

# Polarization-resolved laser-induced breakdown spectroscopy

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Received October 21, 2008; accepted November 17, 2008;  
posted January 9, 2009 (Doc. ID 102966); published February 12, 2009

It is shown that plasma polarization measurements can be used to enhance the sensitivity of laser-induced breakdown spectroscopy (LIBS). The polarization of the plasma emission is used to suppress the continuum with only slight attenuation of the discrete atomic and ionic spectra. The method is demonstrated for LIBS detection of copper and carbon samples ablated by pairs of femtosecond laser pulses. © 2009 Optical Society of America

*OCIS codes:* 300.6365, 140.3440, 260.5430.

Laser-induced breakdown spectroscopy (LIBS) is a versatile tool for elemental analysis with many practical applications [1,2]. In particular, LIBS may be used for real-time detection of multiple elements by tracing their respective atomic (or ionic) and/or molecular spectral fingerprints emitted by the laser-generated plasma. With little or no requirements for pretreatment of the analyte, LIBS may be utilized universally to measure the composition of samples in any physical state, including particles and aerosols. Although LIBS does not have the sensitivity of some other established methods of chemical analysis, it is a superior technique for stand-off detection in harsh environments [3], such as blast furnaces [4], nuclear reactors [5], biohazardous areas [6], and the Martian landscape [7].

It is well known that the plasma spectrum produced by laser ablation of materials consists of a series of discrete lines and a broadband continuum [8,9]. Reducing the continuum background is one of the key challenges for improving the analytical capability of LIBS. A number of techniques have been introduced to increase the line-to-continuum ratio. Among them, time-resolved nanosecond LIBS is most frequently used to extract line emission signals from the continuum background, taking advantage of their different temporal-evolution characteristics [10,11]. This technique is very sensitive, however, to the selection of the time gate, because each resonant line has its own temporal profile that depends strongly on the laser-excitation conditions and sample properties [11,12]. Moreover, inevitable variation of experimental conditions during laser ablation of the samples greatly deteriorates the reproducibility of the measurement. Spatially resolved detection and buffer-gas-assisted methods have also been proposed to improve the signal/background capability of LIBS [13,14]. Nevertheless, because of the strict experimental requirements of these methods, temporally and spatially integrated spectral measurement is still the best choice in the practical application of LIBS, provided that the continuum background can be suppressed [14,15]. A comparison of time-integrated nanosecond and femtosecond (fs) LIBS spectra with identical fluences revealed a much

larger ratio of the discrete to continuum emission in the fs regime [15].

In this Letter, we describe a new technique for reducing the continuum background. In a previous study, we found that the plasma continuum emission produced by ablation of solid materials with pairs of fs laser pulses is strongly polarized, whereas the discrete fluorescence lines are much less polarized [16]. Taking advantage of this phenomenon, we show here that by placing a simple polarizer before the detector, the ratio of the discrete line to the continuum spectrum may be significantly increased in the temporally and spatially integrated LIBS. We refer to this technique as polarization-resolved LIBS (PRLIBS).

The apparatus used for PRLIBS is similar to that used in our previous studies [16–18], with experimental parameters chosen to maximize the polarization of the continuum [16]. Pairs of fs laser pulses with durations of ~65 fs and a central wavelength at 800 nm were generated by a Ti:sapphire laser and a Michelson interferometer. The two pulses had equal energies of 14  $\mu\text{J}$ , and the time delay between them was fixed at 80 ps. The laser was focused onto the sample surface by a convex lens ( $f=100$  mm), and the total fluence was 8.9  $\text{J}/\text{cm}^2$ . A comparatively long focal length (and thus larger Rayleigh range) was selected to reduce the sensitivity of the polarization to the location of the focal point [16].

Industrial copper (OHFC, 99.9%) and semiconductor grade graphite (DFP-3-2, Poco) samples were mounted in air on a computer-driven  $xyz$  stage. The incidence angle of the laser beam was 30° from the normal direction of the sample surface, and its polarization plane was parallel to the sample surface ( $s$  polarized). The plasma plume was imaged normal to the direction of the laser beam by a pair of lenses with focal lengths of 75 and 50 mm, respectively, onto the 50- $\mu\text{m}$ -wide entrance slit of a spectrograph (Spectrapro 2300i, Princeton Instruments). A 300 lines/mm grating blazed at 500 nm was typically used to disperse the spectrum, which was recorded by a nongated CCD (PIXIS 400, Princeton Instruments) camera. A Glan-Thompson polarizer mounted in a motorized rotation stage (PR50, Newport) was in-

served in front of the entrance slit of the spectrograph to measure the polarization of the plasma emission. The spectrum was measured at each position of the polarizer by summing the signals generated by 20 laser shots. A fresh sample position was irradiated at each polarizer angle.

Figure 1 shows the plasma emission spectra of copper and graphite measured with and without the polarizer in place. The upper panel is the time- and space-integrated LIBS spectra, whereas the lower panel shows the improvement in signal-to-background ratio (SBR) obtained by PRLIBS. For example, the SBR for the green Cu lines at 511, 515, and 522 nm are increased from 1.5, 1.7, and 2.2 in LIBS to 4.2, 5.3, and 8.2 in PRLIBS, respectively. Additionally, Cu and Cu<sup>+</sup> lines (especially those at short wavelengths) that are embedded in the continuum background of LIBS spectrum are resolved in the PRLIBS spectrum. For graphite, the C<sub>2</sub> Swan bands [14,19] as well as carbon atomic and ionic lines such as C I at 437 nm, C II at 515 nm, and C III at 388 nm are much better resolved by PRLIBS.

To understand how the polarizer suppresses the continuum radiation and thereby enhances the SBR, we measured the plasma polarization spectra for both samples. The polarization spectra shown in Fig. 2 were obtained by fitting a Malus function to the signal intensity in each 0.21 nm interval [16]. A comparison of the LIBS emission spectrum and the polar-

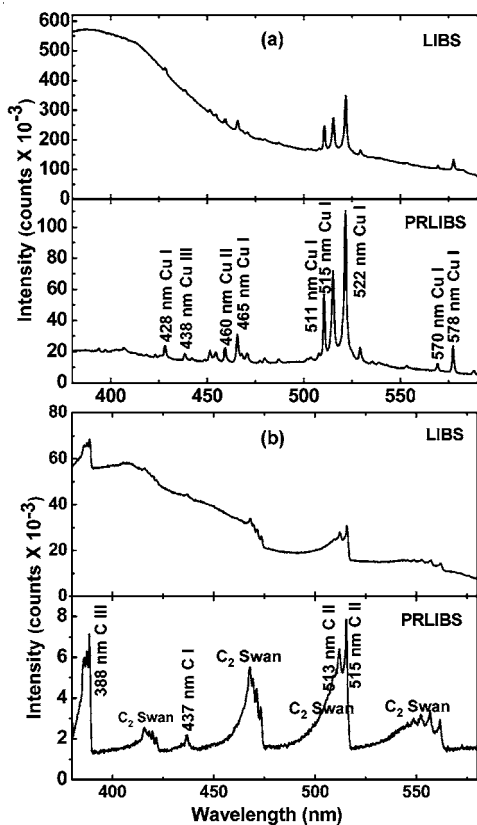


Fig. 1. Plasma emission spectra produced by fs laser ablation of copper and graphite. Upper graphs, LIBS measured without the polarizer; lower graphs, PRLIBS measured with the polarizer in place with its polarization plane perpendicular to that of the laser.

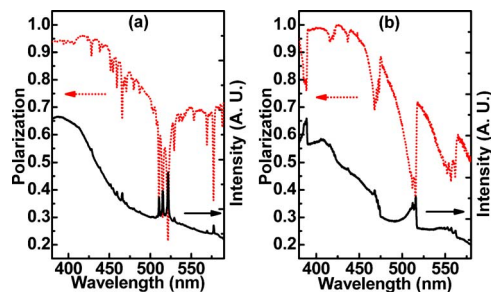


Fig. 2. (Color online) Comparison of the intensity (solid curves) and polarization (dotted curves) spectra for (a) copper and (b) graphite samples.

ization spectrum, both measured without temporal gating, shows that the continuum is much more strongly polarized than the discrete line emission. The spectra recorded with the polarizer positioned at different angles are plotted in Fig. 3. When the polarizer is positioned with its polarization plane vertical to that of the plasma continuum radiation, the background is filtered out significantly, while the emission lines retain their intensity.

The spectra shown in Fig. 4 demonstrate a practical application of PRLIBS. Shown here are the LIBS and PRLIBS spectra of a Cu sample and a U.S. dime coin. The latter is composed of 95% Cu and 5% Ni. In the conventional LIBS spectrum, the Ni I 548 nm peak is visible, but Ni lines at shorter wavelengths are buried in the continuum. In contrast, in the PRLIBS spectrum the Ni I 386 and 548 nm lines, as well as the Ni II 403 and 499 nm lines, are readily observed.

The underlying mechanisms of the different polarization states of the discrete and continuous spectra are not yet fully understood. The continuum is primarily generated by inverse Bremsstrahlung (free-free) and recombination (bound-free) transitions,

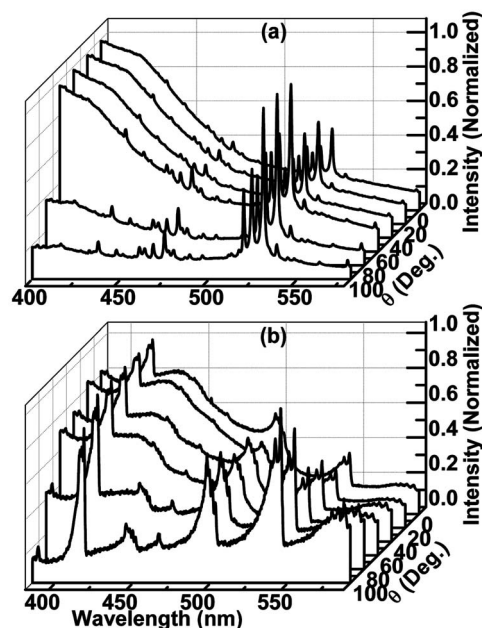


Fig. 3. Copper and carbon spectra measured with the polarizer at different angles. 0° corresponds to the polarization plane of the polarizer parallel to that of the incident laser.

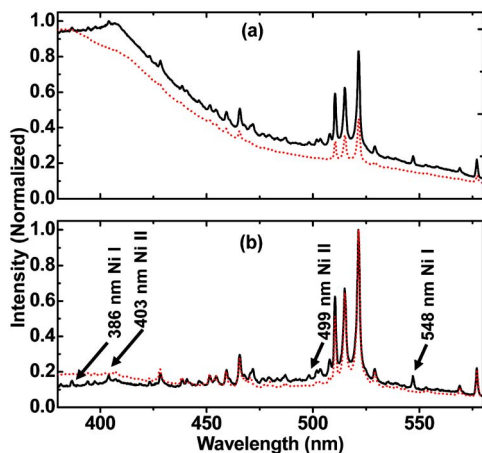


Fig. 4. (Color online) Comparison of (a) LIBS and (b) PRLIBS spectra for a copper sample (dotted curves) and a US dime coin (solid curves).

whereas the discrete lines stem from resonant (bound-bound) transitions [8]. Polarization of the continuum is a consequence of a highly anisotropic velocity distribution of the free electrons, whereas polarization of the discrete spectrum is caused by a nonstatistical population of the magnetic states of the emitting species. The origin of these distributions is under investigation.

In summary, we demonstrated the usefulness of PRLIBS as compared with conventional LIBS. The results demonstrate that the SBR is significantly enhanced by using a polarizer to suppress the the strong continuum background produced in femtosecond ablation of materials. Moreover, because temporally and spatially integrated spectra are employed by this technique, PRLIBS has good reproducibility, simplicity and stability and a high signal-to-noise ratio, as compared to time-gated or spatially resolved LIBS.

We wish to thank Tana Witt for her assistance with some of the experiments. Support by the National Science Foundation (NSF) under grant CHE-0640306 and by the U.S. Air Force Research Laboratory

Materials and Manufacturing Directorate is gratefully acknowledged.

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