Spectrochimica Acta Part B 100 (2014) 137–146

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

journal homepage: www.elsevier.com/locate/sab

Investigation of the spatial and temporal distribution of plasma excited species produced in laser ablation–glow discharge ☆

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ARTICLE INFO

Article history:
Received 27 March 2014
Accepted 10 July 2014

Keywords:
Laser ablation
Glow discharge
Optical emission
Afterglow

ABSTRACT

Laser Ablation and Glow Discharge (LAGD) plasmas have been coupled and optical emission measurements have been performed in order to study the spatial and temporal distribution of LA and GD species and hence to get further insights into the interaction between them. The relative delay between the laser event and the emission measurement along the GD pulse has been found as a crucial parameter. In addition, no post excitation of the ablated material has been observed when laser ablation takes place during GD prepeak or plateau. In contrast, emission enhancements (e.g. Al I lines at ~877 nm presented an enhancement of up to 4 times in the LAGD plasma) were obtained during the afterglow or late plateau, when firing the laser at delays close (<100 μs) to GD pulse termination. Penning ionization of the ablated material within the GD afterglow, followed by recombination processes, seems to account for the emission enhancements obtained when combining laser ablation and glow discharge.

1. Introduction

Nowadays there is a growing need for complete material characterization, including bulk elemental analysis and surface characterization with lateral and depth resolution of solid samples, as well as chemical speciation of organic materials. In this sense, glow discharge (GD) either coupled to optical emission spectroscopy (OES) or mass spectrometry (MS) has become a powerful analytical technique for trace elemental analysis of conducting and also insulating materials [1]. GD spectroscopies also provide exceptional capabilities in the field of thin and ultra-thin film analysis offering a very high depth resolution, and have become comparable to other surface analytical techniques, such as secondary ion mass spectrometry (SIMS) [2–4].

The use of pulsed GDs has been explored over the last years since it provides additional advantages: higher instantaneous powers can be applied increasing the ionization/excitation efficiency without overheating the sample, which make pulsed GDs more suitable for the analysis of thermally sensitive materials [5–7]. Another interesting feature is that the pulsed GD is a transient plasma that passes through different temporal regimes (prepeak, plateau and afterglow), characterized by different physical and chemical processes [8]. Gated acquisition allows selective measurements within a single pulse, taking profit of the sensitive temporal regimes and reducing the signal to background ratio (SBR) since analyte and gas-background species seem to be formed at different times [9–12]. In addition, elemental, structural and molecular information can be achieved when performing temporally resolved measurements within one single pulse, based on the different ("softer" or "harder") ionization characteristics of prepeak, plateau and afterglow [13–15].

Laser ablation (LA) is a versatile sampling technique that can be used as direct ionization (LA–MS [16]) or atomic emission (LIBS [17]) source. It is also commonly used as a direct solid sample introduction tool in combination with secondary excitation/ionization sources, especially in combination with inductively coupled plasmas (ICP) [18]. In general LA sampling can be performed in both conductors and non-conductors, with high lateral resolution [19,20].

Therefore, the combination of laser ablation as sampling technique with a pulsed glow discharge (LAGD) as post-excitation/ionization source would present a priori significant advantages: since sampling and ionization steps are spatially and temporally separated they can be independently optimized, offering less matrix dependence. The use of radiofrequency powered GDs would not be necessary anymore in order to analyze insulating materials. Moreover, the different temporal domains of the pulsed GD would provide the possibility of chemical speciation.

☆ This paper is dedicated to Nicoló Omenetto, on the occasion of his 75th birthday, in recognition of his outstanding contributions to the field of laser spectrochemistry and as an editor of Spectrochimica Acta Part B.

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http://dx.doi.org/10.1016/j.sab.2014.08.008
0584-8547/

A few works concerning the LAGD coupling have been reported so far. In combination with OES, several studies have demonstrated the capabilities of the glow discharge plasma to excite the ablated material. For instance, Iida used a hollow cathode GD to excite the material ablated by LA within an adjacent cell, achieving analytical sensitivities in the range of μg/g [21]. Wagatsuma and co-workers have also employed a hollow cathode GD, but the ablation process was performed inside the hollow tube under He atmosphere, and were able to determine minor elements in low-alloyed steel samples [22,23]. In the previous experiments the GD was operated in continuous mode. Concerning the use of a pulsed GD, Tereszchuk et al. developed a system where the ablated sample acts also as the GD cathode, finding that they can effectively reduce the laser pulse energies below the excitation/ionization thresholds in order to only produce the ablation of the material, which is subsequently excited by the synchronous μs-pulsed GD. Significant enhancements in the analytical signal (up to 75 times) have been reported when comparing the results obtained with LAGD with those obtained from LIBS or GD experiments under similar conditions [24]. Moreover, increased SBR and improved depth resolutions were obtained with the same setup [25,26]. Lewis et al. characterized a ms-pulsed glow discharge laser ablation system, in which sample and cathode were introduced in the same chamber by using two direct insertion probes [27]. They performed the ablation process at certain times during the GD pulse (before pulse termination), finding that apart from the emission signal generated directly from the laser event, further excitation was observed during the afterglow. The later the laser was fired within the GD pulse, the higher was the LAGD signal detected during the afterglow. They considered that the excitation of the ablated material was induced by the argon metastable atoms (Ar^*_m) created after GD pulse termination.

Early works by Barshick and Harrison have also demonstrated the ability of the GD to ionize the ablated material by coupling the laser ablation with an auxiliary GD to a quadrupole mass spectrometer [28]. More recently, Tarik et al. have coupled LA to a pulsed GD-time of flight mass spectrometer (TOFMS), and the resulting ion signals have been compared to those from LA–TOFMS [29]. The post ionization of the ablated material in the afterglow was found to be enhanced up to 7 times, while the ion signal from GD sputtered species decreased significantly. It has been assumed that Ar^*_m are responsible for the ionization of the ablated material through Penning collisions after GD pulse termination. This Ar^*_m population in the pulsed GD has been characterized in the GD chamber used in the LAGD–TOFMS experiments through optical emission and absorption measurements by Lotito et al. [30]. It has been found to maximize about 6–8 mm far from the cathode surface, at about 50–75 μs after GD pulse termination. In terms of applicability, the same LAGD–TOFMS experimental setup has been proved to provide complementary and quasi-simultaneous elemental and molecular information from organic compounds by introducing the ablated material into the different temporal regions of the GD pulse [31].

In order to fully exploit the capabilities of the LAGD combination, in particular when coupled to MS, the spatial and temporal overlap between the ablated material and the exciting/ionizing species within the GD must be optimized. In this sense, not only temporally resolved measurements are necessary, but also the spatial characterization of the ablated material–plasma interaction is crucial. In this work, the spatial and temporal distribution of the different plasma species produced in laser ablation–glow discharge was investigated by optical emission spectroscopy. Two dimensional images of laser-induced (LA), GD and LAGD emission were obtained using an intensified charge coupled device (iCCD) provided with an optical objective. Different bandpass filters were applied to select the wavelength of interest in order to study the emission from the ablated material, the sputtered species and the filling gas. The relative delay between the beginning of the GD pulse and the LA event was studied in detail, covering the different temporal regimes of the pulsed GD (prepeak, plateau and afterglow). The aim of this study was to gain more insights into the laser plasma–GD interaction, in particular when evaluating the possible post-excitation/ionization processes that take place within the GD and the LA plume dynamics within the GD reduced pressure atmosphere. Besides that, the results of this work can support further experimental and modeling studies to determine the capabilities and limitations of combining LA and GD, compared to other techniques such as LA–ICPMS and MALDI.

2. Experimental

Fig. 1a shows a schematic diagram of the experimental setup used in this work. The LAGD configuration has been described in detail in previous works [29,31], although several modifications were carried out for this study. The GD chamber consists of a six-way stainless steel cross equipped with two perpendicular direct insertion probes where sample and cathode are placed. The cathode–anode distance was set to be 10 mm, and the sample surface remained 8 mm far from the central cathode–anode axis. A frequency quadrupled Nd:YAG (266 nm) laser (Brilliant B laser, Quantel Group, France) was focused on the sample surface by means of two mirrors and a lens. The laser pulse energy used for ablation ranged from 0.5 to 0.7 mJ. A window was also placed on top of the GD chamber allowing the observation of the region defined by cathode, anode and sample and allowing the optical emission measurements to be performed. With this configuration the emission measurements give information about the transport of the ablated material into the GD area and towards the sampler cone. In this sense an iCCD (Andor iStar, Andor Technology, US) provided with an optical objective (Edmund Optics, York, UK) was used to carry out the 2D imaging of the LAGD emission. An example of a resulting image of the region of interest obtained through the top window is shown in Fig. 1b.

The GD was powered by a pulsed DC power supply (RUP3-3A, GBS, Grosserkmannsdorf, Germany). The applied voltage was 630 V, and a pulse width of 2 ms at a frequency of 10 Hz was applied in all measurements. The working gas was pure argon (>99.99%) at a pressure of 0.8 mbar.

The anode in the GD chamber acts as the sampler (first extraction cone) of an orthogonal TOFMS from TOFWerk AG (Thun, Switzerland). The TOF software allows triggering the GD pulse generator and the flash lamp of the laser. The delay of the laser pulse with respect to the beginning of the GD pulse, which is defined as laser pulse delay, was varied to produce the ablation process during prepeak, plateau or afterglow. Moreover, a digital multi-channel delay box (DG-535, Stanford Research Systems Inc., Sunnyvale, CA, USA) was used to trigger the iCCD at a frequency of 1 Hz, by using the 10 Hz signal from the TOF as input signal. The read out time needed by the CCD sensor fixed the maximum frame rate at 1 Hz. The CCD software (Andor SOLIS) allows the temporally resolved acquisition of the emission images, by setting the acquisition delay (time between the beginning of the GD pulse and the start of the acquisition) and the acquisition gate width (duration or exposure time). Furthermore, the signal can be accumulated over a sufficient number of pulses or laser shots. A schematic diagram of the triggering concept is shown in Fig. 2.

Two different sample-cathode configurations were used, always under argon atmosphere: ablation of an aluminum sample was performed when using a copper cathode (Cu–Al configuration); and in addition, the ablation of copper was studied when using a tantalum cathode (Ta–Cu configuration). These two configurations allow the study of the Cu emission in both situations, when it is ablated and when it is sputtered and consequently differences in the processes taking place can be investigated. In this second configuration, Ta was selected since it is usually employed in LAGD studies because of its low sputtering rate. The values of the experimental parameters chosen for these studies are summarized in Table 1.

In order to evaluate the spatial distribution of the species involved in the LAGD plasma (Ar, Cu, Al), several bandpass optical filters were implemented as wavelength selectors. The theoretical center of the transmission band together with the band width (represented by the full width at half maximum, FWHM) is listed in Table 2 for the different