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Spectrochimica Acta Part B 60 (2005) 948 – 954

SPECTROCHIMICA ACTA PART B

www.elsevier.com/locate/sab

Thermal-to-plasma transitions and energy thresholds in laser ablated metals monitored by atomic emission/mass spectrometry coincidence analysis☆

José M. Vadillo, Carmen C. García, José F. Alcántara, J. Javier Laserna *

Department of Analytical Chemistry, University of Malaga, E-29071 Malaga, Spain

Received 28 January 2005; accepted 13 June 2005
Available online 22 July 2005

Abstract

A simultaneous laser-induced plasma spectrometry/laser ionization mass spectrometry experiment has been used to follow the ion and photon intensity in laser plasmas generated over pure metallic targets as a function of fluence. The excitation conditions have been chosen to cover the range from low fluence levels, where surface desorption and thermoemission are the common processes, to the high fluence regime, characterized by plasma formation. The fluence thresholds for ion formation and plasma formation have been calculated. The dependence of both processes with melting temperature has been demonstrated.

Keywords: Laser ablation; Thresholds; LIPS; LIMS; Coincidence analysis

1. Introduction

Laser microanalysis of solids involves the local laser excitation of the target and the subsequent collection and interpretation of the detected signal, which carries the information on the chemical composition of the probed spot [1,2]. Several analytical techniques make use of the lasers in such way, among which laser ionization mass spectrometry (LIMS) and laser-induced breakdown spectrometry (LIBS) are the most versatile [3,4].

It is generally accepted that laser–solid interaction is based on a thermal process, where as a result of the laser impact onto the solid target, the temperature of the surface rises, and eventually, the target can melt, and even vaporize [5]. Under this model, the amount of energy reaching a solid sample greatly influences the type of phenomena occurring at the sample surface. While at high irradiance, extensive fragmentation, particle emission, and plasma formation are the dominant situations; at low irradiance levels, surface desorption and thermoemission are the common processes. Different efforts to rationale the details of laser–matter interaction have led to the distinction of at least three regimes in opaque materials exposed to Q-switched lasers: (a) a low fluence regime (10^{-3}–10^{-2} J cm^{-2}) dominated by surface heating and soft ionization of target particles and characterized by a negligible mass transfer across the solid/vacuum interface; (b) a medium fluence regime (10^{-2}–10^{-1} J cm^{-2}) where evaporation of the sample becomes significant, the laser energy is absorbed by both the ionized vapor in front of the target and the target itself and several secondary and non-linear processes occur in the expanding plume; and (c) a high fluence regime (over 1 J cm^{-2}) where the deposition of laser energy is governed by the strong absorption of the expanding plasma cloud. So, as laser irradiance energy increases, different sequential processes occur that in the simplest case

☆ This paper was presented at the 3rd International Conference on Laser Induced Plasma Spectroscopy and Applications (LIBS 2004), held in Torremolinos (Málaga, Spain), 28 September – 1 October 2004, and is published in the special issue of *Spectrochimica Acta Part B*, dedicated to that conference.

* Corresponding author.
E-mail address: laserna@uma.es (J.J. Laserna).

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doi:10.1016/j.sab.2005.06.003

involve the following macroscopic events: surface heating with thermal desorption, surface melting with surface evaporation, volume evaporation, formation of an optically thick plume, plasma absorption in the plume and optical breakdown [6].

As monitoring of laser-produced events in direct solid analysis is commonly carried out by atomic emission spectroscopy (AES) or mass spectrometry (MS), and ion formation and plasma expansion take place at different fluence intervals, it is interesting to determine precisely the transition between the different regimes in order to tune the excitation conditions to the analysis needs. Besides, simultaneous monitoring of the mass spectrum and emission spectrum can also provide information on issues such as calculations of density of ions compared to neutrals, electronic temperature and target surface temperature, among others.

The aim of the present work is exposing seven pure metallic elements to different laser energies and detecting simultaneously the produced ions and photons to describe the transition between the different processes. The detection is performed with two sensitive low-noise multichannel detectors (an intensified optical spectrometer and a time-of-flight mass spectrometer) that provide accurate measurements, while the energy is varied in a precise and controlled way not affecting the spatial distribution of the incoming laser beam.

2. Experimental

Fig. 1 shows the experimental setup used. The samples were introduced in a multiport stainless steel vacuum chamber using a direct insertion probe previously described [7]. The chamber was pumped down to 5×10^{-7} mbar.

The 532-nm output of a Nd:YAG laser was focussed using a 150-mm focal-length lens (FL) onto the sample at normal incidence to the sample surface. The laser was operated at its maximum flashlamp voltage and repetition rate to avoid distortions in the spatial profile due to thermal lens effect in the laser rod. Under these conditions, the maximum output was 250 mJ per pulse. In order to obtain accurate control over the laser energy, a set of spectroscopic-grade coloured glass filters (GF) exhibiting absorption in the spectral green region was used to lower the laser energy per pulse to a maximum of 22 mJ. Additional control over the delay in the Pockels cell in the range between 120 and 155 μs allowed the generation of pulses between 14 and 21 mJ with RSD values better than 2% as shown in Fig. 2. The RSD values correspond to the average of 25 laser shots. A fixed value of 140 μs was selected, providing constant pulses of 20 mJ per pulse. For our fluence-controlled experiments, the laser energy was modified in the range between 0.1 and 7 mJ using a variable polarizer crystal. A thin microscope slide was inserted in the optical path after the polarizer in order to generate a calibrated reflection of

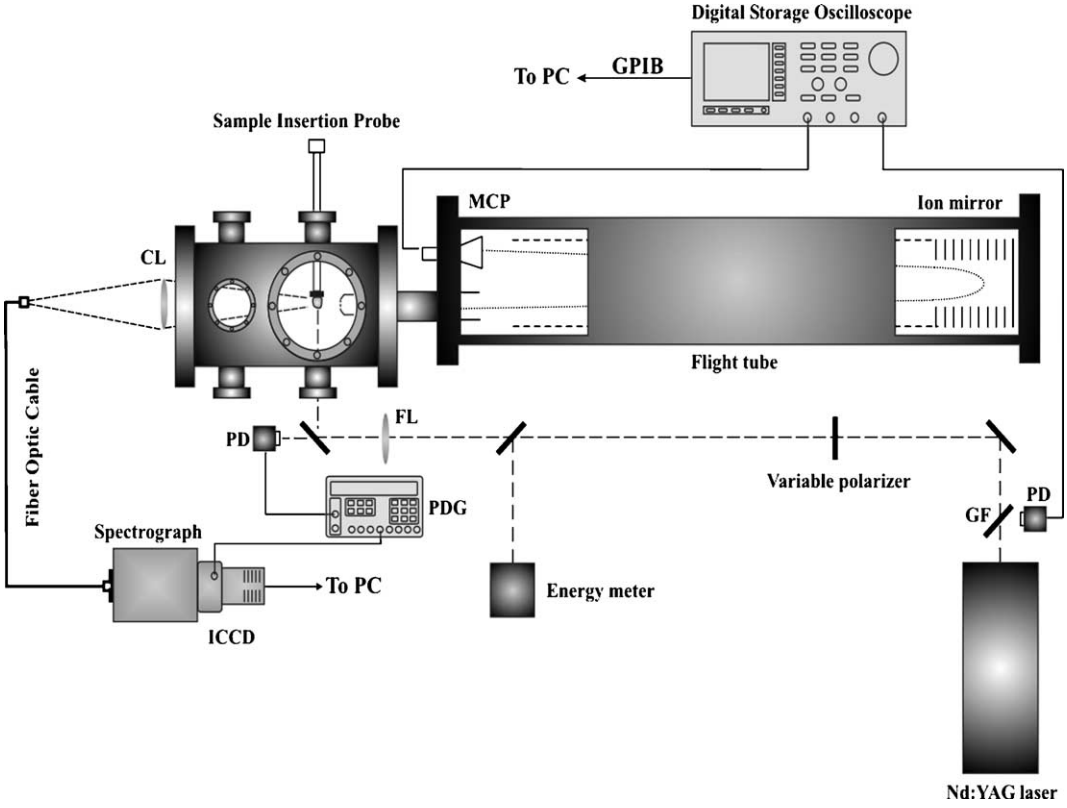

Fig. 1. Experimental setup. CL: Collection lens; MCP: Microchannel plate; PD: Photodiode; FL: Focusing lens; GF: Glass filter; ICCD: Intensified Charge Coupled Device; PDG: Pulse/Delay Generator.