The polarization characteristics of single shot nanosecond laser-induced breakdown spectroscopy of Al*

Liu Jia(刘 佳), Tao Hai-Yan(陶海岩), Gao Xun(高 勋), Hao Zuo-Qiang(郝作强), and Lin Jing-Quan(林景全)†

Changchun University of Science and Technology, Changchun 130022, *China*

(Received 5 July 2012; revised manuscript received 27 September 2012)

The polarization-resolved laser-induced breakdown spectroscopy (PRLIBS) technique, which can significantly reduce the polarized emission from laser plasma by placing a polarizer in front of the detector, is a powerful tool to improve the line-to-continuum ratio in LIBS applications. It is shown that the continuum emission from the plasma produced through ablating an Al sample by nanosecond laser pulses is much more polarized than the discrete line emission with the single-pulse PRLIBS technique. The effects of laser fluence and detection angle on the Al polarization spectrum are systematically explored experimentally. The calculated result of the polarization spectrum as a function of laser fluence shows that it is in agreement with the experimental observations.

Keywords: polarization-resolved laser-induced breakdown spectroscopy, laser plasma, S/N ratio

PACS: 42.62.Fi, 52.38.Mf **DOI:** 10.1088/1674-1056/22/4/044206

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is one of the most promising options for the rapid, quasi-nondestructive, and standoff determination of the elemental composition of materials in numerous applications such as environment monitoring,[1–4] explosive residue detection,[5,6] biomedicine,[7–9] and space exploration.[10,11] This technique is based on the observation of emission from excited atomic, ionic, and other particles produced in plasma formed by the focused laser irradiation on a sample. It is well known that a typical laser induced plasma spectrum consists of a series of discrete lines covered by a broadband continuum. Although LIBS has been applied to various fields, it is still lacking in sensitivity, reliability, precision, and accuracy compared with other analytical techniques. One of the major reasons for that is the presence of strong continuum background radiation at the early stage of plasma evolution.[12–16]

In order to improve the LIBS technique, different methods have been introduced to suppress the continuum emission or enhance the line intensity. Time-resolved laser-induced breakdown spectroscopy is the most well-known technique to reduce the effect of the continuum by using an expensive intensified charge-coupled device (ICCD) camera and a appropriate delay time before each measurement.[17,18] Another technique usually used is dual pulse LIBS which can enhance the intensities of discrete lines, but this technique is also highly dependent on experimental conditions.[19,20]

Recently, a new technique called polarization-resolved laser-induced breakdown spectroscopy (PRLIBS) has emerged, which can significantly filter out the continuous background and increase line-to-continuum ratio by placing a polarizer in front of the detector of a non-gated CCD camera. Liu *et al*.[21] and Penczak *et al*.[22] have systematically investigated the dependence of polarization of plasma emission of an Al sample on experimental parameters such as laser pulse energy, focal position, incident angle, detection angle, and laser polarization with a femtosecond laser, and found that continuum emission is much more polarized than discrete line emission from the plasma. In addition, they also studied the effects of laser pulse energy and laser focus position on polarization spectrum by using nanosecond laser pulses.[23] However, Asgill *et al*.[24] found that there is no significant polarization difference between the continuum and discrete emission from N_2, steel, and Cu samples. This apparent discrepancy could be reduced when laser fluence and polarization are taken into account.[22] The polarization of the plasma needs more detailed investigations, which is important for the optimal design of the detection system of a practical LIBS instrument based on the discrimination of the continuum obtained using the technique. In the present paper, we focus on the polarization characteristics of optical emission from the single nanosecond pulse ablation of Al samples at relatively low laser energy, and systematically investigate the influences of laser pulse energy and detection angle on the polarization characteristic. The experimental results are compared with the calculated results using an established theoretical model of continuum emission from plasma. The underlying mechanism of the polarization spectrum as a function of laser fluence

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60978014, 11074027, 61178022, 11274053, and 11211120156), the Funds from Science and Technology Department of Jilin Province, China (Grant Nos. 20090523, 20100521, 20100168, and 20111812), and Funds from Education Department of Jilin Province.

†Corresponding author. E-mail: linjingquan@cust.edu.cn

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which is in agreement with the experimental observations is analyzed.

2. Experimental setup

The experimental setup used in this work is sketched in Fig. 1. A single pulse of 8-ns duration at wavelength of 1064 nm from the YAG laser is focused on the sample surface by a convex lens (L1, $f = 25$ mm). A half-wave plate (HWP1) and a Glan–Taylor polarizer (P1) are employed to adjust the pulse energy. Another half-wave plate (HWP2) is used to change the polarization of the incident laser. Polished aluminum alloy samples are mounted on a computer-driven three-dimensional (3D) stage (Sigma, Inc.) which can supply a fresh surface for each laser shot. The incident laser beam is horizontally polarized and perpendicular to the sample surface. Our detection system is also in the horizontal plane (x–y plane in Fig. 1). Emission from the plasma is focused onto an optical fiber by a pair of lens (L2 and L3) with focal lengths of 75 mm and 35 mm respectively. A Glan–Thompson polarizer (P2) is installed between the two collecting lens to reduce polarized optical emission from the plasma. The intensity of transmitted spectrum after the polarizer depends on the angle of the polarizer. We continuously rotate the polarizer in steps of 20° and take 15 spectra at each polarizer angle. We use a filter bank to eliminate the possible influence from fundamental laser light. The optical emission from the laser induced plasma passes through a spectrograph (SpectraPro 2500i, Princeton Instruments, Inc.) with a 150-groove grating blazed at 550 nm and a non-gated CCD camera (Princeton Instruments Inc.) is used to record the spectra. The exposure time of 200 ms is used in our experiment.

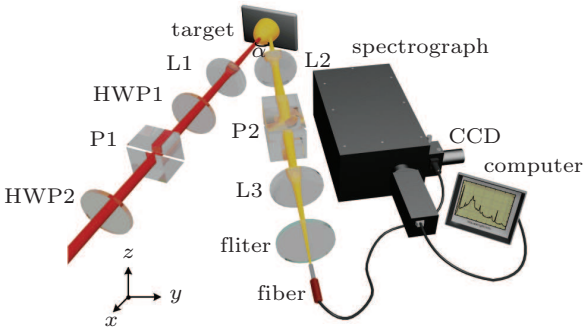


Fig. 1. (color online) Schematic plot of the experimental setup.

The intensity of spectrum depends on the angle of the polarizer. The magnitude of the polarization P at each wavelength is determined by $P = (I_{MAX} - I_{MIN})/(I_{MAX} + I_{MIN})$. The P is calculated by choosing the minimal spectral intensity denoted as I_{MIN} and maximal represented as I_{MAX} from among 18 polarizer angle settings. Each spectrum is an average of 15 spectra.

3. Experimental results

3.1. Comparision of emission intensities with LIBS and PRLIBS

Figure 2 shows LIBS and PRLIBS spectra taking with Al target for horizontally polarized single laser shot at 45° of detection angle with laser fluence of 10 J/cm^2. Figure 2(a) shows conventional LIBS spectrum obtained without the polarizer. The spectrum contains a strong and broad continuum, especially in a wavelength range of 400 nm–580 nm. Figure 2(b) shows a typical PRLIBS spectrum at minimum transmission angle of the polarizer. In this case, most of the continuum is suppressed by the polarizer and it is interesting to note that some weak peaks which are submerged in the continuum like Al II at 443.28 nm and Cu II at 455.59 nm become distinguishable. From Fig. 2 we can see a comparison made in terms of the improvement of the signal-to-noise ratio (S/N) and the signal-to-background ratio (S/B). This enhancement is particularly evident from the Al II peak at 422.80 nm. In the case of conventional LIBS, the S/N and S/B are 52.5 and 1.08 whereas in the case of PRLIBS, they are 112.5 and 3.13, respectively. The S/N and S/B of PRLIBS spectrum are nearly 2 and 3 times higher than those of LIBS spectrum, respectively. The polarization spectrum which is used to determine P in 0.25-nm interval is shown in Fig. 2(c). It clearly shows

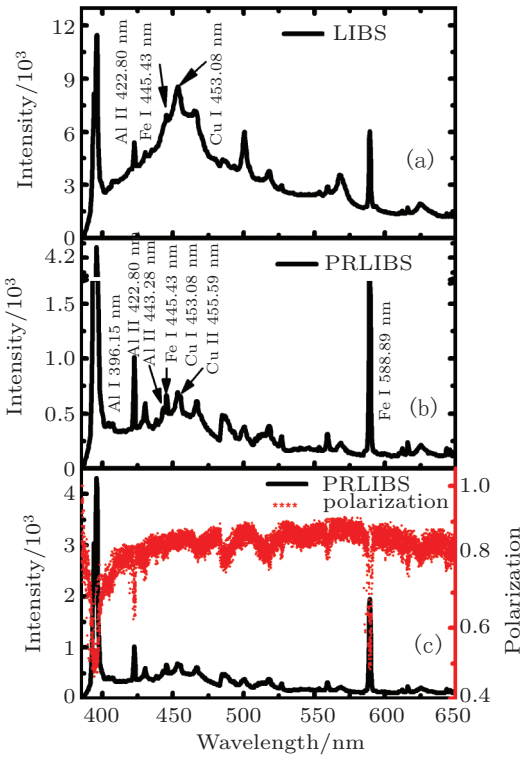


Fig. 2. (color online) Typical spectra of PRLIBS and polarization spectra, the spectra of Al plasma are taken at 45° of detection angle with laser fluence of 10 J/cm^2. The spectra are taken without the polarizer (a), and with polarizer (b). The polarization spectra are calculated by 15 spectra for each wavelength. A PRLIBS spectrum is plotted in panel (c) for comparison.

that the continuum emission is strongly polarized with the polarization almost exceeding 80% in the detection region but the discrete lines are much less polarized. All the peaks in the PRLIBS spectra correspond to dips in the polarization spectrum as shown in Fig. 2(c).

3.2. Dependence of the emission intensity in PRLIBS on laser parameters

Figure 3 shows the dependences of the emission intensities for LIBS (Fig. 3(a)) and PRLIBS (Fig. 3(b)) on laser fluence at detection angle of $\alpha = 45^\circ$ with horizontally polarized single laser shot, and polarization spectra (Fig. 3(c)) calculated based on Fig. 3(b). We can see clearly that the LIBS spectra are dominated by the strong and broadband continuum with laser fluences of 10 J/cm^2, 20 J/cm^2, and 40 J/cm^2 respectively, and the intensities of continuum and discrete lines both increase with laser fluence increasing. After the polarizer is used, the continuous emission is effectively suppressed as shown in the PRLIBS spectra, which has also been demonstrated by other groups.[21] In both cases, the intensity variations of continuum and discrete lines have the same trend with the increase of laser fluence. This behavior may be explained by the fact that an increase in laser fluence produces a larger ablation rate[23–25] and larger number density of excited species. However, there are noticeable differences between the two cases. For example, some line emission in a wavelength range of 400 nm–470 nm cannot be well distinguished in the LIBS spectra, while they become prominent in the PRLIBS spectra. The calculated polarizations of PRLIBS spectra at different laser fluences are plotted in Fig. 3(c). We can clearly see that the value of polarization decreases with laser fluence increasing. At the lowest laser fluence, the polarization of the continuum is above 0.8 nearly in the whole detection range, while the polarizations of discrete lines are much lower than the polarizations of adjacent continuum emission. Therefore we observe the discrete lines as dips in the polarization spectrum. With the increase of laser fluence, the polarizations of continuum and discrete lines decrease and the difference of the polarizations between continuum and discrete lines becomes smaller. It indicates that an increasing temperature of electron, owing to the enhancement of laser fluence, affects the polarization.

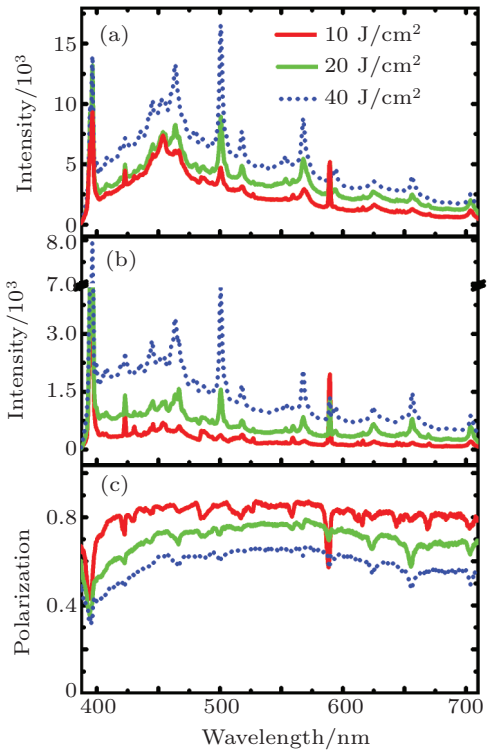


Fig. 3. (color online) Effect of laser fluence: LIBS spectra (a) and PRLIBS spectra (b) taken at 45° detection angle with laser fluences of 10 J/cm^2, 20 J/cm^2, and 40 J/cm^2; (c) polarization spectra.

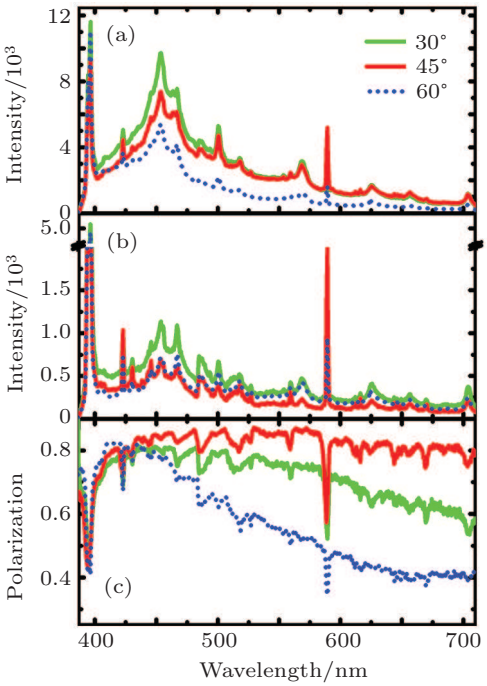


Fig. 4. (color online) Effects of detection angles; (a) PRLIBS spectra taken with laser fluence of 10 J/cm^2 at 30°, 45°, and 60° detection angles; (b) polarization spectra.

The effects of detection angle on the emission intensities in PRLIBS and polarization spectra are also investigated. Figure 4 shows the dependences of PRLIBS and polarization spectra at laser fluence of 10 J/cm^2 on detection angles of $\alpha = 30^\circ$, 45°, and 60° with horizontally polarized single laser shot respectively. In Fig. 4(a), PRLIBS spectra at minimum transmission of the polarizer are shown. It is found that, at 45° detection angle, the peaks are more noticeable than those at the other two angles. Figure 4(b) shows the polarization spectra at different detection angles. We can see that the polarization spectra are strongly influenced by the detection angle, moreover, the effect of detection angle on polarization is more significant at longer wavelengths than at shorter wavelengths. As

shown in Fig. 4(b), at $\alpha = 45^\circ$ detection angle, the polarizations of continuum are above 0.85 in the whole detection range and the polarizations of discrete lines are quite low. There are slight differences in polarization at shorter wavelength among the three detection angles, whereas at longer wavelengths the differences are much more obvious. At 45°, the polarization is relatively stable, and at 30° detection angle, the polarization declines slightly with wavelength increasing, whereas under the condition of 60° detection angle, the polarizations fall down dramatically, particularly at longer wavelengths.

4. Discussion

The underlying physics responsible for the effect of laser polarization has been discussed in previous studies,[22,26] while the effect of laser fluence has not been discussed theoretically yet. Some theoretical and experimental studies demonstrated that the bremsstrahlung[22,27–30] and recombination radiation[31,32] are linearly polarized. Milchberg and Weisheit[33] investigated the polarization of recombination radiation by using the differential cross section for recombination and the anisotropy of the electron velocity distribution with a net drift $u_{\rm D}$

$$P(\omega) = \frac{3\beta_\Gamma \cos 2\rho \sin^2\alpha f_2}{20 f_0 + \beta_\Gamma f_2 (3\sin^2\alpha - 2)} \tag{1}$$

where ω is the frequency of a photon from recombination radiation, β_Γ is the anisotropy parameter in excited state Γ, ρ is the angle between the coordinate system of measurement and the coordinate system of the line of sight, and the angle is 0 here, α is the angle between symmetry axis of the plasma and the direction of detection, f_0 and f_2 are the monopole and quadrupole moments of the distribution, respectively, which can be expressed with the same proportionality constant according to the result of Milchberg and Weisheit[33]

$$\begin{aligned} f_0 &\propto S(\eta,\xi), \\ f_2 &\propto -\frac{5}{2}S(\eta,\xi) + \frac{15}{2}\frac{\partial^2 S(\eta,\xi)}{\partial\eta^2}. \end{aligned} \tag{2}$$

The expression of $S(\eta,\xi)$ can be given as

$$S(\eta,\xi) = 2\sum_{n=0}^{\infty}\frac{(-\xi)^n}{n!}\frac{{\rm d}^{2n}}{{\rm d}\eta^{2n}}\left[\frac{\sinh\eta}{\eta}\right], \tag{3}$$

which is characterized by two dimensionless quantities

$$\eta = [2m_{\rm e}(\hbar\omega - \chi_\Gamma)]^{1/2}\frac{u_D}{k_{\rm B}T_\parallel} \tag{4}$$

and

$$\xi = \left(\frac{\hbar\omega - \chi_\Gamma}{k_{\rm B}T_\parallel}\right)(1 - T_\parallel/T_\perp), \tag{5}$$

where $T_\parallel$ and $T_\perp$ are the electron thermal motions parallel and perpendicular to a symmetry axis, respectively; $m_{\rm e}$ is the electron mass, χ_Γ is the binding energy of state Γ, and $k_{\rm B}$ is the Boltzmann constant.

In the limit $\xi \to 0$, the degree of polarization at $\alpha = \pi/4$ detection angle is

$$P(\eta) = \frac{3\beta_\Gamma\left[3\eta\cosh\eta - (3+\eta^2)\sinh\eta\right]}{4(\beta_\Gamma - 2)\eta^2\sinh\eta + 3\beta_\Gamma\left[(1-\eta^2)\sinh\eta - \eta\cosh\eta\right]}. \tag{6}$$

In the case of limit $\eta \to 0$, the polarization P of recombination radiation at $\alpha = \pi/4$ can be expressed as

$$P(\xi) = \frac{3\beta_\Gamma\sum\limits_{n=0}^{\infty}(-\xi)^n n/(2n+1)(2n+3)n!}{\sum\limits_{n=0}^{\infty}\left(4 - \beta_\Gamma\dfrac{n}{2n+3}\right)\dfrac{(-\xi)^n}{(2n+1)n!}}. \tag{7}$$

The expressions of P as functions of η and ξ for the special case $\beta_\Gamma = 2$ (K-shell capture) are plotted in Figs. 5 and 6, respectively. For simplicity $\beta_\Gamma = 2$ is chosen, which does not affect the calculation results. One of reasons responsible for the polarization of line emission is anisotropic velocity distribution, which arises from Maxwellian distributions with different temperatures in different directions in a nanosecond plasma.[34] Other possible mechanisms leading to polarization have been proposed, such as heavy particle collision, recombination mechanism, forbidden line emission due to electric field, self-alignment due to radiation trapping, etc.[35]

For the first case as shown in Fig. 5, only the electron temperature is considered, which rises in a certain range with the increase of laser fluence because the effect of laser field variation on net drift $u_{\rm D}$ can be neglected. According to Eq. (4), η decreases with temperature increasing. As shown in Fig. 5, the decreasing of η leads to a lower value of P. Therefore, $P(\eta)$ decreases with laser frequency increasing in this case.

In the second case as shown in Fig. 6, the value of $T_\parallel/T_\perp$ keeps constant with the increase of temperature for a given velocity direction.[36] According to Eq. (5), if $T_\parallel/T_\perp \geq 1$, then $\xi \leq 0$ and ξ approaches to zero with the increase of temperature; If $T_\parallel/T_\perp < 1$, then $\xi > 0$ and ξ also approaches to zero with the increase of temperature. Furthermore, the $P(\xi)$ also approaches to zero when ξ approaches to zero as shown in Fig. 6. Therefore, polarization decreases with laser fluence increasing.

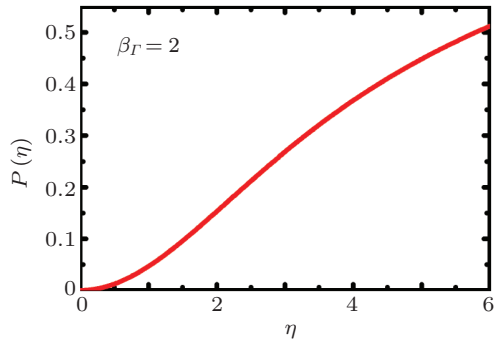


Fig. 5. (color online) Degree of polarization as a function of η.

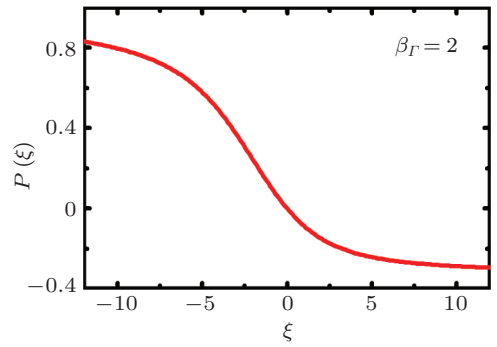


Fig. 6. (color online) Degree of polarization as a function of ξ.

Based on the above analysis, the value of P always decreases with laser fluences increasing for both cases. This simulation results are in qualitative agreement with the experimental observations as shown in Fig. 3(c).

5. Conclusion

A nanosecond single-pulse PRLIBS technique is systematically studied in this paper. We observed that the continuum emission of laser induced plasma is strongly polarized but the discrete line emission is weakly polarized. The experimental results demonstrate that the polarization is very sensitive to the laser fluence and detection angle. The experimental results clearly show a considerable difference in polarization characteristic between the continuum emission and discrete line emission, which should be related to the different generation mechanisms of the continuum and discrete line emissions. Our experimental results suggest that the use of a polarizer is an effective way to filter out the background, thereby improving the S/N and S/B ratios of the discrete line spectrum. Our calculated results could be used to explain the polarization characteristics of the emission from a laser induced plasma to a certain extent. However, further investigations are needed to explore the underlying mechanism.

References

[1] Ferreira E C, Anzano J M, Milori D M B P, Ferreira E J, Lasheras R J, Bonilla B, Montull-Ibor B, Casas J and Neto L M 2009 *Appl. Spectrosc.* **63** 1081

[2] Essington M E, Melnichenko G V, Stewart M A and Hull R A 2009 *Soil. Sci. Soc. Am. J.* **73** 1469

[3] Myriam B, Hao Z Q, Matthieu B, Yu J, Zhang Z and Zhang J 2007 *Chin. Phys. Lett.* **24** 3466

[4] Koch S, Garen W, Müller M and Neu W 2004 *Appl. Phys. A* **79** 1071

[5] Lucia F C D, Gottfried J L and Miziolek A W 2009 *Opt. Express* **17** 419

[6] Stearns J A, McElman S E and Dodd J A 2010 *Appl. Opt.* **49** C8

[7] Baudelet M, Guyon L, Yu J, Wolf J P, Amodeo T, Fréjafon E and Laloi P 2006 *Appl. Phys. Lett.* **88** 063901

[8] Baudelet M, Yu J, Bossu M, Jovelet J, Wolf J P, Amodeo T, Fréjafon E and Laloi P 2006 *Appl. Phys. Lett.* **89** 163903

[9] Hrdlička A, Prokeš L, Staňková A, Novotný K, Vitešníková A, Kanický V, Otruba V, Kaiser J, Novotný J, Malina R and Páleníková K 2010 *Appl. Opt.* **49** C16

[10] Lanza N L, Wiens R C, Clegg S M, Ollila A M, Humphries S D, Newsom H E and Barefield J E 2010 *Appl. Opt.* **49** C211

[11] Knight A K, Scherbarth N L, Cremers D A and Ferris M J 2000 *Appl. Spectrosc.* **54** 331

[12] Feng Y, Yang J J, Fan J X, Yao G X, Ji X H, Zhang X Y, Zheng X F and Cui Z F 2010 *Appl. Opt.* **49** C70

[13] Liu Q J, Fong S K, Cheng Andrew Y S, Luo S R, Tam K S, Zhu J H and Viseu A 2012 *Chin. Phys. B* **21** 087402

[14] Yan L X, Zhang Y S, Zheng G X, Liu J R, Cheng J P and Lu M 2006 *Chin. Phys.* **15** 2271

[15] Park H S, Nam S H and Park S M J 2005 *Appl. Phys.* **97** 113103

[16] Corsi M, Cristoforetti G, Hidalgo M, Iriarte D, Legnaioli S, Palleschi V, Salvetti A and Tognoni E 2003 *Appl. Spectrosc.* **57** 715

[17] Ursu C, Gurlui S, Focsa C and Popa G 2009 *Nucl. Instrum. Method B* **267** 446

[18] Santagata A, Marotta V, Orlando S, Teghil R, Zaccagnino M and Giardini A 2003 *Appl. Surf. Sci.* **208–209** 101

[19] Asgill M E, Brown M S, Frische K, Roquemore W M and Hahn D W 2010 *Appl. Opt.* **49** C110

[20] Vidal F, Chaker M, Goueguel C, Laville S, Loudyi H, Rifai K and Sabsabi M 2008 "Laser and Plasma Applications in Material Science", *First International Conference on Laser Plasma Applications in Materials Science-LAPAMS'*08. *AIP Conference Proceedings*, USA **1047** 25

[21] Liu Y, Penczak J S and Gordon R J 2010 *Opt. Lett.* **35** 112

[22] Penczak J S, Liu Y M and Gordon R J 2011 *Spectrochim. Acta Part B* **66** 186

[23] Borrielli A, Torrisi L, Margarone D, Caridi F and Mezzasalma A M 2008 *Nucl. Instrum. Method B* **266** 3968

[24] Barcikowski S, Hahn A, Kabashin A V and Chichkov B N 2007 *Appl. Phys. A* **87** 47

[25] Scaffidi J, Pearman W, Carter J C, Colston B W and Angel S M 2004 *Appl. Opt.* **43** 2786

[26] Gluckstern R L and Hull M H 1953 *Phys. Rev.* **90** 1030

[27] Eslami Majd A, Arabanian A S and Massudi R 2010 *Opt. Laser Eng.* **48** 750

[28] Gluckstern R L, Hull M H and Breit G 1953 *Phys. Rev.* **90** 1026

[29] Raimbault P A and Shohet J L 1972 *Phys. Fluids* **15** 1477

[30] Motz J W and Placious R C 1960 *Il Nuovo Cimento* **15** 571

[31] Mohamed T, Andler G, Fogle M, Justiniano E, Madzunkov S and Schuch R 2011 *Phys. Rev. A* **83** 032702

[32] Yoneda H, Hasegawa N, Kawana S, Asai H and Ueda K 1998 *Workshop on Plasma Polarization Spectroscopy and the International Seminar on Plasma Polarization Spectroscopy*, 26–28 January, Kyoto, Japan, pp. 247–254

[33] Milchberg H M and Weisheit J C 1982 *Phys. Rev. A* **26** 1023

[34] Sharma A K and Thareja R K 2007 *Appl. Surf. Sci.* **253** 3113

[35] Sharma A K and Thareja R K 2005 *J. Appl. Phys.* **98** 033304

[36] Chen F F 1974 *Introduction to Plasma Physics and Controlled Fusion* (New York: Plenum Press)