Spectrochimica Acta Part B 66 (2011) 186–188

Contents lists available at ScienceDirect

Spectrochimica Acta Part B

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

Research Note

Polarization and fluence dependence of the polarized emission in nanosecond laser-induced breakdown spectroscopy

John S. Penczak, Yaoming Liu, Robert J. Gordon *

Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607-7061, United States

ARTICLE INFO

Article history:
Received 16 December 2010
Accepted 20 December 2010
Available online 3 January 2011

Keywords:
LIBS
Polarization
Ablation
Laser-induced breakdown spectroscopy

ABSTRACT

Several studies have appeared in the past two years reporting that the continuum emission produced by the laser ablation of solid materials is strongly polarized. In a paper that appears to conflict with these findings, Asgill et al. report that they did not observe a significant amount of polarization produced by nanosecond laser excitation of nitrogen gas and laser ablation of copper and steel (M.E. Asgill, H.Y. Moon, N. Omenetto, D.W. Hahn, Investigation of polarization effects for nanosecond laser-induced breakdown spectroscopy, Spectrochim. Acta Part B (2010) xxx–xxx [7]). Here we show that the apparent discrepancy is resolved when laser fluence and polarization are taken into account. Using a 532 nm Nd:YAG laser to ablate Al samples in air, we find that the degree of polarization, P, of the continuum is greater for s- vs. p-polarized excitation and that P decreases with increasing fluence. We show that P would be <10% under the conditions of Asgill et al., whereas P>60% is obtained at low fluences with s-polarized excitation. We also confirm that at high fluence the polarization of the discrete emission is much smaller than that of the continuum.

Laser ablation of solid materials is a complex process that transfers matter into liquid, vapor, and plasma phases in a sequence of non-equilibrium steps. Light emitted by the excited material can provide valuable information about the ablation mechanism as well as a powerful tool for analyzing the elemental composition of the substrate. A number of studies have shown that the light emitted from laser-induced plasmas, especially the continuum radiation, can be strongly polarized [1–5]. This effect was observed for a wide variety of solid materials and for both nanosecond and femtosecond excitation. The polarization was speculated to be related to the non-equilibrium state of the plasma, which may result in an anisotropic velocity distribution of the electrons [6], which in turn transfer their directionality to the polarization state of the emitted photons.

Recently, Asgill et al. [7] investigated these polarization effects in nitrogen gas, steel, and copper with a time-resolved technique using a 10 ns, p-polarized laser. For nitrogen gas they found no polarization of the plasma emission. For the steel sample at oblique angles of incidence they observed a polarization, P, of approximately 5% that is independent of the angle of incidence and delay time. They also report no significant difference between the continuum and discrete polarization levels. For the copper sample the laser was incident normal to the surface, and no polarization was observed. They attribute the polarization effects seen in other laboratories, obtained using non-time-resolved spectroscopic methods, to polarization-dependent Fresnel reflectivity, which causes s-polarized light to be preferentially reflected. They further argue that evolution of the plasma causes the ratio of light emitted directly by the plasma to that reflected by the surface to change in time. The fact that the discrete emission is known to occur at a delayed time with respect to the continuum may therefore explain the polarization effects seen in the other laboratories.

The absence of polarization produced by the copper sample when irradiated at normal incidence agrees with our earlier study of aluminum with a femtosecond laser (see Fig. 7 of Ref. [3]). We also found that the laser-induced breakdown spectrum (LIBS) of air is likewise unpolarized (unpublished data associated with Ref. [8]). The discrepancy with the results of Asgill et al. is therefore restricted to the case of oblique ablation of solid materials.

We believe that the transient optical properties of the plasma as well as Fresnel reflection effects are unable to explain the polarization seen in previous experiments. At an angle of incidence of 30°, the difference in the Fresnel reflection efficiencies of s- and p-polarization are small and could give rise to P<10%. While this effect may explain the small polarizations seen in the experiment of Asgill et al., it cannot account for the very large polarizations seen in previous experiments [1–5], ranging from 20% to almost complete (P = 100%) polarization.

We have performed an experiment that reconciles the differences between the data reported by the three groups that have studied this problem. The second harmonic of a Nd:YAG laser (Continuum Surelite, 532 nm, 4 ns pulse width) was used to ablate an Al sample in air. A variable neutral density filter was placed before the focusing optics to set the pulse energy of the beam, *E*, between 1 μJ and 5 mJ. The polarization state of the laser was changed using a half-wave

* Corresponding author.
E-mail address: rjgordon@uic.edu (R.J. Gordon).

0584-8547/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.sab.2010.12.009

plate. The laser was focused onto the sample by a 100 mm focal length convex lens. Machine-polished, industrial grade aluminum (alloy #7075; 91:0% Al, 6:0% Zn, 2.5% Mg) was mounted on a sub-μm precision xyz translation stage. The stage was computer-controlled to expose a fresh surface for each incident pulse. The laser was incident 30° from the normal direction of the sample surface. The focused laser beam has a radius of $\omega = 22.6 \pm 1.4$ μm, which was measured with a scanning knife edge. This quantity is the Gaussian radius of the electric field, such that the intensity is given by

$$I(r) = I_0 e^{-2r^2/\omega^2}, \quad (1)$$

and the peak fluence is given by

$$F = 2E \cos\alpha / \pi\omega^2, \quad (2)$$

where α is the angle of incidence. The plasma plume was imaged perpendicular to the direction of the laser beam onto the 50 μm wide entrance slit of a spectrograph (Spectrapro 2300i, Princeton Instruments) equipped with a non-gated CCD (PIXIS 400, Princeton Instruments) camera. A Glan–Thompson polarizer mounted on a motorized rotation stage was inserted in front of the entrance slit of the spectrograph to measure the polarization of the plasma emission (Table 1).

Fig. 1 shows the dependence of P on laser fluence for both s- and p-polarization. The polarization was measured at 460 nm, which is free of discrete emission and is representative of the continuum spectrum. The figure also shows data reported by Majd et al. [5] and Asgill et al. [7] at their respective fluences. The fluence of Asgill et al. was calculated without the factor of 2 in Eq. (2) because they used a truncated Gaussian pulse shape [9]. The fluence from Majd et al. was multiplied by a factor of 0.87 to include the cos α factor in Eq. (2) [10].

We propose that the lack of polarization seen by Asgill et al. is a result of two relevant differences in their experimental conditions. First, there is a significant dependence of the polarization of the continuum emission on the polarization state of the laser. Specifically, it is shown in Fig. 1 that s-polarization is much more effective in generating polarized plasma emission than p-polarized light. Second, P depends strongly on the fluence of the incident laser. Fig. 1 shows that the polarization falls dramatically as the fluence is increased from 5 to 500 J/cm^2. For s-polarized excitation, P drops by a factor of 3, whereas for p-polarization P drops below 5%, in good agreement with the findings of Asgill et al.

Fig. 2 shows emission (LIBS) and polarization spectra over the range of 385–505 nm taken with a fluence of 13.2 J/cm^2. These spectra are similar to our previous work [4] as well as that of Majd et al. Specifically, the polarization of the continuum radiation varies slowly with wavelength in this spectral region. The strong Al lines near 400 nm in the LIBS spectrum appear as windows in the polarization spectrum, indicating that the polarization of the discrete emission is smaller than that of the continuum emission. A precise value of P for the discrete lines is difficult to determine because they sit on top of the broad continuum. As the fluence is increased, the difference between discrete and continuum polarization decreases until the polarization spectra are nearly flat, resembling the results of the work of Asgill et al.

Table 1
Laser parameters for the three experimental setups.

Parameter	Present study	Asgill et al. [7]	Majd et al. [5]
Pulse energy (mJ)	0.05–4.6	40	51
Spot radius (mm)	22.6 ± 1.4	30	95
Fluence (J/cm^2)	5.4–497	1200	310
Irradiance (GW/cm^2)	1.02–94.0	120	40

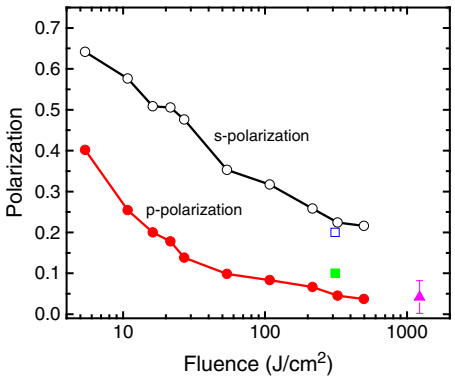

Fig. 1. Polarization of the 460 nm emission vs. laser fluence generated with s-polarized (open symbols) and p-polarized (filled symbols) radiation. The circles are from the present study, the squares are from Majd et al. (Ref. [5]), and the triangle is from Asgill et al. (Ref. [7]).

Other differences between the experimental conditions used by the various groups include the target material and laser wavelength. Majd et al. used copper at 1064 nm, Asgill et al. used steel at 1064 nm, and we used aluminum at 532 nm. The excellent consistency between the three sets of data shown in Fig. 1 suggests that these factors do not play a primary role in the polarization mechanism. Corroborating evidence is provided by our femtosecond experiments, in which we observed high values of P for silicon [1], copper [2] and graphite [2] at 800 nm. The insensitivity to material and wavelength (but not necessarily to pulse duration) suggests that the polarization depends more on the properties of the plasma than of the underlying substrate.

The mechanism responsible for the plasma polarization is still unknown. Possible effects include an alignment of the plasma that persists after termination of the pulse, reflection and scattering of the fluorescence as it emerges from the plasma, and parametric frequency conversion of the laser beam itself. It is possible that more than one mechanism plays a role at different times and fluences. Experiments designed to elucidate the mechanism are ongoing in our laboratory.

Acknowledgement

This project was supported under Contract Number FA7014-07-C-0047, with the U.S. Air Force Surgeon General's Office (AF/SG) and administered by the Air Force District of Washington (AFDW).

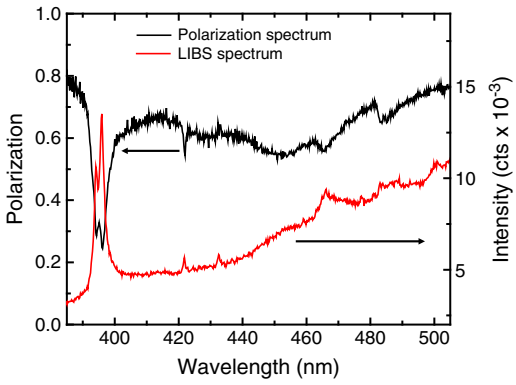

Fig. 2. LIBS spectrum (red, lower trace) and polarization spectrum (black, upper trace) taken with an s-polarized laser with a fluence of 13.2 J/cm^2.

References

[1] Y. Liu, S. Singha, T.E. Witt, Y. Cheng, R.J. Gordon, Observation of near total polarization in the ultrafast laser ablation of Si, Appl. Phys. Lett. 93 (2008) 161502.
[2] Y. Zhao, S. Singha, Y. Liu, R.J. Gordon, Polarization-resolved laser-induced breakdown spectroscopy, Opt. Lett. 34 (2009) 494–496.
[3] J.S. Penczak, Y. Liu, R.J. Gordon, Polarization resolved laser-induced breakdown spectroscopy of Al, J. Phys. Chem. A 113 (2009) 13310–13317.
[4] Y. Liu, J.S. Penczak, R.J. Gordon, Nanosecond polarization-resolved laser-induced breakdown spectroscopy, Opt. Lett. 35 (2010) 112–114.
[5] E. Majd, A.S. Arabanian, R. Massudi, Polarization resolved laser induced breakdown spectroscopy by single shot nanosecond pulsed Nd:YAG laser, Opt. Lasers Eng. 48 (2010) 750–753.
[6] H.M. Milchberg, J.C. Weisheit, Polarization of recombination radiation from nonequilibrium plasmas, Phys. Rev. A 26 (1982) 1023–1029.
[7] M.E. Asgill, H.Y. Moon, N. Omenetto, D.W. Hahn, Investigation of polarization effects for nanosecond laser-induced breakdown spectroscopy, Spectrochim. Acta Part B 65 (2010) 1033–1040.
[8] Y. Zhao, T.E. Witt, R.J. Gordon, Efficient energy transfer between laser beams by stimulated Raman scattering, Phys. Rev. Lett. 103 (2009) 173903, [1-4].
[9] D. Hahn, private communication.
[10] R. Massudi, private communication.