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Influence of electron dynamics on the enhancement of double-pulse femtosecond laser-induced breakdown spectroscopy of fused silica

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ABSTRACT

Femtosecond laser pulse train induced breakdown of fused silica was studied by investigating its plasma emission and the ablated crater morphology. It was demonstrated that the electron dynamics in the ablated fused silica play a dominant role in the emission intensity of induced plasma and the volume of material removal, corresponding to the evolution of free-electron, self-trapped excitons, and the phase change of the fused silica left over by the first pulse. For a fluence of 11 J/cm^2, the maximum plasma intensity of double-pulse irradiation at an interpulse delay of 120 ps was about 35 times stronger than that of a single-pulse, while the ablated crater was reduced by 27% in volume. The ionization of slow plume component generated by the first pulse was found to be the main reason for the extremely high intensity enhancement for an interpulse delay of over 10 ps. The results serve as a route to simultaneously increase the spatial resolution and plasma intensity in laser-induced breakdown spectroscopy of dielectrics.

1. Introduction

Femtosecond (fs) laser machining of dielectrics has attracted much research interest due to the high peak intensity caused nonlinear absorption of the photons over a wide band-gap [1]. Although a single-pulse (SP) fs laser is powerful enough for the precision ablation of dielectric as fused silica, the machining precision can be improved by shaping the fs pulses temporally. Extensive studies about ultrafast laser interaction with fused silica have been carried out over the past few decades to understand its mechanism. These studies have demonstrated the apparent advantages of fs laser pulse trains in controllable micro-/nanofabrication.

Li et al. measured the optical breakdown threshold of fused silica and found an ultrafast decay of plasma energy lasting for only 100 fs, which was coupled with multiphoton and avalanche ionizations. In consequence, a decay term was added in the electron density rate equation to describe the electron decay [2]. Stoian et al. reported a significant improvement in the microstructure quality of dielectrics using temporally shaped ultrafast laser pulse trains with subpicosecond separation. They believed that the material softening by the initial excitation of the first pulse changed the energy coupling of the subsequent pulses, which could be used for machining optimization [3]. Ihtesham et al. used pump-probe experiments to study the high-intensity, ultrafast-pulse ablation dynamics of fused silica [4]. Rapid change in reflectivity and transmissivity after the pump pulse interaction with the material and the apparent influence on the ablated morphology in double-pulse fs laser ablation were reported. The creation of the free-electrons by the first pulse was responsible for the reflectivity increase within the interpulse delay time range of 2 ps. The rapid reflectivity decline from 2 to 10 ps contributed to rapid structural damage at the surface. In addition, the reflectivity experienced a slow decrease for interpulse delays of 10–100 ps, which indicated plasma plume expansion. In this stage, both the reflectivity and the transmissivity were very low, implying a high absorption by the materials. To date, most researches only explored the ablation morphology rather than the plasma properties, resulting in a lack of information on the electron dynamics of the fs interaction with the fused silica. Further theoretical explanation was clarified at the electronic level by Jiang et al. with the plasma model [5,6]. And the effectiveness of the electron dynamics was further verified by serials of experiments on fused silica [7,8]. Still, most explorations focused only the ablation morphology, while the ejected plume shared part of the laser energy and seriously influenced the ultrafast laser processing of fused silica. Therefore, the plasma emission research could provide a deeper understand for the ablation process through the Laser-induced Breakdown Spectroscopy (LIBS) technique.

Lately, Labutin et al. presented a review on the advantages and applications of femtosecond laser-induced breakdown spectroscopy (fs-

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LIBS) [9]. The limitations of this technique and different approaches to overcome its constrains were discussed, including depth profiling, lateral resolution, signal enhancement, and self-absorption. It is hard to improve the lateral resolution of fs-LIBS because of the diffraction limit. Zorba et al. achieved a resolution of 450 nm in fs-LIBS research on mica using a 50× objective lens, which was the smallest ever reported [10]. The signal enhancement in the low fluence can help to improve the lateral resolution further.

The most common and efficient technique for achieving signal enhancement in fs-LIBS is the use of a double-pulse (DP) regime consisting of two fs laser pulses or one fs laser combined with a nanosecond laser in the collinear or orthogonal configuration. The enhancement effect of the DP regime has already been demonstrated on metals [11–18], semiconductors [19], organic material [20], and gases [21]. The leading mechanism of signal enhancement can be related to plasma reheating [16–18,20,21] and atomization of nanoparticles [15,19]. Most enhancement factors in the DP fs-fs collinear scheme LIBS were below 10 benefited from the plasma reheating. But for the orthogonal scheme, the enhancement factors over 10 were achieved with the help of high-power nanosecond pulse as additional excitation of nanoparticles [9].

Due to the wide bandgap of fused silica, the DP fs-LIBS of fused silica has its own features. This paper confirmed the enormous distinction between SP and DP ablation not only in ablated crater morphology but also in plasma emitting intensity. In DP irradiation, the plasma intensity also differs from case to case in terms of interpulse delays because of different electron dynamics left by the first pulse. Component distribution of SP and DP laser-induced plasma plume was researched to verify the enhancement mechanism at different interpulse delays. Finally, the plasma temperature and the electron density were calculated through Boltzmann plot and Stark broadening, respectively. Apparently, the transient electron dynamics induced by the first pulse influence the energy deposition process of the second pulse, which explains the plasma and morphology change with respect to the interpulse delay.

2. Material and methods

The experimental setup of the DP fs-LIBS is shown in Fig. 1. The Ti: sapphire fs laser system produced fs laser pulses with center wavelength of 800 nm and pulse duration of 45 fs. The pulse energy was adjusted by using a half-wavelength plate and a polarizer. The individual pulse was split into two pulses (reflected and transmitted arms) and recombined using a pair of 50/50 beam splitters in a Mach-Zehnder interferometer. For all the comparisons, the total energy input was kept equal for both SP and DP measurements ($E_{SP} = E_{DP} = E_{first} + E_{second}$). The transmitted arm was blocked for the SP laser-material interaction. What's more, the spatial overlapping of those pulses was ensured by monitoring the ablation morphology of both pulses with an imaging system consisting of an illumination lamp and a charge-coupled device camera. The reflected arm was delayed for 0 to 120 ps by using a micron-precision translation stage in the reflected arm, while the transmitted arm was fixed. The temporal zero delay of two pulses was validated using an autocorrelator. Then, the collinear double pulses were focused normally on the front surface of fused silica ($10 \times 10 \times 0.5\ mm^3$ wafers) by a plano-convex lens (100 mm focal length). The pulse energy arriving on the sample surface varied from 30 to 100 μJ. Under these circumstances, the $1/e^2$ Gauss beam radius was estimated to be 17 μm using the epitaxial method for the SP situation [22]. The corresponding laser fluence varied from about 3.3 to 11 J/cm^2. To guarantee the repeatability for each laser ablation, the target was translated to deliver a fresh surface for each ablation with the scan speed of 500 μm/s and the laser repetition frequency of 10 Hz. The optical emission of the laser-induced plasma was collected by two quartz lenses (50 mm and 100 mm focal lengths) and coupled into a Czerny-Turner spectrograph (Andor Shamrock 750) through a quartz fiber bundle. The image ratio of collection lenses is about 2. The fiber optics bundle (Andor, SR-OPT-8024) consists of 19 fibers bundled together closely in three circles, and the core diameter for each is 200 μm. Therefore, the whole diameter of the fiber optics entrance is 1000 μm. A gate width of 100 ns and a gate delay of 22 ns, with respect to the laser pulse, were applied to acquire the strongest line emission and avoid the bremsstrahlung radiation through the spectrograph and the Intensified Charged Coupled Device (ICCD, Andor iStar DH320T). Meanwhile, images of the plasmas were recorded by the ICCD camera placed after an imaging system consisting of a 5× objective and a close-focusing macro video lens. The spatial resolution of the imaging system is 12.5 μm for each pixel in the ICCD camera. The gate delay and the gate width for the plasma image collection were 22 ns and 20 ns, respectively. The flat-field correction has been done for the spectrometer, ICCD and the collection lens system in the temperature calculation, respectively. The ICCD was cooled down to −25 °C to reduce the dark

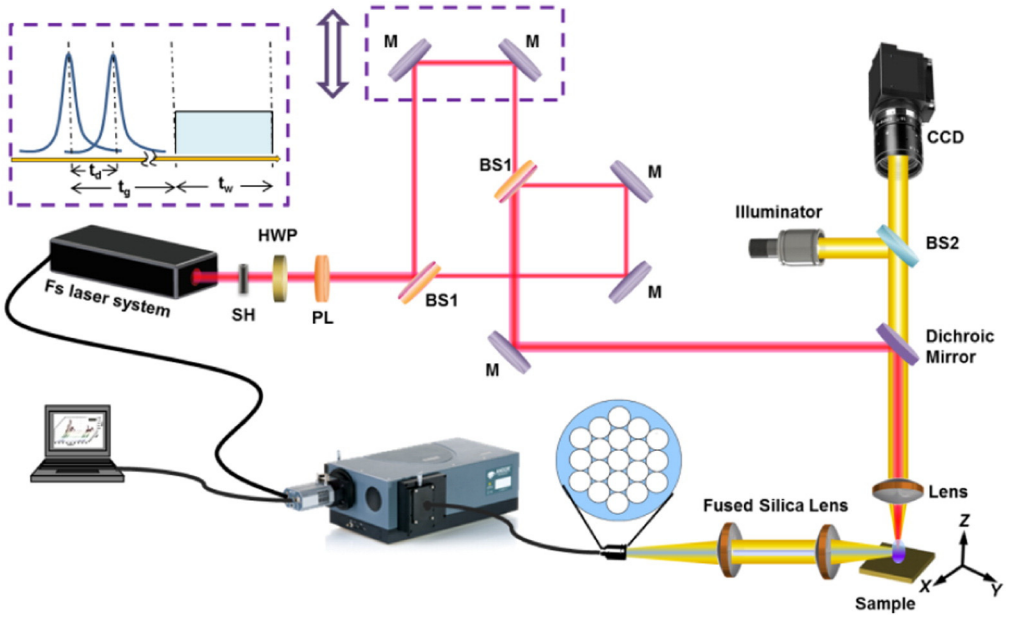

Fig. 1. The experimental setup of the DP fs-LIBS (SH: shutter, HWP: half-wave plate, PL: polarizer, M: mirror, BS1: beam splitter for fs laser, BS2: beam splitter for visible lights, t_d: interpulse delay, t_g: gate delay, t_w: gate width).