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Fundamental characteristics of laser–material interactions (ablation) in noble gases at atmospheric pressure using inductively coupled plasma-atomic emission spectroscopy

Richard E. Russo^{a,*}, Xianglei L. Mao^a, Manuel Caetano^b, Mark A. Shannon^c

^a Lawrence Berkeley Laboratory, Berkeley, CA 94720, USA

^b Escuela de Química, Universidad Central Venezuela, P.O. Box 47102, Caracas 1020-A, Venezuela

^c Department of Mechanical Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA

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Abstract

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is used to study fundamental behavior underlying the explosive removal of solid material by high power pulsed laser irradiation. The influence of power density (irradiance) and carrier gas environment on the mass ablation rate behavior is discussed. Data are presented for nanosecond and picosecond laser ablation of metals.

1. Introduction

Understanding the fundamental processes occurring during high-powered laser–material interactions (laser ablation) is important to numerous applications, including chemical analysis, thin film deposition, lithography, medical, and numerous others [1–6]. In this work, inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is employed for studying the behavior of laser ablation at atmospheric pressure, as a function of power density and gas environment. The ICP is widely used in analytical atomic spectroscopy because of its ability to dissociate chemical species and excite the resultant vapor to optical emission. Simultaneous multi-element quantitative analysis provides a direct measure

of the mass ablation behavior. These studies serve to elucidate issues related to energy coupling to the target surface, based on power density and gas environment. These studies also serve to define the conditions for using laser ablation as a sampling approach for direct solid chemical analysis.

2. Experimental

A diagram of the experimental system is shown in Fig. 1. A XeCl excimer laser (Questek Impulse, $\lambda = 308$ nm) and Nd:YAG laser (Continuum, $\lambda = 266, 1064$ nm) were used for the ablation studies. The excimer laser has a pulse width of 30 ns and pulse energy of 200 to 550 mJ. By varying the distance of the target from lens L1, the focused spot size of the laser beam on the target is changed, thereby changing the incident power density. For the

* Corresponding author.

excimer laser, typical power density at the target surface was in the range of 10^7 to 10^9 W/cm². The Nd:YAG laser has a pulse width of approximately 35 ps and pulse energy of 10–40 mJ. Power density could be varied from approximately 10^9 – 10^{11} W/cm², by changing the lens to target distance. The target (sample) is placed in an ablation chamber in which the carrier gas can be varied. The gas carries the ablated vapor into the ICP where it is excited to atomic emission. The gases are mixed in a T-connector so that the ICP temperature and excitation characteristics can be kept constant during studies of gas effect on the laser ablation process. A CCD detector coupled to a monochromator is used to monitor multiple wavelengths simultaneously or to study the vertical profile of emission lines throughout the ICP.

3. Roll-off

Changes in atomic emission intensity in the ICP are directly related to changes in the quantity of mass ablated from the target. ICP-AES measurements for both picosecond and nanosecond laser ablation versus power density are shown in Fig. 2. These data are for Cu emission during laser sampling of pure copper samples (pure materials are used for demonstration). Several important observations are apparent from these data. First, the lower-energy (6 mJ) picosecond laser ($\lambda = 266$ nm) provides over an

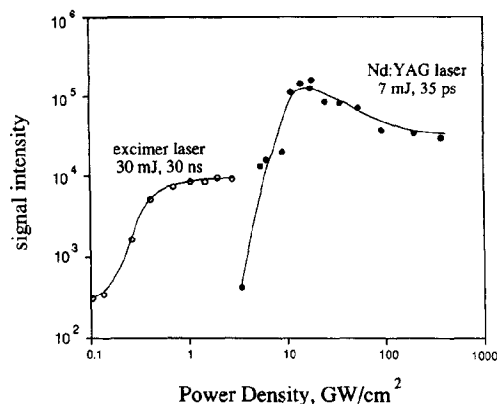


Fig. 2. Nanosecond and picosecond laser ablation of copper measured using ICP-AES. The curves show the roll-off in intensity for each laser as the power density is increased.

order of magnitude greater ICP-AES intensity than the higher energy (30 mJ) nanosecond laser ($\lambda = 248$ nm), pointing out the importance of the energy-deposition per unit time in ablating material from the target. Second, for both lasers, the quantity of material ablated increases with power density. However, for both nanosecond and picosecond laser ablation, the quantity of ablated material reduces as the power density is further increased, indicating a change in the coupling efficiency of laser energy to the target. The plateau or *roll-off* in mass ablation is likely due

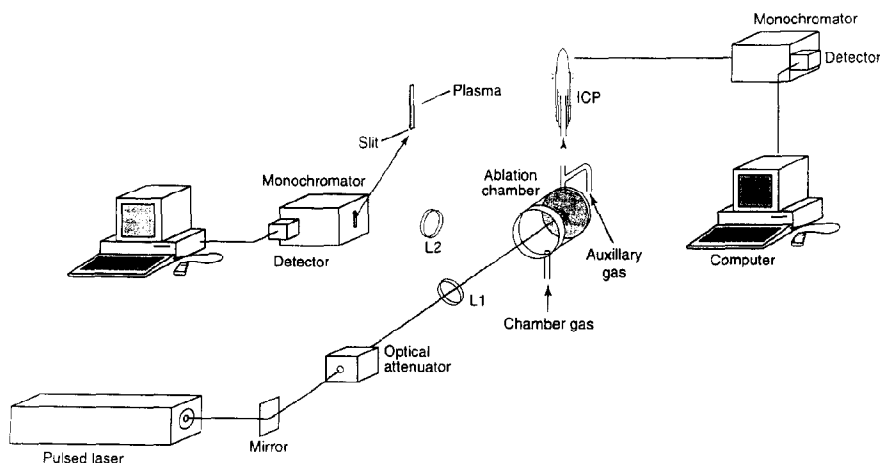


Fig. 1. Experimental setup of the laser ablation ICP-AES system. Atomic emission is measured in the ICP as a function of gas environment in the ablation chamber. The second monochromator can monitor the laser induced plasma.

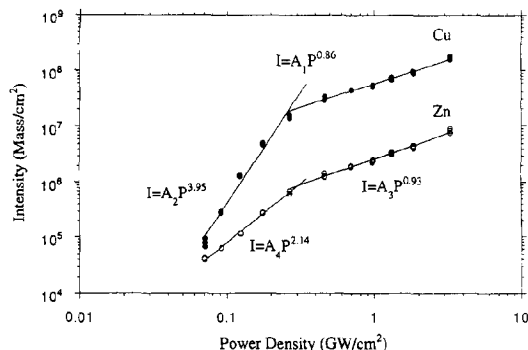


Fig. 3. ICP-AES intensity normalized to laser beam spot area. Nanosecond laser ablation of brass (Zn and Cu) versus power density.

to increased absorption and/or reflection from the laser-induced surface plasma (plasma shielding) by Inverse Brehmstrahlung [5]. A complete discussion of plasma shielding is outside the scope of this paper. We have performed several supporting experiments to confirm that the change in mass ablation is not due to the sampling process, but to the laser material interaction itself. Similar behavior was measured for numerous samples, including metals, alloys, oxide insulators, and glasses [7–10].

Mass ablation *rate* is defined as the total mass ablated per unit time and unit area. Therefore, ICP emission intensity divided by laser-beam area is proportional to mass ablation rate. The mass ablation rates for Zn and Cu (brass sample) versus power

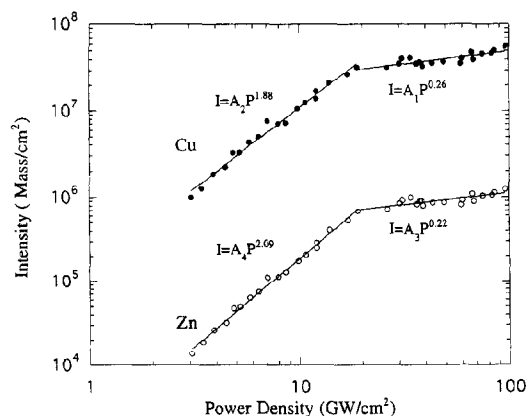


Fig. 4. ICP-AES intensity normalized to laser beam spot area. Picosecond laser ablation of brass versus power density.

density are shown in Figs. 3 and 4, using nanosecond and picosecond laser sampling, respectively (the same laser conditions as above were used for these measurements). Brass is an excellent sample to demonstrate capabilities of these studies. The brass sample composition is 60% copper (bp. 2567 K) and 40% zinc (bp. 907 K). The rates follows a power law dependence with two distinct slopes over this power density region. The mass ablation rate exponentially increases in the low power density regime and drops to near unity at high power densities, again demonstrating the roll-off in efficiency of laser ablation. For the UV nanosecond sampling, Zn and Cu exhibit a different mass ablation rate versus power density before the roll-off. Unfortunately, this difference means that the ratio of Zn to Cu varies versus power density; i.e., fractionation occurs in the lower power density regime. The rates and ratio become constant after the roll off. For the picosecond case, the rates and the ratios are essentially the same in both regions, indicating that fractionation is not significant for picosecond ablation.

4. Inert gas dependence

Gas environment can be varied to study its effects on laser ablation behavior at atmospheric pressure using ICP-AES. As long as the total gas composition is constant, the ICP temperature and excitation characteristics should be constant for studying effects of

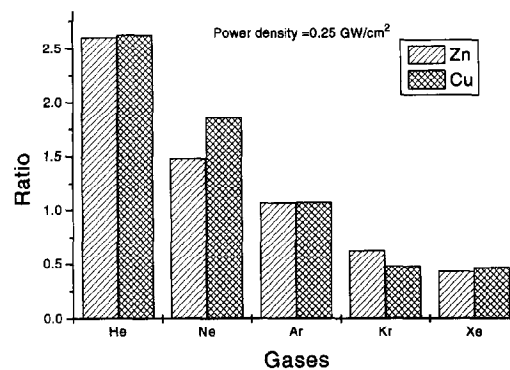


Fig. 5. Zn/Cu ratio relative to Ar measured in the ICP using different inert gas environments in the ablation chamber. Nanosecond laser ablation with power density = 0.25 GW/cm².

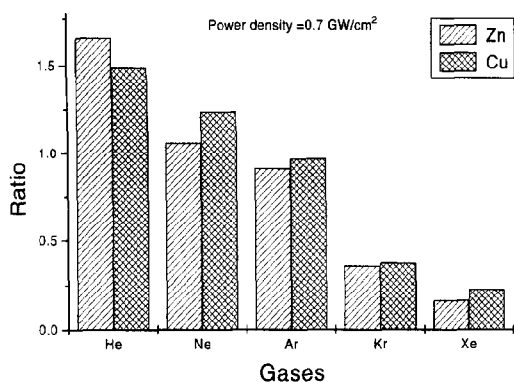


Fig. 6. Zn/Cu ratio relative to Ar measured in the ICP using different inert gas environments in the ablation chamber. Nanosecond laser ablation with power density = 0.7 GW/cm^2 .

gas environment. The data in Figs. 5 and 6 show the atomic emission intensity in the ICP for Zn and Cu from laser ablation of brass, versus inert gases with decreasing ionization potential. The power density at the brass target was 0.25 GW/cm^2 and 0.7 GW/cm^2 for Figs. 5 and 6, respectively. The data represent the ratio of the Zn and Cu emission intensity from laser ablation in each gas to that in Ar. Because the data are the ratio to Ar, the change in ICP-AES signal intensity represents the change in laser ablation versus carrier gas. For these initial data, the intensity ratios appear to be related to the ionization potential of the gas; the amount of ablated mass is highest in He and decreases as the ionization potential of the gas decreases. Zn and Cu appear to be equally effected by the gas environment. The increase or decrease (depending on the inert gas) in intensity (mass ablation) compared to Ar is also power density dependent. At 0.25 GW/cm^2 , the enhancement in He was a factor of 2.5, compared to only approximately 1.5 at 0.7 GW/cm^2 . The data in Fig. 7 show the effect of inert gas on the Zn ratio as a function of power density. The lower the power density, the greater the influence of ionization potential. These data indicate that the ionization potential of the gas may have an effect on plasma screening, the power density level in which laser energy is coupled to the laser induced plasma instead of the target surface. An alternate effect could be transport changes since the mass density of the gases is different in these

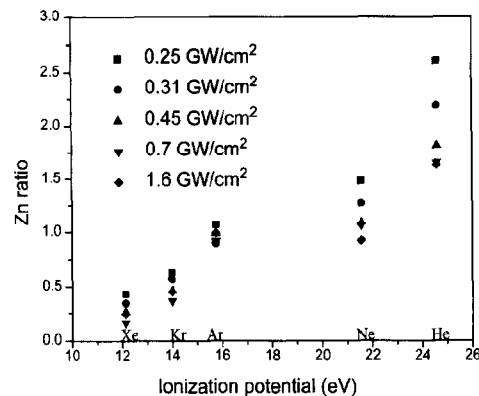


Fig. 7. ICP-AES intensity of Zn in different five inert gas environments relative to intensity in Ar. Nanosecond laser.

experiments. However, the Zn and Cu intensity change versus power density (cf. Fig. 7) for each gas, indicating that the change is due to the laser ablation process and not primarily transport. The initiation and propagation of a laser-induced shock wave is mass density dependent, which can also have an influence on the total mass ablated in each gas environment. The influence of mass density and resultant shock wave pressure has not been investigated in this preliminary work.

If plasma shielding is a primary mechanism for the roll off in mass ablation rate versus power density, then the gas environment should influence the

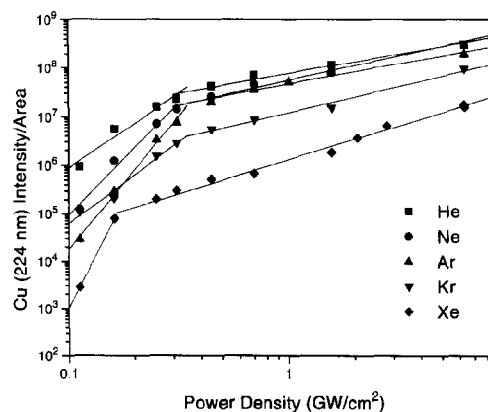


Fig. 8. ICP-AES mass ablation rate behavior as a function of power density and inert gas environment for nanosecond UV laser ablation.

power density at which roll off occurs. The data in Fig. 8, although preliminary, indicate that the roll-off in mass ablation occurs at a lower power density for lower ionization potential gases, especially for xenon. These data were obtained using the nanosecond excimer laser ($\lambda = 308$ nm) as the power density was increased. The absolute intensity scale is not valid for comparison among the gases in this figure because the data are not rationed to Ar; the excitation temperature in the ICP is not normalized.

5. Conclusion

ICP-AES is a unique technology for studying laser ablation at atmospheric pressure and versus different inert gas environments. ICP-AES intensity which represents the quantity of mass ablated shows a roll-off in mass ablation rate as a function of power density. The change in mass ablation rate (roll-off) is proposed to be due to plasma shielding by Inverse Brehmstrahlung. Nanosecond laser ablation was found to cause fractional vaporization before the measured roll-off, whereas fractionation was not significant for picosecond laser ablation in both mass-ablation rate regions. Finally, preliminary data indicate that the ionization potential of the gas environment may influence plasma screening by shifting the point at which roll off occurs.

Acknowledgements

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