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Signal enhancement in laser-induced breakdown spectroscopy using fast square-pulse discharges

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ABSTRACT

A fast, high voltage square-shaped electrical pulse initiated by laser ablation was investigated as a means to enhance the analytical capabilities of laser Induced breakdown spectroscopy (LIBS). The electrical pulse is generated by the discharge of a charged coaxial cable into a matching impedance. The pulse duration and the stored charge are determined by the length of the cable. The ablation plasma was produced by hitting an aluminum target with a nanosecond 532-nm Nd:YAG laser beam under variable fluence 1.8–900 J cm^{-2}. An enhancement of up to one order of magnitude on the emission signal-to-noise ratio can be achieved with the spark discharge assisted laser ablation. Besides, this increment is larger for ionized species than for neutrals. LIBS signal is also increased with the discharge voltage with a tendency to saturate for high laser fluences. Electron density and temperature evolutions were determined from time delays of 100 ns after laser ablation plasma onset. Results suggest that the spark discharge mainly re-excites the laser produced plume.

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a laser-based technique for measuring the chemical composition of a wide range of materials [1–5]. Elemental composition can be performed in situ, in a fast way and with practically null sample preparation. Despite the great LIBS capabilities, its low sensitivity, about parts-per-million (ppm), is the main drawback of this technique compared with other conventional elemental analysis techniques [1]. The use of an additional laser pulse in a double pulse configuration (DP), improves the LIBS sensitivity without losing its advantages [5–9].

Other methods to reduce the limit of detections (LOD) include the use of additional excitation sources, such as inductively coupled plasma [10], hollow cathode [11,12], glow discharge [13], microwave [14], etc. However double laser pulses and other excitation techniques increase the cost and complexity of the whole detection system. The glow discharge method combines a low pressure discharge with laser ablation. Although this method is effective in enhancing the lines it has the disadvantage of requiring a vacuum chamber to produce the glow discharge as this is strictly a low pressure one [13]. Microwaves have been effectively used to enhance emission in the plasma by about an order of magnitude but the method has the disadvantage that it requires that the sample be inside a resonant cavity and the use of a radio-frequency source [14].

A low cost alternative to increase LIBS sensitivity relies on the combination of a high voltage discharge with the laser plasma [15–23]. Spark-assisted methods have the advantage that they can be implemented at ambient pressure and only require a simple capacitor and a high-voltage supply. The high voltage pulse is used to re-excite the laser produced plasma reducing the LODs and the signal's relative standard deviation [19]. This scheme has been used to analyze metals [18, 22], soils [15,19,21] and Si [20]. In the work of Zhou et al. [16] a nanosecond discharge circuit was employed. The laser induced plasma triggers an electric oscillating discharge that enhances the signal-to-noise ratio SNR by a factor of ~3 for a deposited energy of 45 mJ. Besides, the SNR could also be enlarged increasing the capacitance [17]; however no improvement of LIBS signal was obtained when the voltage was raised due to the increment of the background noise. Plasma physics properties were also investigated to elucidate the signal enhancement. In an oscillating discharge of 200-ns period Li et al. [24], found a clear correlation between the increment of the line transitions with the time integrated electron temperature and the electron number density. Conversely, no temperature changes were observed in a microsecond discharge [18]; the LIBS signal increment observed there was attributed to a larger duration of the plasma and an increment of its size. Besides, in this work an oscillating behavior of the electron density was obtained due to the fluctuating electric power.

The dynamics of the discharge was investigated using fast photography [25]. Their results suggest that the enlargement of the plasma size and an increment of the ablated material is the main cause of the enhancement of plasma emission. Wei et al. [26] investigated the electron

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number density and plasma dynamics of spark laser-triggered discharges. They didn't found noticeable changes of the refractive index of laser produced plasmas. Their schlieren result shows a formation of a stagnation layer after laser onset and a dynamic modeling predicts an increment of the pressure shock front.

The discharge-enhancing techniques described above employ an alternating circuit that oscillates at high frequency and, consequently, the electric current becomes null several times (consequently making zero the electric power each time) during the lifetime of the plasma. The aim of this work is to use a square, submicrosecond, unipolar, high-power current pulse to re-excite the laser produced plasma (LIP). The electric discharge is guided by the expanded LIP to the grounded target to increment the LIBS signal without interruptions in the power fed to the discharge.

2. Generation of square pulses using transmission lines: fundamentals

The discharge of a capacitor is a common means of generating a spark discharge in the lab. Unfortunately, a conventional capacitor tends to discharges in an oscillatory, alternate, fashion which means that the current will be null several times during the duration of the spark. The power transfer from the electric circuit will consequently cease every time the current crosses the zero baseline. The coaxial cable, having two adjacent conductors isolated from each other, can also be considered as a type of capacitor but as it is a distributed-parameters device its discharge behavior can be markedly different from that of a conventional capacitor.

A coaxial cable is a type of transmission line. As in any other transmission line, electromagnetic waves take a finite time τ to propagate along its length l. If the cable has capacitance C and inductance L then the propagation speed inside it will be $v = (LC)^{-1/2}$. For non-magnetic media this becomes $v = c/\varepsilon_r^{1/2}$ for an infinite media with permittivity ε_r, where c is the speed of light. So an electric pulse will take a time $\tau = l/v$ to cross from one end to the other of a cable of length l.

When the electric pulse reaches an interface terminated with a different impedance, part of it will reflect and part of it will transmit. So, for example, if a cable is open on one end a voltage pulse will reflect with the same amplitude and polarity. On the other hand, if the cable is terminated in a short-circuit, the pulse will reflect with inverted polarity [27]. These properties can be exploited to generate fast unipolar, square pulses. Furthermore the temporal length pulses can be controlled at will, as will be shown below.

Consider the circuit shown in Fig. 1, where it will be assumed that the load Resistance R_L has the same value as the cable's characteristic impedance Z_0. If we assume that the cable is already charged with voltage $+V_0$ then when the switch SG is closed at $t = 0$ a voltage $V_0/2$ will appear at the load marking the beginning of a sharp current pulse with amplitude $I = V_0/2R_L$. Concurrently, at $t = 0$ a pulse of amplitude $-V_0/2$ will propagate along the cable from right to left bringing down the local voltage to $V_0/2$ as it travels along the way. When the front reaches the other end, at $t = \tau$, it will reflect with equal amplitude and polarity ($-V_0/2$) and as it now travels to the right it will bring local voltage down to zero along the way. When this front arrives to the switch at $t = 2\tau$ the load's voltage will become zero thus ending the current pulse [28]. The end product of this process is a square pulse of constant amplitude $I_{max} = V_0/2R_L$ and finite duration 2τ.

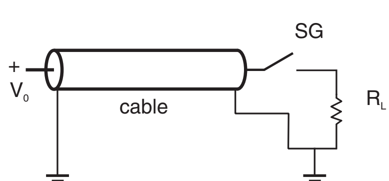

Fig. 1. Schematics of the square-pulse generation principle. V_0: high voltage source; SG: spark gap switch; R_L: load resistance.

3. Experimental

The schematic diagram of the experimental setup is shown in Fig. 2. The ablation laser was a Nd:YAG (Surelite III, from Continuum) delivering 5 ns width Gaussian pulses at 532 nm and was operated at a 1 Hz repetition rate. The output energy was varied from 2 to 100 mJ and was focused by a 10 cm plano-convex lens (L) onto the target producing a spot diameter of ~120 μm. Hence, the ablation laser fluence was 18 to 900 J cm^{-2}. The shot-to-shot stability, monitored in real time by an energy meter EM (1918-C from Newport, using the 818E-03-12-L detector head), was about 97%. The ablated sample was a polished aluminum slab from a commercial aluminum 6463 alloy containing 98% Al, 0.8% Mg, 0.5% Si, 0.2% Cu, 0.2% Fe, plus traces of other elements. The target was mounted onto a translation stage x-y-z to adjust the focusing distance and to shift the target in order to have an undamaged surface in each run of data collection. Each acquisition consisted of 20 shots on the same spot before moving to a new position. Experiments were performed in atmospheric pressure environment at 23 ± 1 °C and 35 ± 5% of relative ambient humidity.

Typically a high voltage discharge circuit consists of a high voltage power supply, connected to a capacitor that discharges through a spark gap. In this implementation of the discharge circuit, a high voltage power supply (model 205 B, from Bertan) giving an output up to 30 kV, charges through $R_1 = 10$ kΩ, a $l = 50$ m length of 50-Ω RG58 cable which serves as a capacitor. The cable output is connected to a stainless-steel cylindrical rod of 5 mm diameter with a hemispherical tip that acts as the anode of the spark-gap. The aluminum target acts as the cathode and it was grounded through a 50 Ω resistance, R_2. The distance between the electrode and the target was also varied from 2 to 12 mm with the axis of the rod at an angle of ~30°. The separation chosen depended on the maximum discharge voltage employed as the self-triggering of the discharge ought to be avoided. The expanding LIP triggered the discharge from the Al target towards the HV rod. The current flowing through R_2 was monitored by means of a Rogowski coil on the low-voltage side of the circuit, and was connected to a digital oscilloscope (DPO 4104B from Tektronix).

The spatially integrated emission was collected by a fused-silica optical fiber bundle located at ~6 cm from the laser focal point and sent to a 50-cm focal length spectrometer (SpectraPro 2500, from Acton Research). The entrance slit of the spectrometer was 10 μm wide, providing an instrumental broadening of 0.04 nm, which was determined by using a Hg spectral lamp. The collected light was dispersed by a 1800 grooves mm^{-1} diffraction grating, sent to an intensified charge-coupled device (ICCD) camera (PiMAX 1024 × 1024, from Princeton Instruments) where the spectra were recorded.

The laser and diagnostic system were synchronized through an 8-channel pulse/delay generator DG (575-8C, from Berkeley Nucleonics).

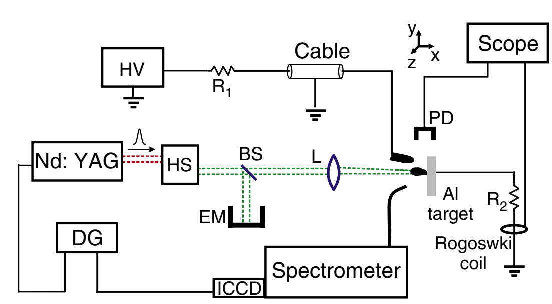

Fig. 2. Scheme of the experimental arrangement for spark discharge assisted laser ablation (SD-LA). HV: high voltage source; DG: pulse/delay generator; HS: harmonic separator; EM: energy meter; PD: photodiode; R: resistance; L: lens; BS: beam splitter; Scope: oscilloscope.