The high dependence of polarization resolved laser-induced breakdown spectroscopy on experimental conditions*

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It is shown that the continuum emission produced by an Al alloy ablated by femtosecond laser pulses is much more polarized than the characteristic lines of elements. A Glan–Thomson polarizer is used in the laser-induced breakdown spectroscopy experiment to investigate the polarization effect. The use of the polarizer at its minimal transmission increases the signal-to-noise ratio. The effects of angle of detection, focal position, and pulse energy on the signal-to-noise ratio are also studied.

Keywords: laser-induced breakdown spectroscopy, femtosecond laser, plasma, polarization

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1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a powerful analytical technique, whcih can be used for the detection and characterization of materials. A high-power laser beam (commonly 10-ns pulsed infrared 1.06 mm radiation) is focused through a lens to produce plasma. The emitted light is collected by a second lens or often through a fiber, and directed into a spectrometer.[1,2] Each atom in the plasma emits a unique set of spectral lines. Therefore, this technique can be used to determine the chemical composition of a sample.[3−5] With LIBS, we can analyze gas, liquid, and solid samples. The major limitation to LIBS performance is the production of strong continuum radiation in the early stages of plasma formation. The main sources of the continuum emission are generally the inverse bremsstrahlung (free-free) and radiation recombination (bound-free) within the hot dense plasma.[6]

Different techniques have been developed in the LIBS method to increase the signal-to-background ratio (SBR) and the signal-to-noise ratio (SNR). The strong white light at the early time can be removed from the measurements by turning the detector on after this white light has significantly subsided in intensity, while the atomic emissions are still present. This technique is called time-resolved laser-induced breakdown spectroscopy (TRLIBS), which is the most well known technique to reduce the level of noise related to the background continuum emission.[7−9] But this technique is very sensitive to the choice of an appropriate time delay (the time between the plasma formation and the start of the observation of the plasma light) and the gate width (the time period over which the light is recorded) for each spectral line, and the intensity of laser as well as the physical and chemical proprieties of the sample.

Recently, the plasma continuum emission has been found to be strongly polarized, whereas the characteristic lines of elements are much less polarized.[10−12] It is possible to reduce the continuum emission by placing a polarizer in front of the detector. This technique is called polarization-resolved laser-induced breakdown spectroscopy (PRLIBS). Elsami *et al.*[13] used this technique to study the effect of laser beam polarization on the direction of polarization of the continuum emission. In the present paper, femtosecond laser pulses are used to study how the PRLIBS results depend on polarizer angle, detection angle, focal position, and laser pulse energy.

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2. Experimental set-up

A schematic diagram of our experimental set-up is shown in Fig. 1. The laser beam generated by a femtosecond Ti: sapphire amplifier (pulse duration 50 fs, repetition rate 1 kHz, wavelength 800 nm, and pulse energy around 4 mJ) is used to ablate the aluminum sample. Our sample is Al 2024(YL 12) consisting of Al ($\sim$ 91%), Si ($<$ 0.5%), Fe ($<$ 0.5%), Cu (3.8–4.9%), Mn (0.3%), Mg (1.2–1.8%), Cr (0.1%), Zn (0.25%), Ti (0.15%), and the others. To reduce the pulse energy, neutral density filters are used. The laser beam is focused through a lens L_1 (f = 200 mm) on the aluminum alloy in air. At the pulse energy of 400 μJ, the laser spot diameter is $\sim$ 100 μm at the focal point.

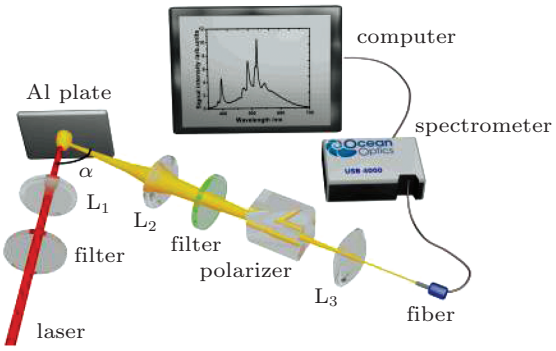


Fig. 1. (colour online) Schematic diagram of experimental set-up.

A two-dimensional translation stage is used to make each laser pulse fall on a fresh target surface. The radiation emitted by the plasma plume is collected and focused on the fiber by using a pair of lenses L_2 (f = 75 mm) and L_3 (f = 35 mm). To reject the fundamental laser light, four attenuators (GRB3) are placed behind lens L_2. In order to investigate the polarization effect, a Glan–Thompson polarizer is placed in front of the detector at the focal point of L_2. The emission from the plume is recorded by using a spectrometer (Ocean Optics USB 4000) in conjunction with an optical fiber placed at the right angle.

During our experiment, an integration time of 100 ms is used, and the dark current background of the detector is subtracted from the measured spectroscopic data for each measurement.

3. Results and discussion

During the whole experiment, the laser beam is normal to the sample surface, and the detection system is adjusted manually. To explore the polarization effect, in each measurement, the polarizer is rotated twenty times with increments of 20°, and we compare the results obtained without using a polarizer (time-integrated LIBS[3]) with those obtained using the polarizer at its minimal transmission (PRLIBS).

3.1. Polarization spectrum

Rotating the polarizer with increments of 20° changes the intensity transmitted by the polarizer. The minimal transmission is obtained when the angle of the polarizer is at 20°, and the maximum transmission occurs at 100° (Fig. 2).

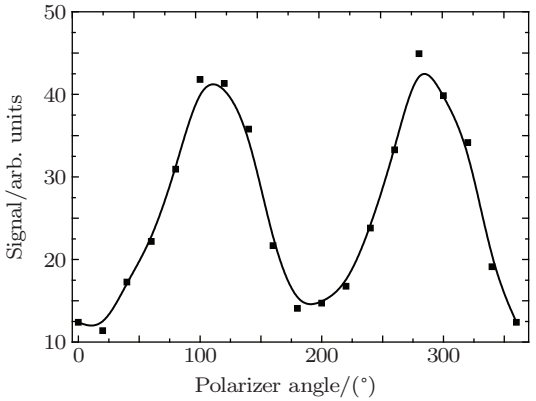


Fig. 2. Typical plot of emission intensity at a given wavelength recorded at 20° intervals. The data correspond to a wavelength of 650 nm. The curve is a sine type function fitted to the data.

In this study, we calculate the polarization degree of the spectrum obtained by the spectrometer. The polarization degree is calculated as

$$P = (I_{\max} - I_{\min}) / (I_{\max} + I_{\min}), \qquad (1)$$

where $I_{\max}$ and $I_{\min}$ are chosen among all the nineteen measurements at each wavelength. The polarization spectrum can be obtained by plotting P as a function of wavelength.

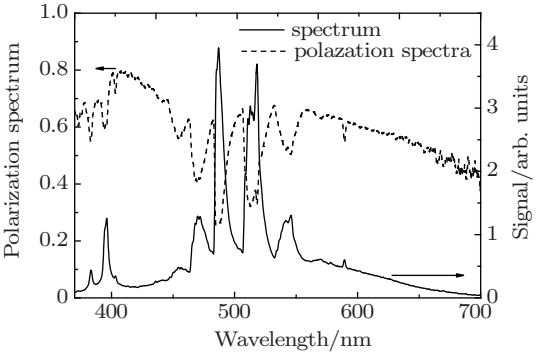


Fig. 3. Plasma emission and polarization spectra of Al.

A comparison between the LIBS emission spectrum and the polarization spectrum shows that the

continuum emission is much more polarized ($\geq 75\%$) than the discrete line emission ($\leq 30\%$) (Fig. 3). The emission and the polarization spectra are nearly mirror images of each other.

3.2. Time-integrated LIBS and PRLIBS comparison

The polarization degree of the spectrum shows that the polarizer placed in front of the spectrometer can reduce the continuum emission while the discrete lines are still present. In this experiment, the detector angle is fixed at 60°, and the pulse energy used is 600 μJ.

In Fig. 4(a), only three lines are well resolved. However in Fig. 4(b), the sensitivity and the resolution of LIBS are improved by placing a polarizer at minimal transmission in front of the detector. Some lines like Cu (I) at 470.45 nm, Mg (II) at 545.53 nm, and Fe (I) at 588.38 nm become well resolved. The line Fe (I) at 588.38 nm is used to calculate the SNR and the SBR for each signal, because it is isolated. The SNR obtained using the polarizer at the minimal transmission is about five times higher than that obtained without the polarizer. It is 59.75 at the minimal transmission of polarizer, and 14.61 without using the polarizer. There is also an improvement of the SBR by using the polarizer.

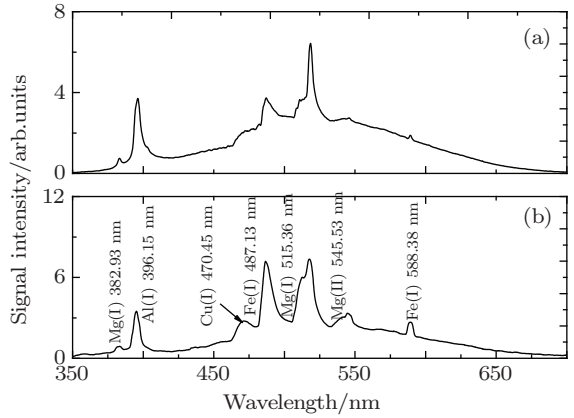


Fig. 4. Plasma emission spectra obtained with (a) time-integrated LIBS and (b) PRLIBS.

3.3. Effect of detection angle

When the plasma is formed, it diffracts in many directions. Thus, it is important to know which direction gives the best result or the effect of changing the detection angle on the LIBS result. In this experiment, the incidence angle is fixed to be 0° (the incident beam normal to the sample surface), and the pulse energy is 400 μJ. In order to explore the difference in the reduction of the continuum emission with the angle of detection, lens L_2 and the optical fiber are placed at angles of 30°, 45°, and 60°, respectively. As shown in Fig. 5, as the detection system moves away from the direction of the laser, the signal increases gradually. At 60° all the peaks are higher than those at 45° and 30°.

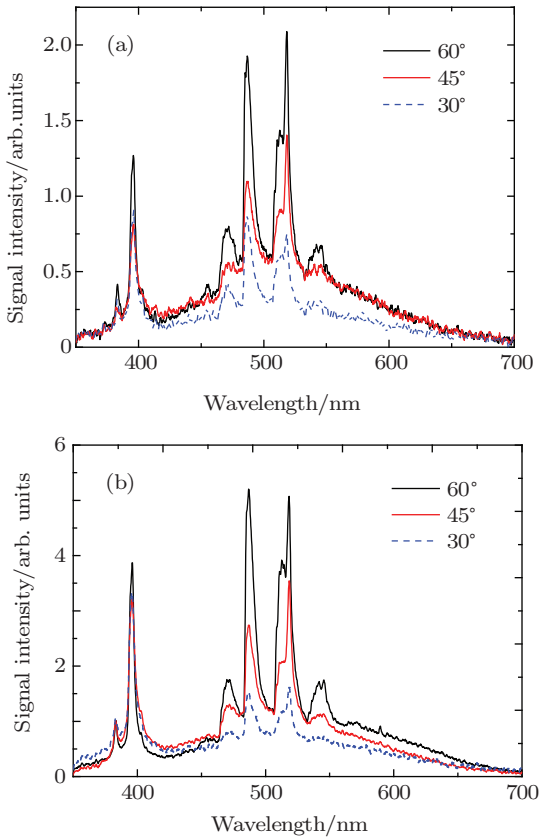


Fig. 5. (colour online) Effects of detection angle on signal in: (a) PRLIBS spectra (with minimal transmission of polarizer); and (b) time-integrated LIBS spectra (without polarizer). The angles are measured with respect to the direction of the laser.

To find the direction that gives the best result, we analyze the SNR, because the SNR refers to the ratio of the level of desired signal to the level of background noise, and the higher the ratio is, the less obtrusive the background noise is. In our study, the signal is measured at its maximal peak intensity $I_{\max}$ after the subtraction of the background $I_{\rm bg}$, while the noise is calculated by the standard deviation $\sigma_{\rm bg}$ of the background emission close to the considered line. The SNR is thus given by[14]

$$\mathrm{SNR} = \frac{I_{\max} - I_{\rm bg}}{\sigma_{\rm bg}}. \tag{2}$$

Using line Mg (II) at 545.53 nm, it is shown that when lens L_2 and the fiber optics are placed at 60°, the SNR is higher than that at the other positions (Table 1).

Table 1. Effects of detection angle on SNR at 545.53 nm.

Angle/(°)	60	45	30
Without polarizer	73.18	42.96	56.75
With polarizer	82.22	48.38	72.65

3.4. Effect of focal position

By conducting this experiment, we also aim to know the effect of the focal position on LIBS results. The sample and the detection system are fixed. We first check the position of lens L_1. When the position of lens L_1 gives the smallest spot on the surface of sample, it means that the surface of sample is on the focal position. Then, we move lens L_1 toward the sample (the focal position is behind the surface) and toward the laser (the focal position is in front of the sample surface) and make the respective measurements.

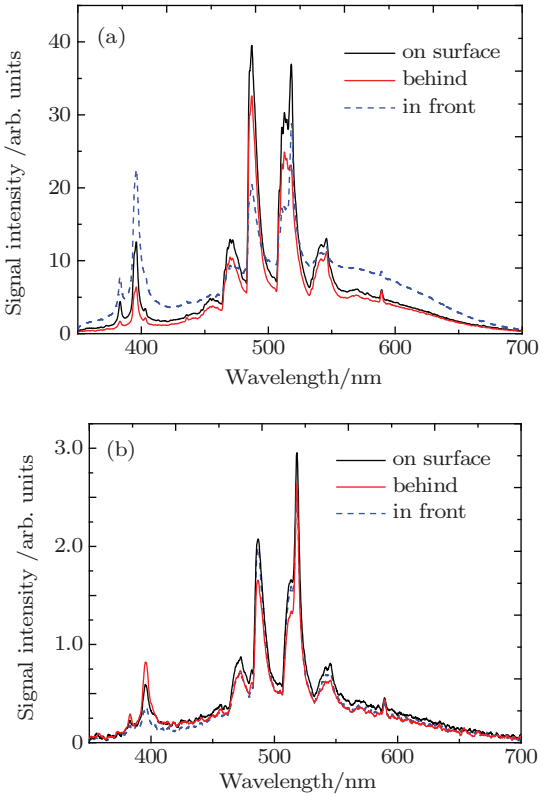


Fig. 6. (colour online) Effects of focal position on the signal taken: (a) without the polarizer; and (b) at the minimal transmission of the polarizer.

It is found that without the polarizer, the SNR is dependent on the position of L_1. As shown in Fig. 6(a), it is found that the maximal SNR (111.66 at 545.53 nm) is obtained when the focus is on the sample surface, and the minimal SNR (20.5 at the same line) is obtained when the focus position is in front of the sample surface. However, the difference in SNR is very small when the polarizer has the minimal transmission (at 20°) (Fig. 6(b)). The SNR is 151.23 when the focus is on the sample surface and 135.56 when the focal position is in front of the sample surface. Thus the polarizer reduces the sensitivity on the focal position. Our result accords with that found in the literature.[13]

3.5. Effect of laser pulse energy

In LIBS, a high-energy laser beam is used to excite the sample and to form the plasma. The LIBS signal is proportional to the laser energy when the laser plasma is in the optical thin region. If the pulse energy is modified, with the focusing distance maintained, the irradiance changes.[15] As a consequence,

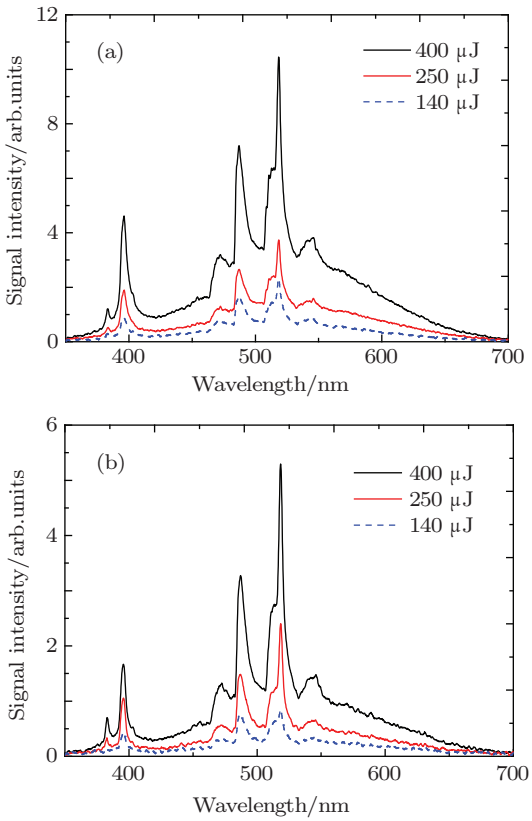


Fig. 7. (colour online) Effects of laser pulse energy on signal, spectra are taken under the same conditions but with the energies being 140 μJ, 250 μJ, and 400 μJ respectively (a) without polarizer and (b) at the minimal transmission of polarizer.

a higher LIBS signal and a larger ablated crater volume are produced with the high energy. Then, the signal and the continuum emission increase. As shown in Fig. 7(a), the signal and the background emission increase when the energy increases. However, using a polarizer at the minimal transmission, the discrete lines grow relatively to the background when the energy increases. In Fig. 7(b), line Mg (I) at 518.36 nm is about 5 times the background at 400 μJ, while it is about 2 times at 140 μJ.

The line Mg (I) at 545.53 nm is used to calculate the SNR. It is found that by increasing the pulse energy from 140 μJ to 400 μJ, the SNR increases (Table 2). Without using the polarizer, the improvement is 3 times when the energy is increased from 140 μJ to 400 μJ, while it is more than 7 times at the minimal transmission of polarizer. Furthermore, with the energy being less than 500 μJ, the line of Fe (I) at 588.38 nm is not well resolved (Fig. 7).

Table 2. Effects of pulse energy on SNR at 545.53 nm.

Energy/μJ	140	250	400
Without polarizer	6.95	14.09	18.88
With polarizer	9.04	14.35	66.10

4. Conclusion

In this paper, it is shown that LIBS results are dependent on experimental conditions. The characteristic line of the element is less polarized. The SNR increases when a polarizer at the minimal transmission is placed in front of the detector. It is also shown that when the incidence angle is 0° (normal to the sample surface), it is better to collect data at 60°. Without using the polarizer, the signal is also sensitive to the position of the focal point, but it is another story when using the polarizer at the minimum transmission.

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