Applications of Femtosecond Laser Induced Breakdown Spectroscopy

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Abstract

Laser induced breakdown spectroscopy (LIBS) has proven to be a versatile tool for analyzing a wide variety of samples with little sample preparation required. In the last decade, the use of short duration (sub-nanosecond) laser pulses has provided improved resolution and reduced pulse distortion, leading to improved measurements in fields including environmental science, semiconductor manufacture, explosives detection, microbiology, and nuclear security. A selection of recent papers is examined exploring these potential benefits. The advantages of the improved resolution, more efficient energy deposition, and reduced peak broadening in these applications are discussed, as are new considerations and obstacles encountered when employing these new techniques. An additional paper on recent developments in long range (meters to potentially kilometers stand-off) LIBS is also discussed.

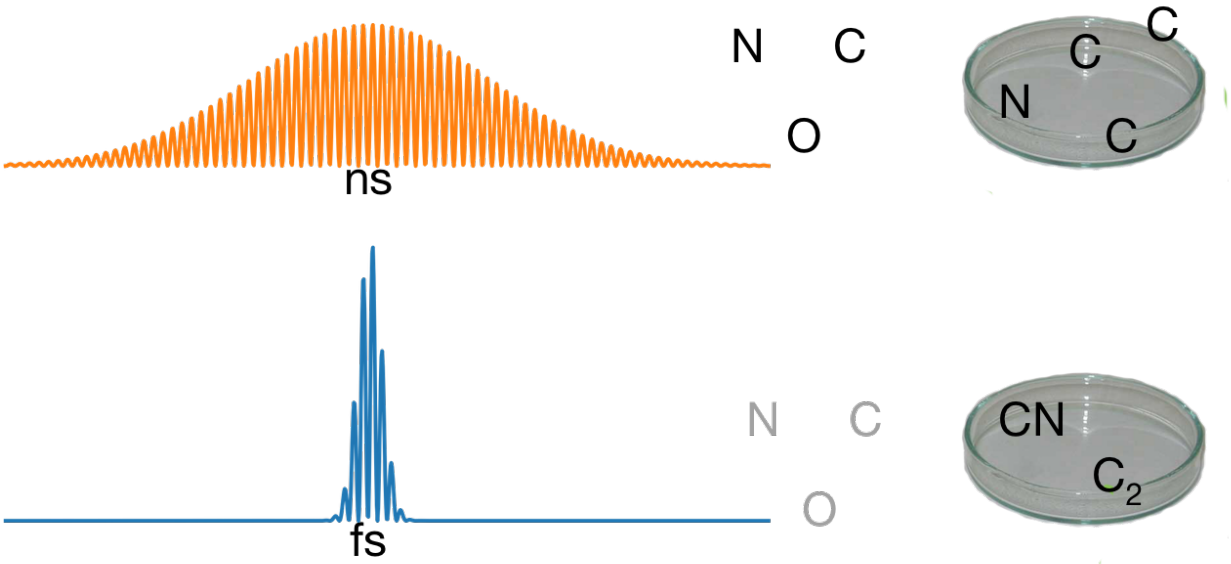

Figure 1: Traditional LIBS uses nanosecond pulses to ablate the sample. This causes heating of the material, producing larger craters, requiring more energetic pulses to develop enough plasma signal for analysis, and potentially confusing atmospheric elements with the sample. Femtosecond pulses excite plasma before sample heating can occur, resulting in smaller crater formation and allowing the use of lower energies—meaning that molecular spectra can be observed, reducing the interference from atmospheric gases.

Introduction

Description of Laser Induced Breakdown Spectroscopy

Laser induced breakdown spectroscopy was first developed as a technique to study solid samples by Brech and Cross in 1962. Its key advantages include that requires little or no sample preparation, can be performed on samples in gas, liquid, or solid phase, and is essentially nondestructive due to the small amounts of material ablated[1]. In the last decade it has been adapted from a purely laboratory technique to a portable device, allowing for spectroscopic analysis in the field. A laser pulse interacts with a sample, forming a small (on order of μg)

volume of plasma. As the plasma cools and deexcites it emits characteristic photons which can be analyzed one dimensionally (using peak location to demonstrate the presence of given analytes) or two dimensionally (measuring the intensity of the peaks to measure the quantity of analyte present). In the latter case it is necessary to account for possible elemental contributions from multiple molecules in the sample, the substrate, or intervening atmosphere which may have also been excited by the laser pulse. Further, the presence of some molecular lines or higher ionization states is influenced by the temperature of the plasma. Accounting for these factors requires understanding of the sample, experimental environment, and laser characteristics.

LIBS Configuration Considerations

The signal collected from a LIBS apparatus depends on several parameters, which can be categorized as pertaining to either the plasma formation or signal collection. For the latter, the main considerations are the delay from the laser pulse to the beginning of signal collection and the signal integration time. Time delays which are too short will not allow the plasma to cool enough to produce signals representative of the sample; overlong time delays will result in weak signal. Longer signal integration times increase the strength of the recorded signal and improve signal-to-noise ratios but may capture different regimes (ion to atom vice atom to molecule transitions). Plasma formation choices include laser power, laser frequency, pulse repetition, and pulse length. Repeated pulses in the same location allow for depth profiling as each pulse excavates a slightly deeper crater. Higher laser power increases the amount of plasma generated but can also introduce convolutions to the measured spectra (in the form of gaussian and Lorentzian broadening). While historically LIBS has employed nanosecond pulse lengths, recent experiments have examined the potential benefits of short pulse (picosecond or femtosecond) lasers.

Femtosecond LIBS

Russo, et al, report that "[i]n general, greater ablation efficiency (amount of mass removed per unit energy), reduced plasma shielding, and reduced fractionation are realized by using short-laser wavelengths (UV) and short laser-pulse durations." This is an outcome of the heat propagation speed ("phonon relaxation time") in materials examined being slower than the energy deposition rate of the laser pulse. As a result of this, the chemical bonds are broken by the photo-physical process before melting, boiling, and vaporization (phononic heating, or heating from the vibrations of the material) can take place.[2] The concentration of energy means that the plasma forms more quickly with less total energy deposited into the material. This allows for the analysis of molecular bonds rather than atomic excitations.

Applications of Femtosecond LIBS

The use of short pulse lasers has opened up new and improved applications for LIBS. Galmed, et al[3], examined the potential for LIBS to analyze the deposition of metal thin films on semiconductors. These thin films are used to electrically connect the semiconductor regions together. The performance of these films depends on the thickness of the metal deposited. This group adapted a technique described by Vadillo, et al[4], wherein repeated laser pulses are delivered to the same location and the number of pulses is used to approximate the ablation depth. The normalized intensities of Titanium (334.8nm) and Silicon (288.1nm) characteristic

lines for each depth was then used to identify the depth (approximated by the number of laser pulses) at which the Ti/Si interface appeared. Longer pulse lengths would have been unsuitable for this analysis as the infrared wavelengths used in the experimental setup have a large penetration depth in the Si substrate being examined.

Femtosecond pulse LIBS can provide improved analysis of samples that share elements with the intervening air—such as explosives. These materials are primarily composed of materials common to both the atmosphere between the instrument and the sample (in the case of stand-off LIBS) and substrate material which might be organic in nature. Femtosecond pulse LIBS, on the other hand, interacts minimally with the atmosphere and underlying substrate[5] and allows for plasma formation with less total energy deposited, meaning that the strength of these interfering lines is reduced and signal to noise ratio increased. These advantages demonstrated by Dikmelik, et al, who analyzed small amounts of trinitrotoluene deposited on an Aluminum substrate. In their experiment, nanosecond pulse LIBS spectra were dominated by the substrate lines at ~395 and ~309nm with some Carbon, Nitrogen, and Oxygen lines from the breakdown of the explosive residue (as in Figure 2). When analyzed with femtosecond LIBS, the excitation energies were an order of magnitude lower (200 J/cm^2 for femtosecond pulse length vice 4300 J/cm^2 for nanosecond pulse length). This meant that the molecular species CN and C_2 remained intact and emitted at 338.32nm characteristic of the first excited electronic state of CN, as shown in Figure 3a, with closeup on the CN lines in Figure 3b[6]. This allowed the experimenters to distinguish between C and N present in the explosive vice present in the atmosphere.

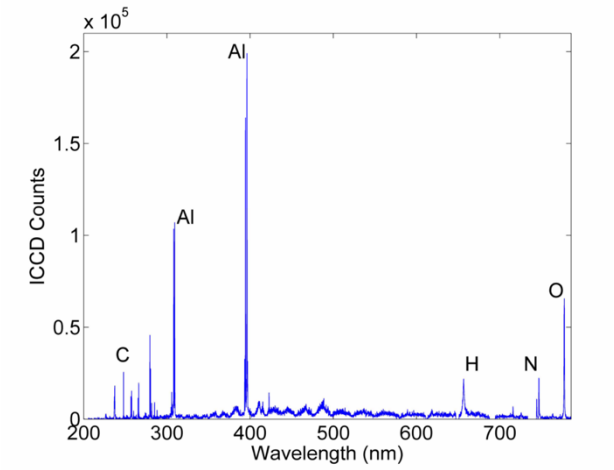

Figure 2:nanosecond pulse LIBS of TNT on Al substrate[6]

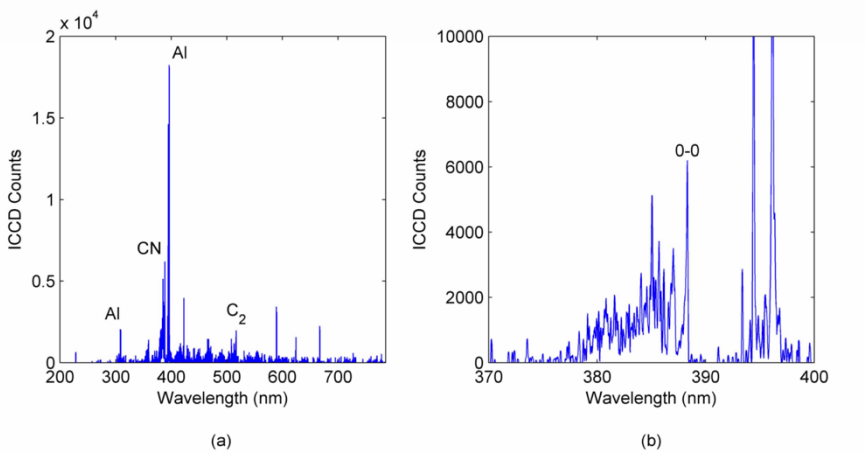

Figure 3: femtosecond pulse LIBS of TNT on Al substrate[6]

This work was extended in 2009 to show that this technique was also useful in the detection of other explosive materials. De Lucia, et al, showed that it was not the pulse length alone that resulted in the appearance of the CN molecular lines appearing in the spectrum, but the reduced power required to induce plasma in the sample[7].

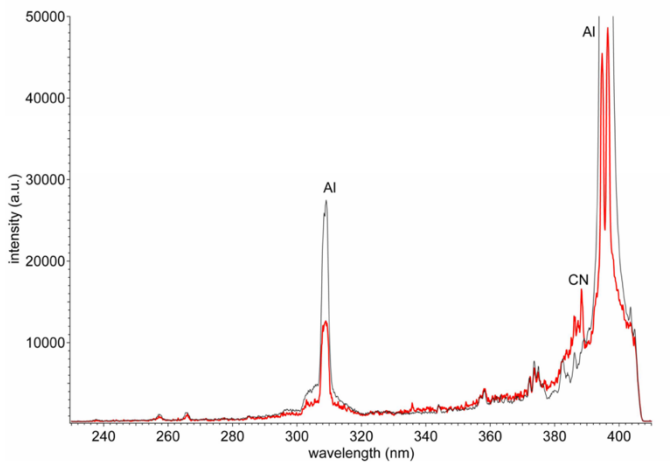

Figure 4: femtosecond pulse LIBS of RDX[7]

The ability to observe molecular emissions also has applications to biology. Bacteria are classified by trace minerals. Detecting these minerals requires high resolution and a minimal background continuum signal since the intensity (not merely the presence) of these mineral lines is required to identify the bacteria. Baudelet, et al, were able to use femtosecond LIBS spectra to identify the presence of bacteria by detecting CN. Then, by analyzing samples with repeated laser pulses and pulse-to-detection delays, they were able to identify the trace minerals and quantify them accurately enough to distinguish between *E. Coli* and *Bacillus Subtilis* by studying the CN and C_2 signal as the plasma relaxed[8].

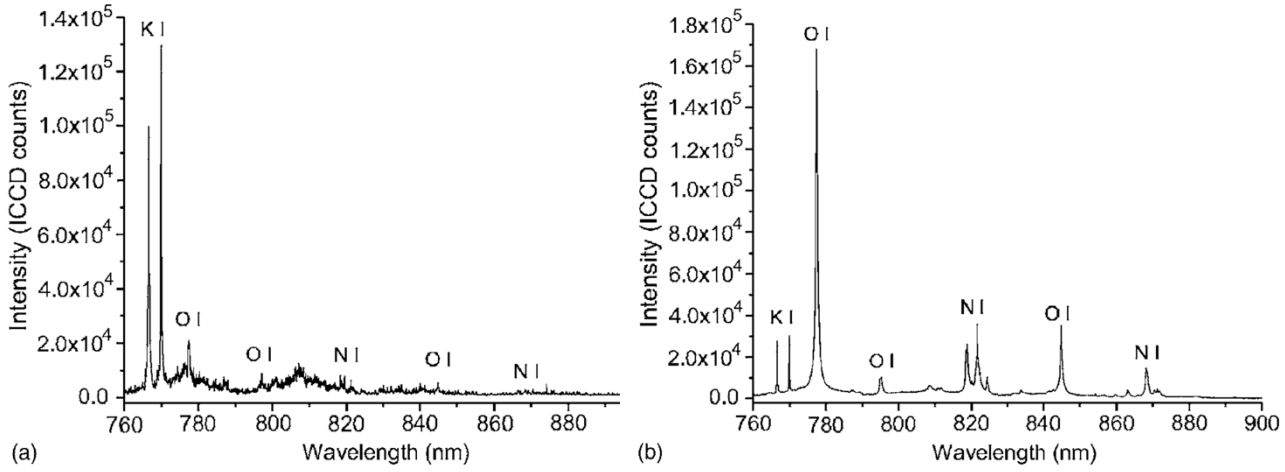

Figure 5: femtosecond (a) vs. nanosecond (b) LIBS spectra of E. Coli *bacteria showing the increased resolution in femtosecond LIBS as well as the reduced intensity of atmospheric elements (Nitrogen, Oxygen)*[8]

Anticipated Future Developments

While nanosecond pulse lasers have demonstrated long standoff detection ranges (on order of 100m), increased spot sizes at these distances require laser power to increase as the inverse of the angle subtended by the spot size at a given range. Femtosecond pulses of sufficient power (as described by equation 1) can form filaments along which they can propagate without appreciable loss or spot size growth at distances on the order of kilometers[9]. This has implications in the field of nuclear safeguards. Nations are often reluctant to allow unfettered access to nuclear facilities by inspectors, fearing that sensitive industrial or national security information will be made available to the governments of the nations from which the inspectors originate. Hartig, et al, were able to demonstrate the ability to discern between isotopes of Uranium in oxide form by identifying a 0.05nm shift in the recombination peak near 593.6nm. Further, they were able to show that the signal to noise ratio did not decrease with length of the filament[10].

$$P_{Cr} = \frac{3.72\lambda^2}{8\pi n_0 n_2} \qquad \text{Eq 1}$$

Conclusion

Femtosecond pulse lasers have improved the performance of traditional LIBS by allowing the use of lower pulse energies to generate the same amount of plasma relaxation signal. This has opened new or improved applications in a variety of fields ranging from microelectronics to forensics to biology. Further, the ability of ultrafast pulses to form and propagate along nonlinear filaments in atmosphere means that very precise spectra can be measured even at long standoff distances.

References

(1) Adrain, R. S.; Watson, J. Laser Microspectral Analysis: A Review of Principles and Applications. *J. Phys. D. Appl. Phys.* **1984**, *17*, 1915–1940.

(2) Russo, R. E.; Mao, X. L.; Liu, C.; Gonzalez, J. Laser Assisted Plasma Spectrochemistry: Laser Ablation. *J. Anal. At. Spectrom.* **2004**, *19* (9), 1084.
(3) Galmed, A. H.; Kassem, A. K.; Von Bergmann, H.; Harith, M. A. A Study of Using Femtosecond LIBS in Analyzing Metallic Thin Film–semiconductor Interface. *Appl. Phys. B* **2011**, *102* (1), 197–204.
(4) Vadillo, J. M.; Laserna, J. J. Depth-Resolved Anaylsis of Multilayered Samples by Laser-Induced Breakdown Spectrometry. *J. Anal. At. Spectrom.* **1997**, *12* (8), 859–862.
(5) Rohwetter, P.; Yu, J.; Mejean, G.; Stelmaszczyk, K.; Salmon, E.; Kasparian, J.; Wolf, J.-P.; Woste, L.; M□jean, G.; Stelmaszczyk, K.; et al. Remote LIBS with Ultrashort Pulses: Characteristics in Picosecond and Femtosecond Regimes. *J. Anal. At. Spectrom.* **2004**, *19*, 437–444.
(6) Dikmelik, Y.; McEnnis, C.; Spicer, J. B. Femtosecond and Nanosecond Laser-Induced Breakdown Spectroscopy of Trinitrotoluene. *Opt. Express* **2008**, *16* (8), 5332–5337.
(7) De Lucia, F. C.; Gottfried, J. L.; Miziolek, A. W. Evaluation of Femtosecond Laser-Induced Breakdown Spectroscopy for Explosive Residue Detection. *Opt. Express* **2009**, *17* (2), 419.
(8) Baudelet, M.; Guyon, L.; Yu, J.; Wolf, J. P.; Amodeo, T.; Frájafon, E.; Laloi, P. Femtosecond Time-Resolved Laser-Induced Breakdown Spectroscopy for Detection and Identification of Bacteria: A Comparison to the Nanosecond Regime. *J. Appl. Phys.* **2006**, *99* (8).
(9) Xu, H. L.; Bernhardt, J.; Mathieu, P.; Roy, G.; Chin, S. L. Understanding the Advantage of Remote Femtosecond Laser-Induced Breakdown Spectroscopy of Metallic Targets. *J. Appl. Phys.* **2007**, *101* (3).
(10) Hartig, K. C.; Ghebregziabher, I.; Jovanovic, I. Standoff Detection of Uranium and Its Isotopes by Femtosecond Filament Laser Ablation Molecular Isotopic Spectrometry. *Sci. Rep.* **2017**, *7* (October 2016), 1–9.