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Emission enhancement of femtosecond laser-induced breakdown spectroscopy by combining nanoparticle and dual-pulse on crystal SiO_2

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ABSTRACT

Metal nanoparticle deposition on sample surface is a promising approach to enhance the emission signal during laser-induced breakdown spectroscopy (LIBS). In this article, strong optical emission enhancement was achieved by combining nanoparticle enhanced LIBS (NELIBS) and double pulse LIBS (DP-LIBS) on a crystal SiO_2 sample by using femtosecond laser. Thermal dewetting was used to deposit gold (Au) nanoparticles (NPs) on sample surface and NPs with different size were obtained by altering the thickness of the Au film. It was found that both the size and distribution of Au NPs significantly affected the enhancement effect of NELIBS and the Au NPs made from 7.5 nm gold film had the best enhancement effect. The fundamental features of NELIBS enhancement for dielectric target were investigated by studying the photon absorption process. At a low laser fluence of 4.4 J/cm^2, an enhancement factor of about 13 for spectrum intensity was obtained in NELIBS and reached to 30 after being combined with DP-LIBS.

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) is a popular chemical analysis technique. This technique is carried out by analysis of optical emission from laser-induced plasma on target surface to identify elements and organic compounds in the ablated area. LIBS allows for a rapid, almost nondestructive, remote and multi-element analysis, which makes it applied in many fields, such as archeological research [1,2], explosives [3], environmental science [4,5], space exploration [6], and medical science [7,8]. However, compared with other atomic spectral analysis techniques, the standard LIBS has the disadvantages of low precision and poor repeatability. In order to improve the sensitivity and accuracy of LIBS, a large number of studies have been devoted to obtain enhanced signal intensity of LIBS.

To date, many methods have been used to improve the sensitivity of LIBS, such as double-pulse [9], plasma confinement [10], microwave [11], spark discharge [12,13], magnetic field [14], and flame [15]. Among methods mentioned above, double-pulse has been proved a very effective way to improve analytical performance of LIBS. Detailed enhancement mechanism of double pulse LIBS (DP-LIBS) was studied in recent decades [16,17]. Recently, nano-structure has been studied to obtain enhanced LIBS signal, which provides a new direction for the improvement of the sensitivity of LIBS technique. The enhanced LIBS emission from nano-based target instead of bulk-based ZnO was reported with the average enhancement of 8-fold. Besides, compared with the bulk-based samples, strong enhanced emission was observed for plasma from iron oxide nanomaterial [18,19]. In particular, De Giacomo et al. reported nanoparticle-enhanced LIBS (NELIBS) of metallic samples with an increase of 1–2 orders of magnitude in LIBS signals by depositing silver nanoparticles (NPs) on metal samples [20]. In another article, they discussed the basic mechanisms of NELIBS in detail [21]. They pointed out that a faster and more efficient production of seed electrons was produced with NPs during the laser ablation process.

In this article, combination of NELIBS and collinear DP LIBS on dielectric was firstly studied. Different from experiment method reported above [20,21], a new method of depositing nanoparticles was used and femtosecond laser (fs) was applied instead of nanosecond laser because ultrashort pulse duration has unique advantages, such as little sample damage, low ablation threshold, and periodic microstructure fabrication [22,23]. In this study, an enhancement factor of about 30 for spectrum intensity was obtained in combination of NELIBS and DP-LIBS on crystal SiO_2 sample, compared to conventional single pulse (SP)LIBS. Detailed study of effect of size and distribution of Au NPs on NELIBS was carried out.

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2. Experiment methods

2.1. Sample preparation

In this study, Au NPs were deposited on crystal SiO_2 ($10 \times 10 \times 0.5\ mm^3$, 001, twin polishing) surface by thermal dewetting [24]. The first step was to cover gold nano-film (2–30 nm) on the target surface by an ion beam sputtering (Gatan 682 PECS), where the film thickness was controlled by the sputtering time. Then a muffle furnace (GHA12/300, Carbolite) was used to heat the Au-coated sample for thermal dewetting. The temperature rise rate of muffle furnace was set to 30 °C per minute and the maximum temperature was kept at 950 °C for an hour. It's easy to get Au NPs attached on SiO_2 surface with good dimensional stability in a large area in this way. Scanning electron microscope (SEM) (FEI, XL30 S−FEG) was used for characterization of the Au NPs. The voltage of SEM was set to 10 kV and the working distance was 20 mm.

2.2. Experiment setup

Fig. 1 shows the schematic diagram of the LIBS system used in this study. A Ti: sapphire laser with wavelength of 800 nm and pulse duration of 75 fs was used for plasma generation. The maximum repetition frequency of the fs laser was1 kHz and the maximum energy of single pulse was 4 mJ. The double pulses were created through a Mach-Zehnder interferometer consisting of two beam splitters (50:50) with a maximum delay of 120 ps and then passed through a half wave plate and a polarizer, where the transmitted laser beam was p-polarized and the pulse energy could be changed from 20 to 150 μJ. After passing through a plano-convex lens (focal length, 100 mm), the laser beam was focused onto the sample surface and the spot diameter was about 34 μm. The sample was fixed on a computer-controlled three-dimensional platform. The emission from the laser-induced plasma was coupled into an optical fiber by two quartz plano-convex lenses (focal length, 50 and 100 mm) and then transmitted into a spectrometer (Shamrock 750, Andor). The spectral lines were detected by an intensified charge-coupled device (ICCD) (DH334T-18U-03, Andor, pixel: 1024 × 1024), which was attached to the exit focal plane of the spectrometer. To guarantee that the sample ablated location was new before each laser shot, laser fre-

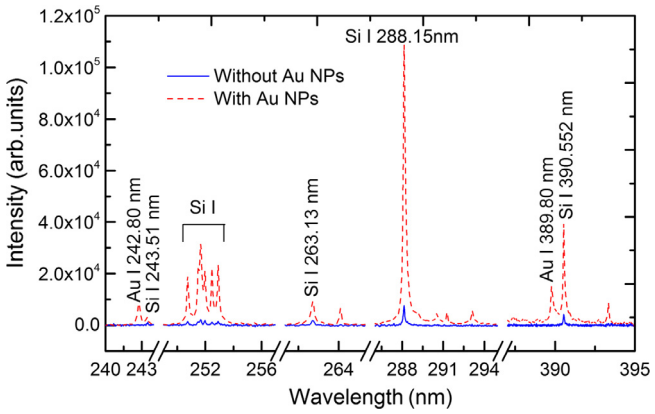

Fig. 2. Typical spectra of crystal SiO_2 irradiated by fs laser with (red and dotted line) and without (blue and solid line) Au NPs at the fluence of 6.6 J/cm^2. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Summary of spectral lines from Fig. 2.

λ/nm	Lower level configuration	Upper level configuration
Si I		
243.515	$3s^23p^2$ (^{1}D 2)	$3s^23p3d$ (^{1}D 2)
250.690	$3s^23p^2$ (^{3}P 1)	$3s^23p4s$ (^{3}P° 2)
251.432	$3s^23p^2$ (^{3}P 0)	$3s^23p4s$ (^{3}P° 1)
251.611	$3s^23p^2$ (^{3}P 2)	$3s^23p4s$ (^{3}P° 2)
251.920	$3s^23p^2$ (^{3}P 1)	$3s^23p4s$ (^{3}P° 1)
252.411	$3s^23p^2$ (^{3}P 1)	$3s^23p4s$ (^{3}P° 0)
252.851	$3s^23p^2$ (^{3}P 2)	$3s^23p4s$ (^{3}P° 1)
263.128	$3s^23p^2$ (^{1}S 0)	$3s^23p3d$ (^{1}P° 1)
288.158	$3s^23p^2$ (^{1}D 2)	$3s^23p4s$ (^{1}P° 1)
390.552	$3s^23p^2$ (^{1}S 0)	$3s^23p4s$ (^{1}P° 1)
Au I		
242.795	$5d^{10}6s$ (^{2}S 1/2)	$5d^{10}6p$ (^{2}P° 3/2)

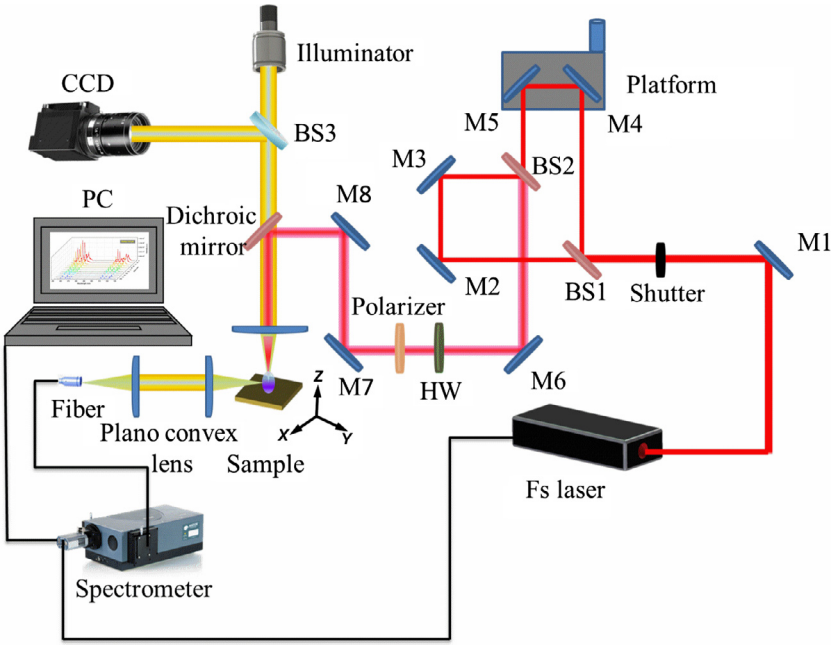

Fig. 1. Schematic diagram of the experiment setup (M: mirror, HW: half-wave plate, BS: beam splitter).