Ge\(_2\)O\(_{20}\), a photorefractive material with potential applications in spatial light modulators, under the same experimental conditions as for LiNbO\(_3\). In Bi\(_{12}\)Ge\(_2\)O\(_{20}\), strong radiative transitions of excited ions are observed, thus enabling the comparison of the expansion dynamics of neutrals to that of ions. Fig. 5a shows a 1D-spatial and spectral hybrid image recorded with \( \Delta t = 100 \text{ ns} \) and \( t_1 = 200 \text{ ns} \), averaged over 10 laser pulses in order to increase the signal-to-noise ratio. The spatial distributions of the emitting species shown in Fig. 5a correspond essentially to radiative
transitions of neutral atoms of the three target constituents: Bi* at 412.2 nm, Ge* at 422.7 nm and O* at 431.2 nm. In addition, several other emission lines that correspond to Bi ions (Bi***) are observed at 407.9, 425.9 and at 430.2 nm. The different spatial distribution of Bi ions compared to neutrals can best be appreciated in Fig. 5b, showing distribution profiles for the Bi* line at 412.2 nm and for the Bi** line at 425.9 nm, which have been extracted from Fig. 5a. It can be seen that the center of the ion distribution is spatially advanced with respect to that of the neutrals. This indicates that the average velocity of ions is considerably higher than that of neutrals, which is most likely related to the attractive force exerted by the even faster electrons expelled at the very early stages of plasma expansion. An earlier study using a single-point detection technique reported similar velocities for neutrals and ions in this material [15]. We attribute this difference to the lower electron density of a LiNbO 3 plasma compared to Bi 12Ge 1O 20 near-surface emission of excited neutrals (Li*, Nb*, Bi*) hundreds of nanoseconds after the laser pulse. Finally, we have found in both target materials a long lasting expansion velocity is higher than that of excited Bi neutrals. This indicates that the average velocity of ions is considerably higher than that of neutrals, which is most likely related to the attractive force exerted by the even faster electrons expelled at the very early stages of plasma expansion. An earlier study using a single-point detection technique reported similar velocities for neutrals and ions in this material [15]. We attribute this difference to the lower electron density of a LiNbO 3 plasma compared to Bi 12Ge 1O 20 near-surface emission of excited neutrals (Li*, Nb*, Bi*) hundreds of nanoseconds after the laser pulse. 

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