Temperature and Emission Spatial Profiles of Laser-Induced Plasmas during Ablation Using Time-Integrated Emission Spectroscopy

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Emission spectra and excitation temperature spatial profiles, within laser-induced plasmas from solid copper targets, are characterized as a function of laser power density with the use of time-integrated emission spectroscopy. This research shows how the measured axial spatial emission intensity of the expanding plasma can be influenced by the time integration. The excitation temperatures calculated from these integrated emission-line intensities may not coincide with the actual temperature spatial profile. Transient plasma dynamics during time-integrated intensity measurements can influence both the excitation temperature and the atomic number density of the emitting species. As a demonstration of the influence of fluid dynamics on time-integrated emission measurements, a shock-wave model was used as an example to show how the spatial emission intensity profile of a laser-induced plasma can be affected by transient expansion. Even for time-resolved emission measurements, the high velocity of a laser-induced plasma can influence spatial intensity data close to the target surface. The ability to accurately measure spatial emission intensity and temperature behavior is shown to be related to the integration time vs. plasma expansion velocity.

Index Headings: **Laser ablation; Laser-induced plasmas; Temperature; Boltzmann distribution; Atomic emission spectroscopy; Shock wave.**

INTRODUCTION

When a high-power pulsed laser beam is focused onto a solid surface, it can cause the removal of material by melting, vaporization, sublimation, and a number of nonlinear processes. A generic term, laser ablation, is regularly used to identify the overall interaction. Laser ablation offers several attractive features for chemical analysis: direct analysis of conductive and nonconductive solid materials, localized micro-analysis, and minimal sample preparation. Qualitative and semi-quantitative analysis of a wide variety of solid samples has been demonstrated with the use of laser ablation sampling with a separate atomization and/or excitation source.[1-10]

The high-power laser material interaction initiates a luminous plasma above the solid surface. Compositional analysis of the sample can be obtained directly by measuring the optical emission spectra of the laser-induced plasma (LIP).[11-17] LIP emission spectra consist of neutral atom and ionic lines superimposed on a spectrally broadband continuum of radiation. The characteristics of the plasma are dependent on the laser irradiance, target composition, atmospheric conditions, and time. The continuum plasma emission background results from free–free or free–bound transitions through electron–ion recombination.[18,19]

With the use of either direct observation of the laser-induced plasma or any of the arrangements that use laser ablation for sample introduction, the analytical figures of merit (accuracy, precision, and detection limits) for quantitative analysis are often not satisfactory. The primary reason is that the violent, nonlinear laser material interaction cannot be predicted accurately; the mass ablation (removal) rate and mass composition may vary, depending on the laser and material characteristics. Shot-to-shot variations in the laser power, temporal pulse shape, and laser spatial profile influence the precision of these nonlinear ablation processes. The mechanical, physical, and chemical properties of the sample influence the interaction, underscoring a strong matrix effect. Finally, variation in experimental conditions (laser focusing, angle of incidence of the laser beam, surface condition, etc.) makes it difficult to compare results from different laboratories or define universal operating conditions for chemical analysis.

To improve laser ablation applications, it is necessary to understand the nonlinear interaction between the laser and solid, and the dynamic processes of plasma initiation and propagation in gases. By understanding the characteristics of the plasma and the influence of experimental conditions, one can optimize analytical sensitivity and detection limits, while minimizing preferential vaporization. For both fundamental understanding of the laser material interaction and chemical analysis, many groups have studied temporal and spatial characteristics of laser-induced plasmas.[20-28] Time-resolved measurements have shown that the plasma may consist of two distinct regions: a short-lived high energy-density plasma just above the target, and a second lower-energy region that expands with time and follows a blast wave model.[25-30] It is this secondary plasma region that is often used for emission spectra-chemical analysis.

In order to examine in detail the characteristics of the secondary plasma, several groups have measured emission spectra, and electron temperature and density profiles (spatial and temporal) under different pressures and laser conditions.[20,28,31-33] The excitation temperatures calculated from Boltzmann plots are from 6000 to 30,000 K, depending on the gas pressure, sample material, laser power density, and measurement position in the plasma. These temperatures are calculated from spectra which were measured by integrating the intensity over the line

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of sight at each position in plasma. For high-velocity transient expansion dynamics of laser-induced plasmas, the calculated spatial temperature profile from integrated emission-line intensity measurements may be spatially skewed. This factor is important to consider, since spatial changes in number density due to recombination, as well as in continuum emission, do not fully explain the calculated temperature profile at high laser densities, nor the offset in temperature with the peak emission of the plasma continuum.

In this work, laser-induced plasmas from solid copper targets in argon at atmospheric pressure are characterized by measuring their emission spectra and calculating excitation temperature spatial profiles, as a function of laser power density. The effect of converting integrated emission line intensities to excitation temperature during a dynamic plasma expansion process is discussed as a possible explanation for a measured offset of temperature and emission intensity. A shock-wave model is used as an example to demonstrate how the transient expansion may influence the position of maximum emission intensity. Relationships among plasma velocity, spatial position, and integration time to the measured emission intensity and temperature profiles are discussed.

EXPERIMENTAL

A diagram of the experimental system is shown in Fig. 1. A pulsed KrF excimer laser (Questek Model 2680) is used as the ablation source. The 248-nm UV beam is directed into the sample chamber with the use of a mirror and focused onto the sample surface with a plano-convex UV-grade quartz lens with a 20-cm focal length. This lens is mounted on a micrometer translation stage so that focusing can be accurately adjusted. The pulse energy is monitored by a power meter. The laser's pulse duration is 30 ns and the repetition rate is 5 Hz. An aperture is placed between the excimer laser and the focusing lens to vary the laser beam spot size and energy at the target surface.

The samples are mounted on an aluminum rod and attached directly to a micrometer tilt stage. The samples are always placed before the effective focus of the lens. The samples are metallic copper (99.9% purity, Aldrich Chemicals) 2-cm-diameter disks and are approximately 1 mm in thickness. A flat and smooth surface of the Cu is obtained by polishing with silicon carbide paper. The polished surface is washed with water and acetone and then dried.

The ablation chamber essentially has the same geometry as used in our previous work,[34–36] but in this work was made entirely of quartz to allow observation of the laser-induced plasma. Gas flow through the chamber is regulated by a needle valve and measured with a mass flow meter (Matheson Model 8112-0423) at 1.0 L min^{-1}.

The central channel of the laser-induced plasma, normal to the target surface, is viewed in these experiments. For axial spatial resolution, the radiation of the plasma is observed at a right angle to the laser beam with the aid of a dove prism and a camera lens (f = 120 mm), in order to get the horizontal plasma image onto the vertical entrance slit of the Czerny–Turner spectrometer (Spex Industries Model 270M with a 1200-grooves/mm grating,

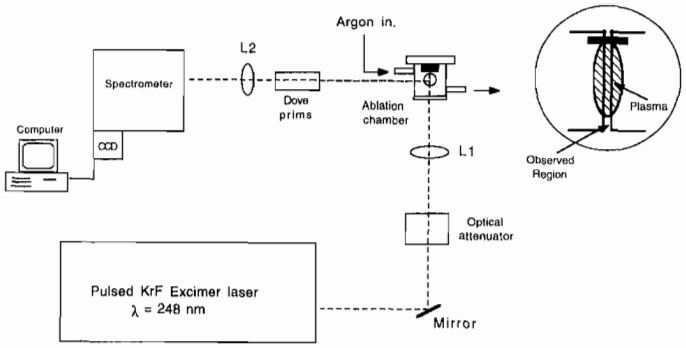

FIG. 1. Diagram of experimental system for measuring spatial emission intensity in laser-induced plasmas. Inset shows axial channel of plasma that is imaged by the lens and CCD spectrometer.

focal length = 270 mm). The spectrometer slit height is set at 10 mm to observe the entire axial extent of the plasma. The slit width is 12.5 μm. The spectrometer is equipped with a thermoelectrically cooled charge-coupled device (CCD) (EG&G Princeton Applied Research Model OMA VISION; 512 × 512 pixels) and controlled by OMA SPEC 4000 software (EG&G Princeton Applied Research). This CCD spectrometer system is able to view a 30-nm wavelength region simultaneously. A mercury lamp is used for wavelength calibration. The spatial resolution of CCD spectrometer plus lens arrangement is 40 μm. The total axial distance that can be measured in the plasma is 3.5 mm. The imaging ratio for the lens and spectrometer arrangement is 1:1.23.

The power density of the excimer laser beam is controlled by using an optical attenuator (Newport 935-10) to vary the laser beam energy, with a fixed beam spot size. Power density at the sample surface is estimated from the energy of the laser beam, the pulse width, and the calculated spot area. The spot area is calculated according to simple geometric optical principles and compared to burn patterns.

Emission intensity from the laser-induced plasma is integrated for 10 s during repetitive laser sampling, at each location on the target surface (the target is not rotated). A 60-s pre-ablation was used. Pre-ablation stabilizes mass removal, providing better reproducibility in the quantity of material removed per laser pulse.[34] The continuum emission background of the laser-induced plasma is subtracted from the copper emission-line intensity measurements. Continuum emission is measured at wavelengths on both sides of each Cu spectral emission line.

RESULTS AND DISCUSSION

Laser-Induced Plasma Spectra. Spectral emission-line intensity, background continuum intensity, and the excitation temperature are important characteristics of laser-induced plasmas for analytical applications. Spatially resolved, time-integrated Cu emission spectra from the laser-induced plasma, obtained with a 100-μm laser-beam spot size and 4.93-GW/cm^2 power density, are shown in Fig. 2. Cu atomic emission lines at 510.55, 515.32, 521.82, and 529.25 nm are observed. Cu-ion emission lines were not observed, in this case because of their short lifetimes in the plasma and the time-integrated measurement tech-

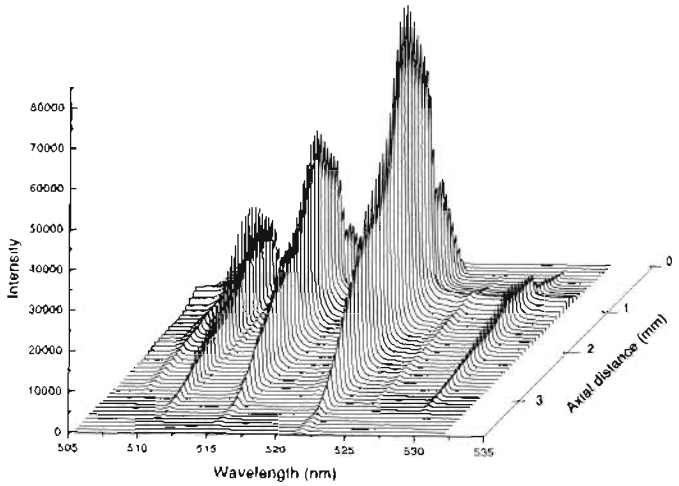

FIG. 2. Integrated Cu emission intensity vs. axial position in the laser-induced plasma with power density = 4.93 GW/cm².

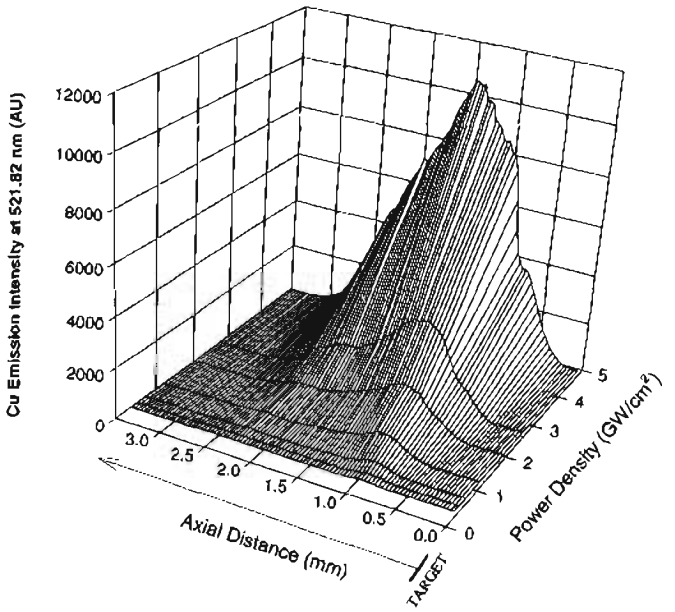

FIG. 3. Spatial distribution of the Cu(I) 521.82-nm emission lines as a function of laser beam power density.

nique. Cu-ion emission has been reported to exist for only about 200 ns after the laser pulse;[37] Cu atomic emission can last for several hundred microseconds.[38] Therefore, for time-integrated measurements, ionic emission intensities will be weak in comparison to the atomic emission. Strong plasma continuum emission from free–free and free–bound transitions (for ablation into atmospheric-pressure gas) occurs on time scales of less than a microsecond.[37]

From the data in Fig. 2, the copper lines extend about 3 mm above the metal surface, with the peak emission intensity at approximately 1.5 mm from the surface. The ratio of line emission intensity can be used to determine the excitation temperature of the plasma at each axial location, discussed later in this paper. Line broadening and self-absorption have been reported for laser-induced plasmas, primarily for short time delays, with the use of time-resolved measurements.[37,39,40] If self-absorption occurs, it should be noticeable at the high power density, and the full width at half-maximum (FWHM) of the emission line will change at the different axial positions, because of different plasma densities. The nonresonance emission lines selected in this work show the same linewidth (within the 0.063-nm spectral resolution of the monochromator) at the different axial positions and the different power densities studied. Therefore, broadening and self-absorption are assumed to be negligible in their influence on the time-integrated emission lines reported in this work.

The axial intensity distribution is primarily dependent on the power density of the laser, which can complicate analytical utility. The spatial distribution of the 521.82-nm Cu emission intensity at laser power densities from 5 to 0.4 GW/cm² with a fixed 100-μm laser-beam spot size is shown in Fig. 3. The spatial extent of the plasma diminishes as the power density decreases. This effect is better shown when the emission intensity is normalized to the maximum intensity for each curve, as shown in Fig. 4 (same experimental data as Fig. 3). The peak emission intensity is closer to the target surface at lower power densities. For low laser power densities, there is only one peak in the Cu emission intensity spatial profile in comparison to extensive shoulders at the higher laser power densities. The position of peak emission intensity occurs farther from the surface as the power density is increased, as shown in Fig. 5.

Laser-Induced Plasma Temperature. Temperature is an important property of an analytical excitation or atomization source, and it needs to be known to understand vaporization, atomization, and excitation processes. In order to calculate the excitation temperature in the laser-induced plasma, the Boltzmann two-line method is used, on the basis of the assumption that the Boltzmann distribution for excitation energy occurs in the second plasma region. The Boltzmann distribution is assumed for two reasons. First, the plasma expands into an atmospheric-pressure gas, resulting in numerous collisions over hundreds of microseconds, thereby equilibrating the thermodynamic excitation temperatures. Departures from local thermodynamic equilibrium at the later time, observed because of the expansion, will be small. Second, the range in wavelengths that are simultaneously observed is narrow, so that differences calculated in the excitation temperature due to wavelength by the Boltzmann method will be negligibly small. The 521.82- and 510.55-nm atomic Cu emission lines are used to calculate the excitation temperatures reported in this work. In an effort to verify local thermodynamic equilibrium, four Cu emission lines were used for the Boltzmann plots at several power densities. These data exhibited a linear fit with a correlation coefficient of 0.98. Temperatures calculated with four emission lines were similar to those from the two-line method. The degeneracies and Einstein coefficients were taken from Reader and Corliss.[41] A good signal-to-noise ratio for the Cu line emission intensity is necessary for excitation temperature calculations. For high incident laser power densities in which high LIP emission intensities are measured, the temperature can be calculated from 0.3 to 3 mm from the target surface. In the

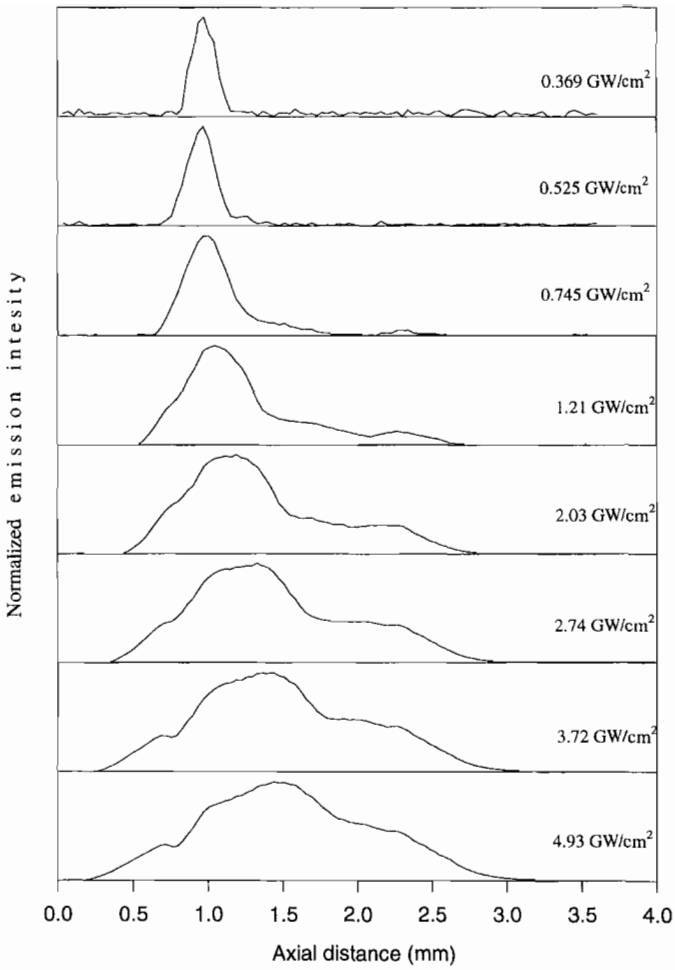

FIG. 4. Normalized axial spatial emission intensity vs. power density from data in Fig. 3.

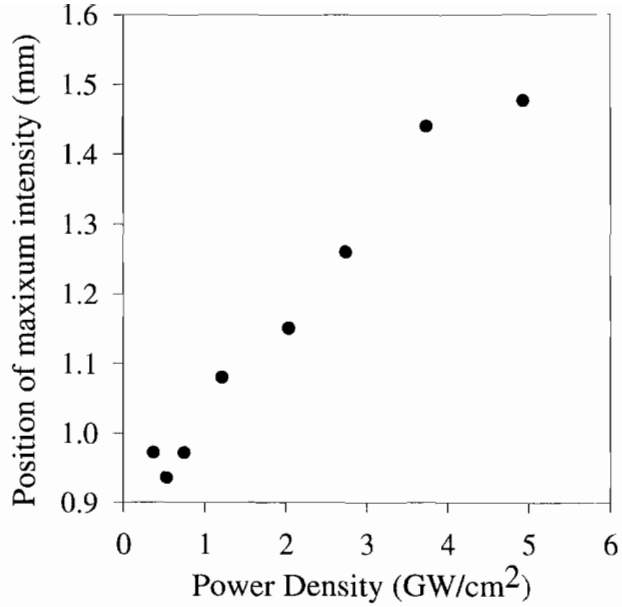

FIG. 5. Measured peak position of Cu(I) emission intensity as a function of power density.

case of low power density, the temperature can be calculated only from 0.7 to 1.8 mm from the target surface.

Excitation temperature spatial profiles calculated from the measured Cu emission profiles at two different power densities are shown in Figs. 6 and 7. For 0.525 GW/cm², the calculated excitation temperature varies from 11,000 to 6000 K and decreases with distance from the surface (Fig. 6). At 4.93 GW/cm², the temperature is 12,000 K at a height of 0.3 mm and then decreases to 7200 K at 2 mm. It then increases to about 8500 K at 2.5 mm and decreases again to 7500 K (Fig. 7). The maximum in the temperature spatial profile does not overlap with maximum plasma emission intensity. The maximum temperature is always closest to the target surface before the emission intensity has peaked. To fully analyze the intensity and temperature spatial distributions requires a complete description of plasma expansion dynamics, excitation, and recombination—which is outside the scope of this paper. At low laser power densities (Fig. 6), plasma conditions based on temperature and number density might coincide with the measured temperature and emission intensity behavior. However, recombination effects alone cannot explain the high laser power density (Fig. 7) temperature and emission behavior. Also, the plasma continuum emission profile (not shown) does not track with the temperature, which should be the case for a stationary plasma.[18] By using a known shock-wave model for laser plasmas, we demonstrate how the offset in these data may be due to the measurement technique, in which time-integrated emission intensity is measured during the plasma expansion processes.

Plasma Expansion. Thermal and fluid dynamic processes can influence the correlation between time-integrated emission intensity measurements and calculated temperature spatial profiles of an explanding ablation plume. Geohegan published time-resolved photographs of visible plasma emission from laser ablation of a YBCO target at 1 J/cm² under 100 mTorr oxygen.[25] Two components of the expanding plasma were identified. The first component with gas velocities of 10^6 cm/s lasted about 1 μs. The second (slower) component appeared after 2 μs, and existed for approximately 500 μs in a vacuum.[27] At atmospheric pressure, the laser-induced plasma propagates into an ambient gas as a shock wave. The expansion boundary of this luminous plume was described as a function of time with the use of a shock model or a drag model.[25–30]

Emission intensities measured in these experiments are along the central channel of the plasma leaving the surface of the target, as shown in Fig. 1. At each distance from the surface, the total emission reaching the CCD detector includes the intensities emitted along the line of sight that extend through the entire plasma, normal to the central channel. The intensity measured at each position x along the central channel is a line integration of plasma emission. Therefore, even though the measured intensity along the central channel is one-dimensional, the overall intensity is still due to a three-dimensional expansion of the plasma. A three-dimensional treatment of plasma dynamics, though, is difficult to tractably analyze. However, some simplifying assumptions may be made for our experiments. The plasma is essentially symmetric about the central channel, and its forward velocity is much greater than the radial expansion, for laser-beam spot sizes that