Laser-induced breakdown spectroscopy using mid-infrared femtosecond pulses

K. C. Hartig,1,2 J. Colgan,3 J. E. Barefield 1,2 and I. Jovanovic1, a)
1) Department of Mechanical and Nuclear Engineering, The Pennsylvania State University, University Park, PA 16802
2) Chemical Diagnostics and Engineering, Los Alamos National Laboratory, Los Alamos, NM 87544
3) Theoretical Division, Los Alamos National Laboratory, Los Alamos, NM 87544

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We report the first laser-induced breakdown spectroscopy (LIBS) experiment driven by mid-infrared (2.05-µm) fs pulses, in which time-resolved emission spectrum of copper was studied. Ab-initio modeling is used to explain the results of new fs measurements at both 2.05 µm and 800 nm. Ablation by mid-infrared fs pulses results in a plasma with a lower plasma density and temperature compared to fs-LIBS performed at shorter laser wavelength.

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Laser-induced breakdown spectroscopy (LIBS) is presently widely used for its versatility, simplicity, and ability to perform in-situ, rapid chemical and isotopic analysis not only in the laboratory setting, but also in the field.1–3 LIBS involves focusing the output of a pulsed laser onto the sample of interest to generate a luminous plasma. The types of pulsed lasers most commonly used for LIBS are the Q-switched Nd:YAG ns-lasers, but an increasing number of LIBS studies report the use of fs-lasers, such as the chirped-pulse amplified Ti:sapphire laser. Laser-matter interactions characteristic for LIBS have been extensively studied in the past, and it is recognized that the plasma production by a laser pulse and its evolution is a process that depends on the wavelength, pulse duration, fluence, and shape of the laser pulse.

Previous single-pulse LIBS experiments have shown that the plasma density and the peak emission intensity of the LIBS signal can be enhanced by 40–50% if shorter wavelength ns pulses are used (532 nm in comparison to 1064 nm).11 In dual-pulse LIBS, an enhancement of the peak intensity, plasma temperature, and plasma density has been reported when the second pulse wavelength is increased.12 Such enhancements are desirable, as they result in a higher intensity and increased stability of the LIBS signal due to the longer plasma lifetime and reexcitation of the plasma with the second pulse.1 One potential avenue for further LIBS enhancement is the use of eyesafe mid-infrared pulses, as recently reported in the ns-pulse regime.13 Mid-infrared ultrafast lasers have undergone a significant development in the recent period, producing pulse durations as short as ∼10’s of fs and pulse energies extending to many mJ.14 Those characteristics make them compatible with LIBS requirements. No LIBS measurement in the fs regime has been reported to date using mid-infrared laser pulses.

Formation of plasmas induced by typical ns-laser pulses involves several processes: surface melting, vaporization, vapor ionization, ambient and evaporating gas breakdown, free electron acceleration within the evaporated cloud, and plasma heating.15 With the advent of high-intensity ultrashort laser pulses, the laser ablation and laser-matter interaction processes noticeably differ from those taking place with ns lasers.16 Ultrashort pulses allow for direct coupling of the laser energy to the sample through inner ionization (1–5 fs), followed by outer ionization within the pulse duration (tens of fs), similar to the ns ablation process. Since the pulse duration is sufficiently short to prevent reheating, plasma formation occurs by Coulomb explosion in a highly unstable multi-ionized system within ∼200 fs. The direct ionization of the sample occurs at near solid density, as there is little or no material removal, which results in reduced threshold fluences and thermal damage.17 Fs-lasers have improved the quantification and trace element identification in LIBS through the direct ionization of the irradiated sample and greatly reduced laser-plasma interactions, resulting in a cleaner ablation and improved repeatability with a low continuum emission and characteristic line emissions that appear within 50 ns after the laser has irradiated the sample surface.3,18–20

In this Letter, we report what we believe to be the first study of the effect of mid-infrared (2.05-µm) fs pulses on the LIBS plasma formation and emission. We find that fs-LIBS conducted by 2.05-µm pulses results in a lower electron temperature, shorter plasma lifetime, and lower electron density in comparison to fs-LIBS conducted at shorter (near-infrared) laser wavelengths. In addition, we present the results of numerical modeling that provide an explanation for the experimentally observed differences in the relative spectral line intensities when two different laser wavelengths are used. The modeling is based on ab initio theory utilizing the Los Alamos National Laboratory (LANL) suite of atomic structure and plasma emission codes (ATOMIC)21, capable of treating both the local thermodynamic equilibrium (LTE) and non-LTE con-

a)Electronic mail: ijovanovic@psu.edu; www.mne.psu.edu/ij
ditions for various electron temperatures and densities.

Our modeling analysis consists of several steps. It starts with atomic structure calculations performed by solving the Hartree-Fock equations for the I and II ionization states of Cu. The energy levels are then adjusted to their experimentally known values reported in the NIST atomic database. The atomic transition probabilities and atomic collision quantities are also computed in an ab initio manner. We perform LTE or non-LTE calculations that generate level populations and, subsequently, the entire emission spectrum for the copper plasma for a range of electron temperatures and densities typical for LIBS.

In our experiments, a two-stage optical parametric amplifier is pumped by a commercial Ti:sapphire chirped-pulse amplification system (Trident X, Amplitude Technologies), which produces 40-fs, up to 15-mJ pulses centered at 800 nm, with a full width at half maximum (FWHM) bandwidth of ≈25 nm at a repetition rate of 10 Hz. The optical parametric amplifier produces 2.05-µm, ≈42-fs pulses with energies of up to 2.2 mJ.

The 800-nm and 2.05-µm laser pulses were both attenuated to 200 µJ and focused on the sample surface by 30-cm focal length BK7 or CaF₂ lenses, respectively. The spot size on the sample surface was approximately 100 µm in both measurements, and was determined by measuring the size of the resulting laser ablation craters using a laser surface profilometer. The copper sample consisted of a copper mirror formerly used for a CO₂ laser system. A fresh sample spot was chosen for each accumulation of 10 laser shots by translating the sample. Optical emission was collected by a 50-mm focal length lens positioned at 45° with respect to the sample surface (f/# = 2.2) and coupled to an optical fiber. The fiber was interfaced to a spectrally calibrated Catalina Scientific SE-200 Echelle spectrometer equipped with an Andor intensified charge coupled device (ICCD) camera and a Horiba iHR 550 Czerny-Turner spectrometer with a 1800 g/mm grating and an Andor i334T iStar ICCD. The spectrometers were calibrated using an Ocean Optics DH-2000 deuterium-tungsten calibration lamp.

Fig. 1 shows the LIBS spectrum of copper in vacuum for both the 800-nm and 2.05-µm fs pulses with three characteristic Cu I emissions clearly present. The spectrum was obtained with a time gating window of 5 µs and a delay of 50 ns following the time at which the scattered 800 nm laser light was first observed in the measured spectrum. In order to provide statistics for the plasma temperature measurement, 10 spectra were taken successively at the same sample location. Emission transitions observed in the full collected spectrum have all been identified to be from neutral copper (Cu I).

The relative differences in characteristic emission line intensities in vacuum shown in Fig. 1 reveal the differences of plasma temperature and density when the two laser wavelengths are used. Further, when there was no delay in the acquisition following the laser pulse being incident on the sample, as shown in Fig. 2, a lower continuum (bremsstrahlung and radiative recombination) emission and peak intensity is observed in the case when 2.05-µm pulses are used. Additionally, emission from low-intensity Cu I lines at 511.19 nm and 520.08 nm with high (7.99 eV and 7.80 eV, respectively) upper energy levels is more intense due to a more efficient ablation and higher plasma temperature occurring following ablation by 800-nm pulses, as shown in Fig. 1.

In order to determine the plasma temperature, we analyzed several Cu I emission lines: 406.26, 427.51, 437.82, 458.69, 465.11, 510.55, 521.82, 529.251, 570.024, and 578.213 nm, which are observable in Fig. 2. The associated spectroscopic data for each emission line an-
analyzed was obtained from the NIST database. The plasma temperature was calculated using the Boltzmann plot method, the two-line method (utilizing the ratio of two closely spaced emission lines associated with different energy levels), and the synthetic spectra method with the criteria and best practices described by Zhang et al. The plasma is assumed to be in quasi-LTE conditions, satisfying the McWhirter criterion, which sets the lower bound on the electron density for LTE conditions as

\[ n_e \geq 1.6 \times 10^{12} T_e^{1/2} (\Delta E)^3 \text{ cm}^{-3}, \tag{1} \]

where the electron temperature \( T_e \) is in K and the energy of the transition is \( \Delta E \) is in eV. For a neutral Cu plasma with transition energies in the range of 3–6 eV and plasma temperature of 0.8 eV, a plasma with density \( \gtrsim 2 \times 10^{15} \text{ e}^-/\text{cm}^3 \) would satisfy this criterion.

The full width at half maximum (FWHM) \( \Delta \lambda_{1/2} \) of the Stark broadened line from neutral atoms due to an electron density \( n_e \), assuming that the contribution from the electron impact width parameter \( \omega \) and the ion-broadening parameter \( A \) are weak functions of temperature, is

\[ \Delta \lambda_{1/2} (A) = 2 \omega (n_e/10^{16}). \tag{2} \]

The plasma density was determined from Stark broadening of the 510.5 nm Cu I emission line using Eq. (2), and was measured to be 0.038 nm and 0.091 nm (FWHM) for the 2.05-μm and 800-nm case, respectively. This corresponds to a plasma density of \( \approx 1.5 \times 10^{17} \text{ e}^-/\text{cm}^3 \) for the 2.05-μm case. The 800-nm ablation resulted in a plasma density of \( \approx 5 \times 10^{17} \text{ e}^-/\text{cm}^3 \). The change in plasma temperature is not sufficient to account for the magnitude of Stark broadening; thus an increase in the plasma density following ablation with 800-nm pulses explains the observed higher emission intensities.

The obtained Boltzmann plot for 2.05-μm LIBS of Cu is shown in Fig. 3, and has a \( \approx 10\% \) error due to the \( \approx 20\% \) error in the spectroscopic data. The Boltzmann plot method resulted in a temperature for the neutral Cu \( T_{\text{Cu}} = 0.62 \) eV for the 2.05-μm case and \( T_{\text{Cu}} = 0.8 \) eV for the 800-nm case. The plasma temperature obtained for the 800-nm case agrees with previously reported Cu fs-LIBS measurements. The ATOMIC code was utilized to produce synthetic spectra for the Cu transitions under LTE conditions at several different plasma temperatures; the 0.62 eV case is shown in Fig. 4 for comparison with the experimental results.

The lack of observed Cu II emission in the full spectrum can be explained by the calculated average ion charge of 0.115 for the 0.62 eV case and \( 1 \times 10^{17} \text{ e}^-/\text{cm}^3 \) density. For the same density and a plasma temperature of 0.8 eV, the average ion charge is predicted to be 0.832. This increased ion charge indicates that a larger fraction of the plasma is ionized, which explains an increased recombination emission in the 800-nm case and the comparative increase in the continuum (when no delay is present).

The ATOMIC calculations presented here employ atomic structure data derived from Cowan’s codes. The fine-structure resolved calculations include full configuration-interaction (CI) between all the configurations included in our model. We include over 50 configurations that span around 1000 levels for neutral Cu.

We find that the lowest (energetically) odd-parity levels arise from strong mixing of the \( 3d^{10}4p \) and \( 3d^94s4p \) configurations, and that transitions involving these levels have line strengths that are quite sensitive to the amount of CI included in the calculation. Including more CI is achieved by adding more configurations to the atomic model, but this can result in more computationally in-

FIG. 3. Boltzmann plot for the calculation of the excitation temperature of Cu I. Scatter symbols: experimental data, red curve: linear fit, green curve: 95% confidence bands.

FIG. 4. Emission spectrum from Cu (red curve) obtained in LIBS driven by mid-infrared fs pulses. The measurements are compared to ATOMIC LTE calculations (black curve) performed at the temperature and density matching the measured value from the Boltzmann plot and Stark broadening.
tensive calculations. The calculations presented here attempt to strike a balance between ensuring sufficient CI effects are included at a manageable computational cost. The effect of the strong mixing and CI sensitivity can be seen in Fig. 4, where the 510.5-nm line is predicted to be more intense than the measured intensity.

The plasma lifetime was observed to be $\approx 450$ ns and $\approx 2400$ ns for the 2.05$\mu$m and 800-nm fs-LIBS copper measurements, respectively. The short plasma lifetime in 2.05$\mu$m LIBS measurements can be explained by two mechanisms: (1) the laser-matter coupling is less efficient for the longer wavelengths, leading to less ablation, and (2) lower plasma temperature and density results in a plasma consisting primarily of neutral atoms, as singly ionized atoms would act as a source for neutral emission following electron recombination.

Further work is being conducted on integrating the radiation transport into the ATOMIC code and implementing a multi-region model to more accurately simulate the LIBS plasma emission. With dense, inhomogeneous plasmas, such as those observed in previous LIBS measurements, an average temperature and density does not accurately represent the plasma that exists with a hot, dense center and cool, rapidly expanding outer layer. Such multi-region models will benefit from further experimental efforts to resolve the spatio-temporal LIBS plasma evolution.

In conclusion, we reported the first LIBS measurements that use mid-infrared fs laser pulses. We demonstrated through experimental analysis and theoretical modeling that the copper plasma resulting from ablation by 2.05$\mu$m fs pulses exhibits a lower plasma temperature and shorter plasma lifetime than fs-LIBS performed at a shorter wavelength (800 nm). The lower plasma temperature combined with the short plasma lifetime leads to low continuum emission and, thus, an improved signal-to-background ratio of 1570 for 2.05$\mu$m LIBS and 630 for 800-nm LIBS with a 50-ns delay.

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