Available online at www.sciencedirect.com
SCIENCE DIRECT
Chemical Physics Letters 423 (2006) 197–201
CHEMICAL PHYSICS LETTERS
www.elsevier.com/locate/cplett

Influence of bandwidth and phase shaping on laser induced breakdown spectroscopy with ultrashort laser pulses

Tissa Gunaratne, Michael Kangas, Sherdeep Singh, Andrew Gross, Marcos Dantus *

Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA
Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, USA

Received 23 November 2005; in final form 8 February 2006
Available online 3 April 2006

Abstract

We report on the influence of pulse duration, bandwidth, and phase shaping on femtosecond laser induced breakdown spectroscopy (LIBS) and micromachining of metallic samples. Shorter pulses gave a lower threshold. Different phase functions were tested, and sample-dependent differences were found. Phase dependence was greater near threshold. When 30 fs pulses were stretched to 10 ps by linear chirp, little or no effect was measured on the LIBS signal, seemingly contradicting the advantages reported for femtosecond pulses. We determine that the bandwidth of the laser pulses is inversely proportional to the LIBS threshold.

1. Introduction

Since the invention of the laser, scientists recognized its ability to generate a spark when focused on any material [1]. The spark, resulting from plasma formation, carries characteristic atomic emissions that can be used to identify the composition of the target. Interest in the technique for its ability to provide atomic composition remotely, with minimal sample preparation, has remained strong and has evolved with laser technology. Here we explore the effect of phase on LIBS signal from metallic samples using ultrashort laser pulses. The present work is relevant to related work on micromachining and desorption with femtosecond lasers.

Nanosecond LIBS suffers some limitations due to inefficient coupling of the laser pulse energy into the sample. The laser creates a plasma, which couples with the bulk (electron–phonon coupling) and supplies the energy for melting, followed by evaporation and excitation of the gas phase atoms [2,3]. The inefficient coupling requires high energies per pulse, typically in the 10–100 mJ/pulse range, and leaves a scar caused by melting [2,3]. The low cost and ease of use of the nanosecond laser has resulted in ns-LIBS applications in the steel industry [4], environmental monitoring of stack emissions [5], trace elements in water [6,7], and soil [8], art restoration [9,10], and even space exploration [11].

The ablation process in femtosecond LIBS is very different. The electric field causes inner ionization of the atoms (1–5 fs), followed by outer ionization within the pulse (~35 fs). This highly unstable multi-ionized system triggers a Coulomb explosion within ~200 fs. Ablation is limited by the optical penetration depth at low fluences. Reduced thermal damage, lower threshold fluences, and less or no material deposition is attributed to the direct transition of material to the vapor or plasma [12–14]. Only at very high fluences (150 mJ/pulse) is melting observed, as evidenced by crater formation and microsecond emission [15,16]. The higher efficiency of fs-LIBS results in higher reliability, making it a potentially valuable analytical method [14,17–20]. The goal of this work is to determine the most efficient method to deliver photons to a sample to produce a reproducible LIBS signal.

* Corresponding author. Address: Department of Chemistry, Michigan State University, East Lansing, MI 48824, USA; Fax: +1 517 353 1793.
E-mail address: dantus@msu.edu (M. Dantus).

0009-2614/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2006.02.110

2. Experimental

Experiments were performed using a regeneratively amplified Ti:Sapphire laser. A MIIPS box pulse shaper [21] was used to correct phase distortions, resulting in transform limited (TL) pulses centered at 800 nm (35 fs, ~750 μJ/pulse at 1 kHz). The laser beam was focused with a 100 mm lens. The focal spot diameter was 26 μm as measured from single pulse holes on metal. Laser intensity was varied from 0 to 150 μJ per pulse. The signal was collected at a ~45° angle with a fiber coupled high-resolution miniature spectrometer (HR4000-Ocean Optics) and averaged 1 s.

Laser power dependence was measured using a monochromator a photomultiplier and was averaged with a boxcar integrator. A time gate was used to avoid the prompt (first 5 ns) broadband plasma emission. The signal collected corresponded to the atomic emission with characteristic 30–60 ns decay time. The samples used for this study were 6061 aluminum, copper, and brass disks spun at ~4800 rpm.

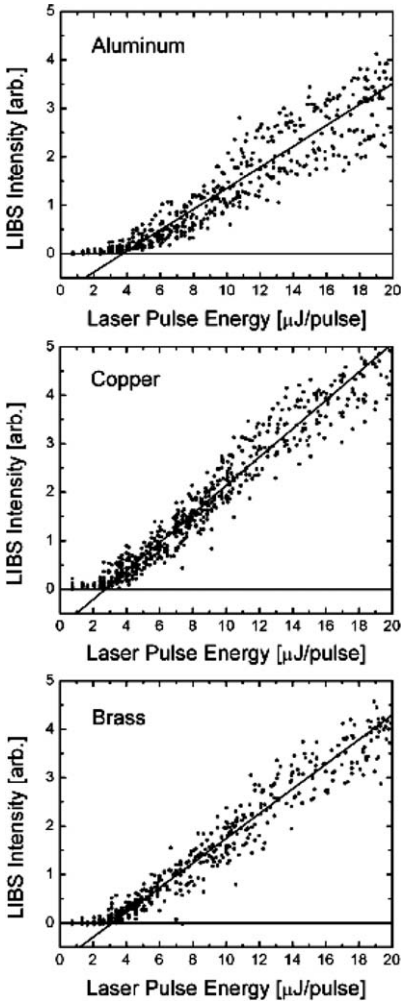

Fig. 1. Femtosecond LIBS laser power dependence recorded for Al, Cu and Brass at 396.152, 521.820 and 481.053 nm, respectively.

3. Results

3.1. Laser power dependence

Laser power dependence measurements were carried out by selecting spectral lines from the LIBS spectra (Cu I at 521.820 nm, Al I at 396.152 nm and Zn I at 481.053 nm in brass). For atomic lines, the fast rise was followed by a slow decay characteristic to atomic emission (30–60 ns). Lack of melting was confirmed by microscopic analysis of clean edged micromachined holes.

Laser power dependence results are shown in Fig. 1, where the LIBS intensity is plotted as a function of laser pulse energy. The threshold values obtained with TL pulses are in the 3–5 μJ/pulse levels and are very low compared to typical LIBS experiments carried out with three to five orders of magnitude higher energy per pulse [13–15]. The threshold energy density was 0.6 for aluminum, 0.5 for copper and 0.8 for brass, all in J/cm^2. This implies micromachining sub-0.5 mm features should be possible with single nano-Joule per pulse lasers.

3.2. Chirp dependence

We evaluated the effect of linear chirp, which has been shown to enhance the yield of multiphoton-initiated chemical reactions [22], and fs-LIBS emission [15]. Measurements from −10,000 to 10,000 fs^2 were carried out precisely using the MIIPS box pulse shaper at 50 and 150 μJ/pulse (not shown). In Fig. 2, we note that chirp pro-

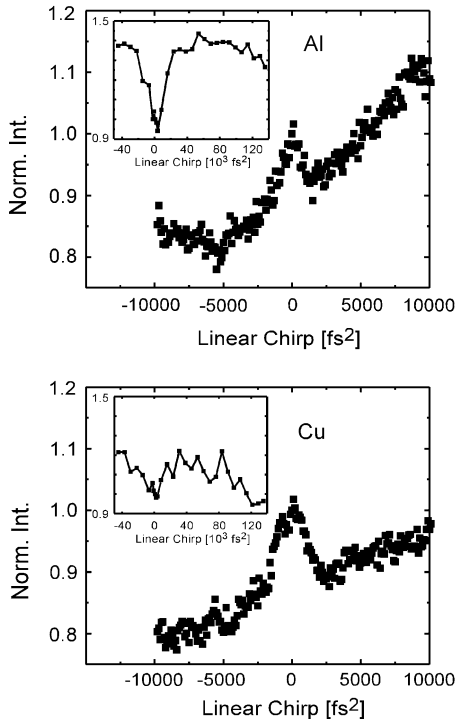

Fig. 2. Femtosecond LIBS dependence on linear chirp recorded for Al and Cu. Insets show measurements for a larger linear chirp scale.

duces a 30% change in the overall LIBS signal for aluminum and a slightly smaller effect for copper. At much greater chirp values (inserts), the signal increases by as much as 40% compared to TL pulses. Signal was still higher than for TL pulses with a chirp of 130,000 fs^2, obtained by moving the compressor grating, implying that 35-fs pulses with energy just above threshold produce the same amount of LIBS signal as a pulses that are 10.3 ps long. This striking result is explored below.

3.3. Effect of sine phase modulation

We evaluated the dependence of femtosecond LIBS on sinusoidal phases inspired by their effect on multiphoton intrapulse interference (MII) and control of multiphoton processes on molecules, proteins, and nonlinear optical crystals [23–26]. The measurements were carried out by introducing phase functions in the frequency (ω) domain defined by $\varphi(\omega) = 3\pi/2\cos(\gamma\omega - \delta)$, where γ is the bandwidth of the pulse ($\sim$1/35 fs) and δ determines the position of the mask with respect to the spectrum of the pulse. The resulting LIBS signal is plotted as a function of δ in Fig. 3.

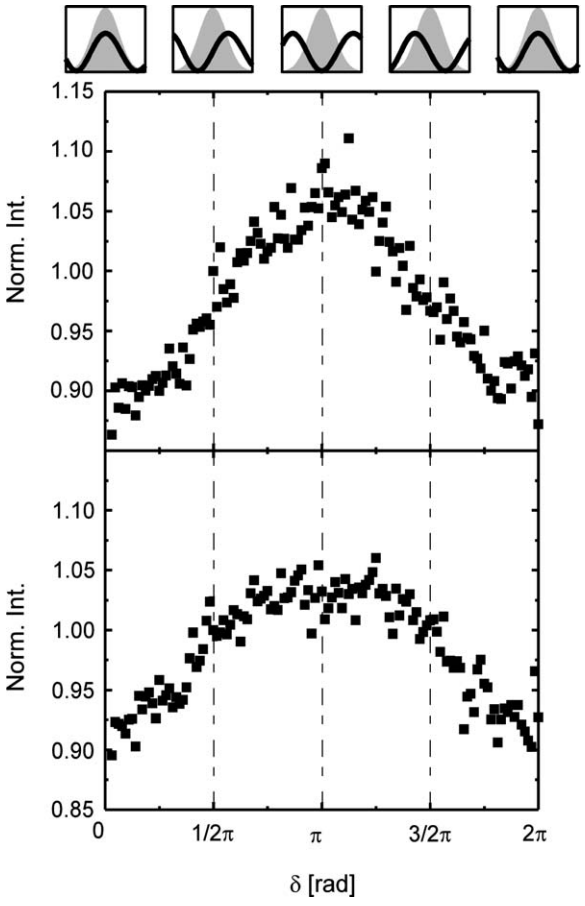

Fig. 3. Femtosecond LIBS dependence on sinusoidal phase functions across the incident pulse bandwidth recorded for Al and Cu samples. The corresponding phase functions as a function of δ are shown in the upper insets and $\delta = \pi$ resembles positively chirped pulses while $\delta = 0,\ 2\pi$ resembles negatively chirped pulses.

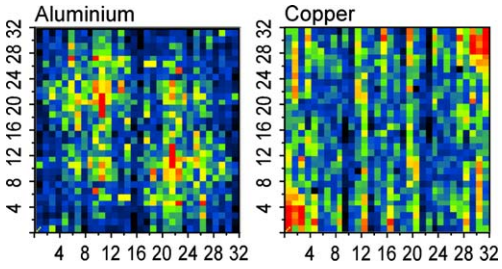

Fig. 4. Femtosecond LIBS dependence on binary phase functions recorded on Al and Cu samples. The data is represented in a 3D map. A rainbow color scheme is used to indicate intensity, with black and blue being the lowest values and red the highest. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

These measurements were obtained with pulse energies three to five times above the LIBS threshold. When the intensity was increased to 30 times the LIBS threshold, the effect of the sinusoidal modulation decreased from 20% to less than 10% (data not shown).

3.4. Binary phase dependence

We explored the effect of binary phase functions (10 bit resolution) on Al and Cu. Binary phase functions have been shown to be effective for achieving selective multiphoton excitation in condensed phase and enhancing selective fragmentation in molecular beam experiments [27–30]. A total of 512 binary phase functions were tested. These experiments explored the ability of tailored pulses to selectively probe different species. The results obtained are given in Fig. 4 as a three-dimensional map in which each binary phase function is assigned an x–y coordinate pair according to its first and last five values $x = b_0 2^0 + b_1 2^1 + b_2 2^2 + b_3 2^3 + b_4 2^4$ and $y = b_9 2^0 + b_8 2^1 + b_7 2^2 + b_6 2^3 + b_5 2^4$. The b_i coefficients correspond to the value the binary phase function takes at that position, zero or π. The different patterns observed in the binary phase maps indicate a fundamental difference in the coupling of the laser energy into the substrate. The pattern obtained for copper indicates TL pulses produce higher LIBS intensity while modulation of the pulse into sub-pulses is best for aluminum.

4. Discussion

Our results with TL pulses confirm very low thresholds for LIBS emission with femtosecond pulses [31]. Positive chirp results in a greater efficiency compared to negative chirp which as observed by Rohwetter et al. using much more intense fs pulses [15,16]. A theoretical model to explain this behavior is currently not available. The most striking result is that stretching the pulse by a factor of $\sim$300 yields signals that are slightly higher than those observed for TL pulses, despite the fact that the laser pulse energy is near threshold. We contrast this observation with the expected signal from a two- or three-photon excitation

process where the effect of stretching the pulse by such a factor would lead to a signal decrease of five or seven orders of magnitude, respectively. This surprising observation indicates that the LIBS process is limited by the timescale of electron–phonon coupling and of atoms leaving the bulk. As the pulses are stretched, there is a transition from the fs-LIBS model, in which the laser energy is confined, to the ns-LIBS model, in which the energy couples to the bulk causing melting.

The relative insensitivity of LIBS to pulse duration would seem to contradict the better efficiencies and better micromachining characteristics found for picosecond and femtosecond laser pulses [12,15]. Therefore, we explored the effect of bandwidth by introducing a set of slits in the compressor of the regenerative pulse amplifier, where the pulse is frequency-dispersed, and measured the LIBS threshold at multiple bandwidths. Results, shown in Fig. 5, indicate that the greater the bandwidth, the lower the threshold. This observation allows us to conclude that efficient LIBS on metallic surfaces is highly dependent on bandwidth; however, for micromachining purposes, pulse durations below 1 ps are required to avoid melting and control depth [31]. Although changes in the bandwidth cause changes in the pulse duration, we have already shown, through the chirped pulse measurements, that pulse duration alone does not affect the LIBS threshold.

The observed effects of sinusoidal modulation are consistent with the observations regarding chirp. When $\delta = \pi$, the phase function can be approximated by a positive chirp, which was observed to yield a higher LIBS signal. When $\delta = 0$, the phase function can be approximated by a negative chirp, which was observed to yield a lower LIBS signal. At $\delta = \pi/2$, the phase function has, within the FWHM of the pulse, a linear dependence resulting in near-TL excitation; inspection of the results in Fig. 3 shows a slight enhancement at this value. The dependence of LIBS on sinusoidal phase modulation, however, was not as significant as that of multiphoton processes [26].

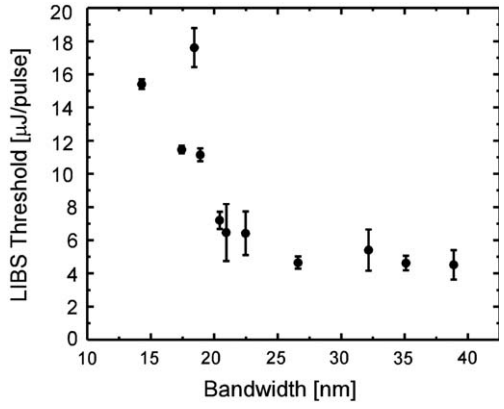

Fig. 5. Femtosecond LIBS threshold dependence on the bandwidth of the pulse (full-width at half maximum). Each data point is the average of three power dependence measurements.

Binary phase functions showed clear differences between copper and aluminum. In copper, TL pulses yielded the highest LIBS signal; Aluminum required greater pulse modulation. This observation can be correlated with the experiments from Rohwetter et al., where fs-LIBS signal was easily obtained from copper but not aluminum [15]. Presumably, this is due to the aluminum-oxide layer. We tested a dual-pulse arrangement to enhance the sensitivity of fs-LIBS and to explore selectivity towards a particular element, to test if we could observe enhancements similar to dual-pulse ns-LIBS [32–35]. Our results showed no enhancement for either TL or binary phase functions over those reported here for single pulses. We attribute this lack of two-pulse enhancement to the fact that we are exciting near the LIBS threshold and that there is no significant delayed emission caused by melting of the sample.

5. Conclusions

We find, as had been reported earlier, that femtosecond pulses lead to lower LIBS thresholds. Here, we determine that the reason for this enhancement is the additional bandwidth of ultrashort pulses, rather than their duration. This was confirmed by our measurements with 30 fs pulses stretched to a length of 10 ps, and also by the dependence of LIBS threshold on bandwidth. A 40% increase in LIBS emission was found for positive linear chirp. The effects of sinusoidal and binary modulation showed more modest enhancements with differences between aluminum and copper. These changes reflect a shift from a highly localized excitation followed by fast Coulomb explosion to a slower process where electron phonon coupling leads to melting. Our experiments show that LIBS efficiency improves with bandwidth well beyond what is available using the typical picosecond laser. This finding, therefore, supports the use of broad bandwidth pulses for efficient LIBS. Phase control of ultrashort (broad bandwidth) pulses will be valuable in laser machining and will improve reproducibility and selectivity in analytical LIBS applications, especially when minimal disturbance of the substrate is required.

Acknowledgements

We gratefully acknowledge funding from the Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, US Department of Energy. Support for A.G. came from the High School Honors Science Mathematics Engineering Program at MSU, and is gratefully acknowledged. We also acknowledge The Innovation in Educational Spectroscopy Grant from Ocean Optics toward HR 4000 spectrometer.

References

[1] F. Brech, L. Cross, Appl. Spectrosc. 16 (1962) 59.
[2] K. Song, Y.I. Lee, J. Sneddon, Appl. Spec. Rev. 32 (1997) 183.

[3] R.A. Multari, L.E. Foster, D.A. Cremers, M.J. Ferris, Appl. Spectrosc. 50 (1996) 1483.
[4] J.A. Aguilera, C. Aragon, J. Campos, Appl. Spectrosc. 46 (1992) 1382.
[5] H.S. Zhang, F.Y. Yueh, J.P. Singh, Appl. Opt. 38 (1999) 1459.
[6] A.E. Pichahchy, D.A. Cremers, M.J. Ferris, Spectrochim. Acta B 52 (1997) 25.
[7] R. Knopp, J.I. Kim, Fresenius J. Anal. Chem. 355 (1996) 16.
[8] A.S. Eppler, D.A. Cremers, D.D. Hickmott, M.J. Ferris, A.C. Koskelo, Appl. Spectrosc. 60 (1996) 1175.
[9] I. GobernadoMitre, A.C. Prieto, V. Zapiropolus, Y. Spetsidou, C. Fotakis, Appl. Spectrosc. 52 (1997) 1125.
[10] D. Anglos, S. Couris, C. Fotakis, Appl. Spectrosc. 51 (1997) 1025.
[11] A.K. Knight, N.L. Scherbarth, D.A. Cremers, M.J. Ferris, Appl. Spectrosc. 54 (2000) 331.
[12] P.P. Pronko, S.K. Dutta, J. Squier, J.V. Rudd, D. Du, G. Mourou, Opt. Commun. 114 (1995) 106.
[13] B. Le Drogoff, J. Margot, M. Chaker, M. Sabsabi, O. Barthelemy, T.W. Johnston, S. Laville, F. Vidal, Y. von Kaenel, Spectrochim. Acta B 56 (2001) 987.
[14] K.L. Eland, D.N. Stratis, D.M. Gold, S.R. Goode, S.M. Angel, Appl. Spectrosc. 55 (2001) 286.
[15] P. Rohwetter, J. Yu, G. Me'jean, K. Stelmaszczyk, E. Salmon, J. Kasparian, J.-P. Wolf, L. Woste, J. Anal. Atom. Spectrom. 19 (2004) 437.
[16] P. Rohwetter, G. Me'jean, J. Yu, E. Salmon, J. Kasparian, R. Ackermann, J.-P. Wolf, L. Woste, Appl. Phys. Lett. 85 (2004) 3977.
[17] A. Assion, M. Wollenhaupt, L. Haag, F. Mayorov, C. Sarpe-Tudoran, M. Winter, U. Kutschera, T. Baumert, Appl. Phys. B 77 (2003) 391.
[18] S.M. Angel, D.N. Stratis, K.L. Eland, T. Lai, M.A. Berg, D.M. Gold, Fresenius J. Anal. Chem. 369 (2001) 320.
[19] J.-B. Sirven, B. Bousquet, L. Canioni, L. Sarger, Spectrochim. Acta B 59 (2004) 1033.
[20] V. Margetic, A. Pakulev, A. Stockhaus, M. Bolshov, K. Niemax, R. Hergenroder, Spectrochim. Acta B 55 (2000) 1771.
[21] V.V. Lozovoy, I. Pastirk, M. Dantus, Opt. Lett. 29 (2004) 775.
[22] I. Pastirk, E.J. Brown, Q. Zhang, M. Dantus, J. Chem. Phys. 108 (1998) 4375.
[23] V.V. Lozovoy, I. Pastirk, K.A. Walowicz, M. Dantus, J. Chem. Phys. 118 (2003) 3187.
[24] I. Pastirk, J.M. Dela Cruz, K.A. Walowicz, V.V. Lozovoy, M. Dantus, Opt. Express 11 (2003) 1695.
[25] J.M. Dela Cruz, I. Pastirk, V.V. Lozovoy, K.A. Walowicz, M. Dantus, J. Phys. Chem. A 108 (2004) 53.
[26] K.A. Walowicz, I. Pastirk, V.V. Lozovoy, M. Dantus, J. Phys. Chem. A 106 (2002) 9369.
[27] M. Comstock, V.V. Lozovoy, I. Pastirk, M. Dantus, Opt. Express 12 (2004) 1061.
[28] J.M. Dela Cruz, I. Pastirk, M. Comstock, M. Dantus, Opt. Express 12 (2004) 4144.
[29] J.M. Dela Cruz, V.V. Lozovoy, M. Dantus, J. Phys. Chem. A 109 (2005) 8447.
[30] I. Pastirk, M. Kangas, M. Dantus, J. Phys. Chem. A 109 (2005) 2413.
[31] S. Nolte, C. Momma, H. Jacobs, A. Tunnermann, B.M. Chichkov, B. Wellegehausen, H. Welling, J. Opt. Soc. Am. B 14 (1997) 2716.
[32] J. Scaffidi, J. Pender, W. Pearman, S.R. Goode, Bill W. Colston Jr., J.C. Carter, S.M. Angel, Appl. Opt. 42 (2003) 6099.
[33] J. Scaffidi, W. Pearman, J.C. Carter, Bill W. Colston Jr., S.M. Angel, Appl. Opt. 43 (2004) 6492.
[34] D.N. Stratis, K.L. Eland, S.M. Angel, Appl. Spectrosc. 54 (2000) 1270.
[35] J. Scaffidi, W. Pearman, M. Lawrence, J.C. Carter, B.W. Colston Jr., S.M. Angel, Appl. Opt. 43 (2004) 5243.