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Single shot depth sensitivity using femtosecond Laser Induced Breakdown Spectroscopy

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ABSTRACT

Depth profiling measurement using multiple pulse Laser Induced Breakdown Spectroscopy (LIBS) can be used to determine the characteristics of buried layers. However for femtosecond pulses the emission spectra does not necessarily reflect the average depth composition for the single shot case and instead has much higher sensitivity for the surface layer of the ablation region. We introduce a concept of "depth sensitivity" to characterize this behavior for single shot LIBS depth profiling. Experiments were carried out using 800 nm femtosecond laser pulses irradiating layered targets while monitoring the plasma emission with a spectrometer system. Laser induced plasma formed at the surface layer exhibits a strong LIBS signature while deeper ablated region contributes very little to the emission spectrum. The sensitive depth region, the source of the major part of the emission, is much less than the ablation crater depth and is shown to be of the order of 3 nm in the case of actual crater depths of 100's of nm. A two temperature model has been used to determine the lattice temperature profile versus depth which qualitatively predicts the observed behavior.

1. Introduction

Laser Induced Breakdown Spectroscopy (LIBS) [1–6] is a technique that employs short laser pulses to ablate a small amount of material and measure the characteristic line emission of the excited atoms and ions in the ablation plume in order to determine the atomic constituents. This is a potentially powerful technique for determination of material composition [7,8], detection of buried layers [9], pollution monitoring [10,11], process control and quality control in industrial settings [12,13]. LIBS offers a small scale non contact probe where the damage to the surface is often negligible. Pulse energies in the micro-joule (μJ) energy range (μLIBS) [14] can improve spatial resolution [15], reduce the energy requirements and lead to inexpensive robust systems in comparison to milli-joule energy systems. Another aspect of spatial resolution using LIBS is depth profiling [16–21]. Depth profiling can reveal the interfaces between different materials at different depths in a layered sample. Multi layer coatings of different material and thicknesses are used in microelectronics industry and it is important to know the location of interfaces between different materials i.e. the depth profile. Microscopic depth information is also needed for characterization of artwork and preservation of cultural heritage items for the future. There are several other techniques which can determine the depth profile of a sample e.g. Secondary Ionization Mass Spectroscopy (SIMS), X-ray Photoelectron Spectroscopy (XPS) and Glow Discharge Optical Emission Spectroscopy (GD-OES). LIBS offers faster online in-situ analysis than the other methods in a relatively compact system that requires no vacuum system. Nanometer range depth resolution analysis using coated steel samples was demonstrated by Vadillo et al. [22]. They have demonstrated a depth resolution of 8 nm/pulse using a spatially flat intensity profile from a XeCl excimer laser beam. They also resolved complex depth profiles of electrolytically deposited brass samples [17]. Häkkänen et al. have measured material distributions in paper and paper coatings in order to characterize the quality of paper [23]. Microscopic variations of pigments in a double coated paper were determined. It was observed, that the two coating layers can be distinguished, if they differ enough in composition. Physical properties of the target sample such as crystal structure, absorption efficiency, melting point and boiling point as well as the laser parameters (wavelength, pulse duration, energy fluence) and incident angle of the laser beam play a key role in this process. Dependence of depth profile on different experimental variables (buffer gas, pressure, laser fluence, focal conditions) were reported by Vadillo et al. [24] and Novotny et al. [25]. Margetic et al. [18] have shown depth profiling of a multi layered Cu–Ag sample on a Si wafer. Depth profile analysis by LIBS was investigated by Pouli et al. [19] with respect to its potential to measure the thickness of different types of thin organic films used as protective coatings on historical and archeological metal objects.

Laser matter interaction and the evolution of laser ablated plasmas are complex phenomena in time and space domains. For metals three distinct steps lead to laser ablation in the ultrafast regime. Firstly the free electrons of the metal absorb laser radiation by the inverse Bremsstrahlung effect [26]. Secondly the electrons transfer their energy to the lattice system via electron-ion and electron-phonon collisions on a picosecond timescale. Thirdly the lattice thermalizes leading to break up of the binding forces leading to laser ablation [27]. The latter steps

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typically follow with a time lag of several picoseconds after the initial energy absorption which can affect the depth of material heated and ablated.

Most depth profile mapping of the elemental constituents in LIBS literature assumes a constant rate of material removal per laser pulse and uniform material ablation with each laser pulse. General practice in the determination of depth resolution is to calculate the Average Ablation Rate (AAR) [22,18,19,21,25] in terms of μm/pulse or nm/pulse i.e. the thickness of the layer divided by the total number of pulses required to reach the bottom of the layer. This AAR is then used to define depth resolution. Depth resolution, $\triangle z$ [28], can be defined as the depth range where the signal intensity changes from 16 to 84%, given by

$$\triangle z = N_s \times AAR \quad (1)$$

where N_s is the number of laser shots needed to go from 84% to 16% of the normalized signal intensity. This depth resolution gives an estimate of the capability of a LIBS system to resolve transitions in material composition of buried layers for a particular layered sample for a given set of material and laser parameters. The transition of emitted spectra from one layer to another typically happens over the range of a μm or more [28,21] for a metallic sample with sharp interfaces. Mixing of layers of different materials because of melting and resolidification during a multiple shot depth profiling also leads to reduced resolution for profiling buried features. Although it is possible to achieve a very shallow ablation depth per pulse such as $\leq$2 nm/pulse [29] the emitted spectra change slowly over several laser shots and thus the depth resolution can be many times the ablation depth per pulse. For single laser shot ablation the question arises whether the observed spectrum reflects the average composition of all the material ablated or whether materials close to the top surface contribute more to the emission. Such a non uniform response was observed previously in the detection and mapping of latent fingerprints by LIBS where the thin layer of finger oil blocked the emission from a silicon substrate even though the ablation crater penetrated well into the silicon substrate [30]. This depth dependence of LIBS emission within a single laser shot is the focus of the present work.

It has been observed in the past that the depth and volume that contribute substantially to spectral emission is less than the total ablation crater volume [14,31] and therefore the scaling of depth sensitivity with laser pulse energy is different than the scaling of ablation depth with energy. In addition, very few photons are emitted compared to atoms ablated for energies of 100 nJ to 100 μJ (120 fs pulse length) i.e. the emission efficiency is much less than unity [14]. We expect that highly excited atoms near the surface will emit more strongly than the bulk of ablated atoms. Therefore, the upper layer of the ablated target material forms the bulk of the plasma that emits the spectra. The material below is ablated and forms a crater but contributes much less to the LIBS spectra. The depth dependence of LIBS emission determines the emission response for a given constituent within the ablated depth of one laser shot. In the current experiment different layered targets on silicon wafer substrates were ablated at laser energies from 1 μJ to 100 μJ to determine the depth sensitivity of the LIBS emission.

2. Experimental

The experimental setup is shown in Fig. 1. A Ti:Sapphire (Spectra-Physics Hurricane) laser which produces ~130 fs (FWHM) pulses at 800 nm with the maximum energy ~600 μJ is used as the excitation source. We have used a half-wave plate and a Glan polarizer to control the output laser pulse energy. The energy delivered to the sample was measured using a photodiode cross calibrated against a Spectra Physics model 407A power meter and monitored throughout the experiment. The maximum energy employed at the target was ~200 μJ. The laser pulse had a Gaussian spatial profile and was focused on the sample surface using a 10 cm focal length lens. The laser spot diameter was 13 μm (FWHM). A target-viewing system consisting of a CCD camera and an f = 15 cm achromatic lens viewing through the same focusing objective that focuses the laser beam was used for target visualization and positioning. The LIBS plasma emission was imaged 1:1 onto the spectrometer (Oriel MS260i) entrance slit with a pair of aluminum coated f/4 off-axis parabolic mirrors. A grating with 1200 lines/mm and a 300 μm entrance slit was used for the experiments reported. Spectra were recorded using a gated intensified CCD camera (Andor iStar ICCD). Focal position alignment and alignment of the plasma imaging optics were checked and adjusted for each experiment to confirm similar experimental background conditions. The targets were mounted on a precise XYZ positioning stage. To improve the signal to noise ratio and

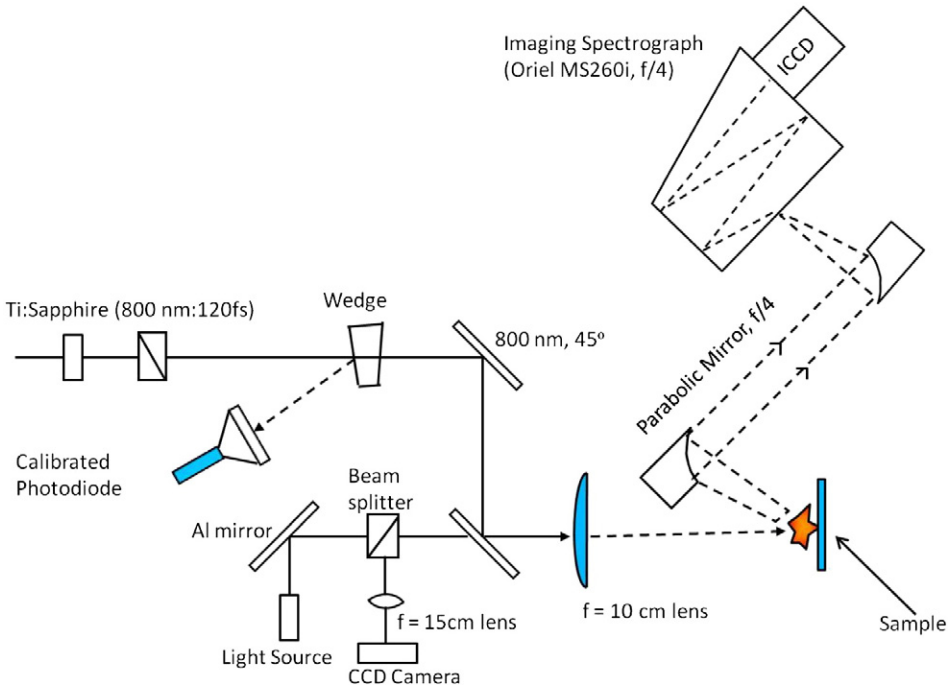

Fig. 1. Schematic layout of the experimental setup.