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Spatial confinement effects on spectroscopic and morphological studies of nanosecond laser-ablated Zirconium

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Spatial confinement effects on plasma parameters and surface morphology of laser ablated Zr (Zirconium) are studied by introducing a metallic blocker. Nd:YAG laser at various fluencies ranging from 8 J cm^{-2} to 32 J cm^{-2} was employed as an irradiation source. All measurements were performed in the presence of Ar under different pressures. Confinement effects offered by metallic blocker are investigated by placing the blocker at different distances of 6 mm, 8 mm and 10 mm from the target surface. It is revealed from LIBS analysis that both plasma parameters i.e. excitation temperature and electron number density increase with increasing laser fluence due to enhancement in energy deposition. It is also observed that spatial confinement offered by metallic blocker is responsible for the enhancement of both electron temperature and electron number density of Zr plasma. This is true for all laser fluences and pressures of Ar. Maximum values of electron temperature and electron number density without blocker are 12,600 K and 14×10^{17} cm^{-3} respectively whereas, these values are enhanced to 15,000 K and 21×10^{17} cm^{-3} in the presence of blocker. The physical mechanisms responsible for the enhancement of Zr plasma parameters are plasma compression, confinement and pronounced collisional excitations due to reflection of shock waves. Scanning Electron Microscope (SEM) analysis was performed to explore the surface morphology of laser ablated Zr. It reveals the formation of cones, cavities and ripples. These features become more distinct and well defined in the presence of blocker due to plasma confinement. The optimum combination of blocker distance, fluence and Ar pressure can identify the suitable conditions for defining the role of plasma parameters for surface structuring.

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) is a rapidly developing and emerging technique for spectro-chemical analysis of materials and plasma diagnostics [1,2]. Multi-elemental analysis of almost all kinds of samples including solids, liquids and gases with minimum sample preparation, capability of micro-area analysis and real-time detection are promising aspects of this popular technique. Therefore, LIBS is widely applicable in different areas of research, manufacturing industry, medicine and space sciences [3]. In this technique, a highly focused pulsed laser beam is employed as an excitation source to generate a high-temperature and high-density plasma [2]. The elemental composition as well as the electron temperature and electron number density of laser assisted plasmas are evaluated by the analysis of the selective atomic and molecular emissions from excited plasma [4]. However, as compared to other spectroscopic methods, LIBS always suffers from relatively poor detection sensitivity. Different techniques have been adopted by various research groups to enhance the detection efficiency and to improve the surface structuring e.g. by optimizing the laser parameters and enhancing the plasma confinement effects. The increased ablation rate, longer plasma durations and higher plasma temperatures are responsible for the enhancement of line emission intensity, improved detection capability and surface structuring of irradiated targets.

Among these methods, the most common approach for the enhancement of LIBS sensitivity and ablation efficiency is the suitable selection of laser parameters such as fluence, pulse duration as well as laser wavelength [5,6]. Laser fluence is one of the most important parameters which directly control the various physical phenomena e.g. energy deposition, ablation rate and shielding as well as confinement effects and generation of shock waves [5,7]. Gondal and Khalil et al. [8,9] studied the optical emission

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characteristics of metallic plasmas and evaluated the plasma parameters as a function of laser fluence. More recently, Shakeel et al. [10] investigated the effect of ambient pressures and laser irradiance of Nd:YAG laser at 1064 nm on Germanium plasma parameters and found the improved analytical performance of LIBS through the variation of ambient pressure from 8 to 250 mbar and laser irradiance from 9 to 33 GW cm^{-2}.

Spatial confinement is another suggested technique for increasing the detection efficiency of LIBS and ablation mechanisms. It plays an effective role for increasing plasma shock wave pressures [4]. There are various experimental techniques which can be employed for the compression and confinement of plasma e.g. environmental gas and their pressures [11], presence of electric and magnetic field [12], plasma plume collisions with obstructing surfaces [13], double pulse discharge enhancement [14], drilling and irregular configurations of target surface etc [15]. All these methods have been shown to be ~~a~~ strongly dependent upon incident laser-target coupling, expanding plume dynamics and plume interactions with the target surface [4,8].

The spatial confinement offered by obstructing surfaces using LIBS has attracted a significant research attention [16,17]. It was found to be effective for the significant enhancement of emission intensity, electron temperature and number density. In the presence of a small obstructing surface placed across the plume expansion path, a propagated shock wave during plasma expansion is reflected back from this immobile obstructing surface and is responsible to modify the plasma shape, size, life time & dynamics [15]. This arrangement results in additional processes like enhanced emissions and enhanced recombination rates at collisional surfaces, which finally lead to a large gradient in electron temperature and electron number density. For such type of plasma confinement, a number of scientific groups have adopted different configurations of obstructing surface [16,18]. Gao et al. [13] used pair of parallel Al plates as confining surfaces for Cu plasma and found 10 mm the best distance for enhancement of electron temperature and electron number density. Recently, Fu et al. [15] have explored physical effects of cavity on enhancement of LIBS spectra of Brass target on the basis of reflected shock wave compression effects.

The aim of present work is to investigate the effects of laser fluence and spatial confinement on Zr plasma parameters (electron temperature and electron number density) and surface morphology. The variation in electron temperature and number density has been evaluated by LIBS analysis, whereas surface modification of irradiated Zr has been analyzed using Scanning Electron Microscope (SEM).

To best of our knowledge, no comparative study of laser induced breakdown spectroscopy and surface modification of Zr at various fluences and blocker distances has yet been reported. The effect of laser fluence ranging from 8 J cm^{-2} to 32 J cm^{-2} on Zr plasma is explored. Two techniques are employed for the spatial confinement of Zr plasma. One is by introducing Ar gas at different pressures ranging from 5 Torr to 50 Torr. The second technique employed for the spatial confinement of Zr plasma is introducing an Al-Metallic blocker which is placed at three different distances of 6 mm, 8 mm and 10 mm from the target surface. The electron temperature and electron number density are evaluated for all pressures and fluences in the presence and absence of blocker. The aim is to investigate the most suitable and optimum combination of laser fluence, Ar gas pressure and Al blocker distance for the enhancement of kinetic energy and charge density of ablated species of Zr which in turn are responsible for the surface modification of Zr. The optimum control over plasma parameters with pronounced spatial confinement effects makes plasma more suitable for thin film deposition, ion implantation as well as micro/nano-structuring of materials.

2. Experimental details

The schematic of experimental set-up used for laser assisted ablation and plasma generation of Zr is illustrated in Fig. 1. Square shaped Zr samples (99.99, Alpha Aesar) with dimensions of $1.5 \times 1.5 \times 0.5$ cm^3 were selected as target material. The mechanically polished and ultrasonically cleaned Zr targets were placed at a distance of 3 mm before the focus in order to minimize the breakdown of ambient gas. The laser beam was focused on to the Zr surface at normal incidence by a lens of 50 cm focal length. The estimated area of laser spot on Zr target was 6×10^{-3} cm^2 which was measured by SEM analysis. Samples were mounted on a motorized rotating stage for the analysis of fresh sample surface for each exposure in order to improve the reproducibility and accuracy of the spectral emission lines. A Q-switched Nd:YAG laser (CFR 200 Big Sky laser Technologies Quantel France) with wavelength of 1064 nm, pulse duration of 10 ns, pulse energy of 25–200 mJ, with repetition rate of 1–10 Hz was employed for ablation and plasma formation. The emissions from Zr plasma were collected by LIBS 2500 plus spectrometer system (Ocean Optics Inc, USA) consisting of LIBS fiber bundle with seven linear silicon CCD array detectors for a broad band 200–980 nm analysis. The optical resolution of LIBS system was 0.1 nm. All the measurements were performed with a time window (integration time) of the order of 2.1 ms and delay time 2.01 μs. Therefore, it should be mentioned that the measured values of electron temperature and electron number density in present study, are time-averaged over $t_i - t_d$; where t_i is total integration time of 2.1 ms t_d is the delay time.

In order to introduce spatial confinement effects to Zr plasma, an experimental set-up was designed and fabricated. It consists of a square Aluminum (Al) plate of dimensions $5 \times 8 \times 0.1$ cm^3 that was inserted as a blocker between the target and the laser beam. The blocker was placed on the holder which was attached to a micro-positioner to control the distance of the plate from target surface. A small hole of diameter 4 mm was drilled in the center of Al plate to allow laser beam to pass and to interact normally with the target surface to produce plasma. For appropriate

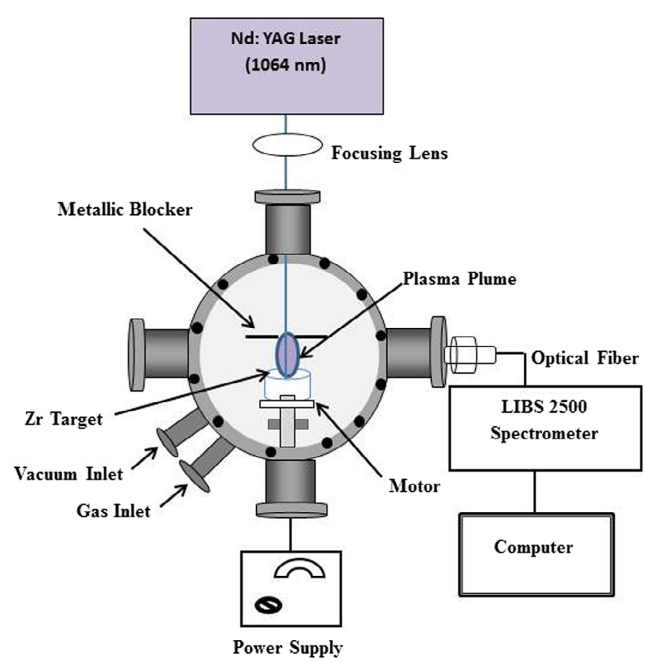

Fig. 1. The schematic of experimental setup for laser-induced breakdown spectroscopy of Zr plasma. Al plate was used as a reflector (blocker) of shock waves for spatial confinement of plasma.