Optical analysis of the ablation processes in pulsed laser deposition

Adam Cohen
Physics Concentrator
The College of William & Mary
Advisor: Anne Reilly
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I. Abstract

Pulsed laser deposition, or PLD, is a powerful technique for growing thin films of many different substances, ranging from high temperature supercondcutors to biocompatible materials. Films are grown onto a substrate from material that is ablated from a target by interaction with a high fluence, pulsed laser. One disadvantage, however, of PLD is that the processes which occur during ablation/deposition are not well understood or controlled. The purpose of this project is to see if optical spectroscopy can be used to monitor and understand the PLD process with a very new laser source, namely, the Jefferson Lab Free Electron Laser. The Free Electron Laser (FEL) has not been used to study PLD. Our work has shown what one can expect with basic optical spectroscopy: temperature measurement from blackbody emission, and superimposed atomic spectral lines.

II. Introduction

Pulsed laser deposition, or PLD, is a technique by which material is ablated from a target by interaction with a high fluence, pulsed laser beam and deposited onto a substrate. As such, it is an extremely adaptable and powerful technique for the growth of thin films.[1] The last decade has seen many experimental and theoretical investigations of PLD, especially for production of high-temperature superconducting films, oxide thin films, and ferroelectric films.[2-3] The process has been revealed to have many advantages, such as, for example, the versatility of the experimental setup. Indeed, the prospects for modifying the system geometry and ambient gas parameters make PLD an admirable technique for growing a wide variety of thin films with excellent properties.[1] In fact, it is due to the relative ease of performing PLD and the ability to grow films that would be very difficult, if not impossible, to grow by other methods that it can be assumed that the applications of the technique will continue to advance.[2]

The great flexibility of PLD is made possible in part by the extreme sensitivity of the resulting film quality on laser parameters such as wavelength, pulse width, and intensity. This may be a hindrance, especially since many of these effects are not well understood. However, if this dependence could be studied and controlled, a greater overall command of the deposition process could be achieved.[2]

The purpose of this project is to see if optical spectroscopy can be used to monitor and understand the PLD process with the Jefferson Lab Free Electron Laser. Using a very simple CCD spectrometer, we hoped to learn something about the ablation process through an analysis of the plasma emission. We were able to see very clear plumes,

significant blackbody emission, and evidence of spectral lines. The results show promise that optical spectroscopy can be used to monitor PLD.

III. Theory

A. *Background Theory*

Pulsed Laser Deposition, or PLD, is a process in which a high fluence, pulsed laser beam strikes a material, interacting with it in such a way as to evaporate some of the matter and form a plasma plume. This plume then interacts with a substrate, condensing into a thin film. The key to understanding PLD lies in the laser-target and laser-plasma interactions. As laser light strikes the target, it is absorbed via the excitation of the outer atomic electrons. When the excitation energy exceeds the binding energy of the target material, bond breaking may occur and target ablation takes place.[3]

The target material absorbs a great deal of the laser energy as heat, which is then conducted along the entire volume of the disk. Thus, the target will get heated to a certain temperature, and will emit electromagnetic radiation. The plasma plume will also contain a great deal of heat, and thus will also emit radiation. A blackbody signature can characterize this radiation, due to the fact that the plasma can be characterized at being at a certain defined temperature. This expectation has been confirmed through experimentation.[4]

B. *Calculating the Temperature of the Target*

A great deal of heat results from the interaction of the laser and the target, and one can approximate the heating process as the propagation of a heat wave into the target in accordance with a one-dimensional heat conduction equation.[3] With the appropriate boundary conditions, the value of the average temperature as a function of the laser and target parameters is calculated to be:[3]

$$\langle T \rangle = \left(\frac{2}{\pi} \right)^{1/2} \frac{I_a (a t_p)^{1/2}}{k} = \frac{1}{\sqrt{2}} T_{\max} \qquad (1)$$

Where I_a is the absorbed laser intensity in [W/cm^2], κ is the heat conduction coefficient in [J/(s cm K)], t_p is the laser pulse duration, and a is the thermal diffusion coefficient, which is defined as:[3]

$$a = \frac{\kappa}{C_p \rho_0} \tag{2}$$

Where C_p is the specific heat in [J/(g K)] and ρ_0 is the target material density in [g/cm^2][3].

This is the case for a single laser pulse. Actual high pulse lasers have single pulse durations on the order of a nanosecond or picosecond. Thus, it is far more useful to discuss things in terms of repetitive pulses. For repetitive pulses, the average temperature over n number of pulses is given by:[3]

$$\overline{T}_n \cong 2T_m \left(\frac{t_p}{t_{pp}} \right)^{\frac{1}{2}} \tag{3}$$

Where t_p is the pulse duration, t_{pp} is the time between laser pulses, and T_m is defined as:[3]

$$T_m = (T_{\max})_1 \tag{4}$$

T_{max} of the first pulse can be derived from the average temperature of the pulse as shown in Equation (1)[3].

As stated above, we expect the plasma plume to exhibit a characteristic blackbody pattern in it radiation. The blackbody curve is given by this relation:

$$u(\lambda) = \frac{8\pi hc\,\lambda^{-5}}{\exp\left(\frac{hc}{kT\lambda}\right) - 1} = \frac{5 * 10^{-24}}{\exp\left(\frac{0.0144}{T\lambda}\right) - 1} \tag{5}$$

Where h is Planck's constant, k is Boltzmann's constant, T is in Kelvin [K], and λ must be in meters [m]. Using this relation, the temperature can be calculated from the experimental data.

As an example of the temperatures we expect, our carbon target has a heat conduction coefficient, ***k***, of 0.063 W/cm K, from which we calculated a thermal diffusion coefficient, *a*, of 4×10^{-2} cm^2/s, according to Equation (2). When running the laser at 75 MHz at a power level of 200 W (focused into a 100-micron size spot), t_p is 650×10^{-15} s and t_{pp} is 53×10^{-9} s. When these numbers are inserted into Equations (1), (4) and (3), we get the approximate values T_{max} = 54000 K and T_n = 3000 K.

IV. Experimental Method

The experiments for this study were conducted primarily at the Free Electron Laser (FEL) at the Thomas Jefferson National Accelerator Facility (TJNAF). The qualities of the TJNAF-FEL set it apart from other commonly used PLD sources such as excimer, Nd:YAG and CO_2 lasers. In the pulsed mode the TJNAF-FEL provides 58 μJ per pulse at a repetition rate of either 18.7, 37.4 or 74 MHz.[2] The wavelength of the FEL was fixed at 3.1 μm for these experiments. Characteristics of some conventional lasers and the TJNAF-FEL are shown in Table 1.

Laser	***Pulse Width***	***Repetition Rate***	***Output Energy (per pulse)***
CO_2	100 ns	50 kHz	0.1 J
Excimer	10 – 30 ns	~100 Hz	0.3 J
TJNAF-FEL	~0.5 – 2 ps	18.7 or 37.4 MHz	25 μJ
Nd:YAG (ultra-fast)	30 ps	10 Hz	50 mJ

Table 1: PLD laser sources and their properties

The experimental setup is shown in Figure 1 below.

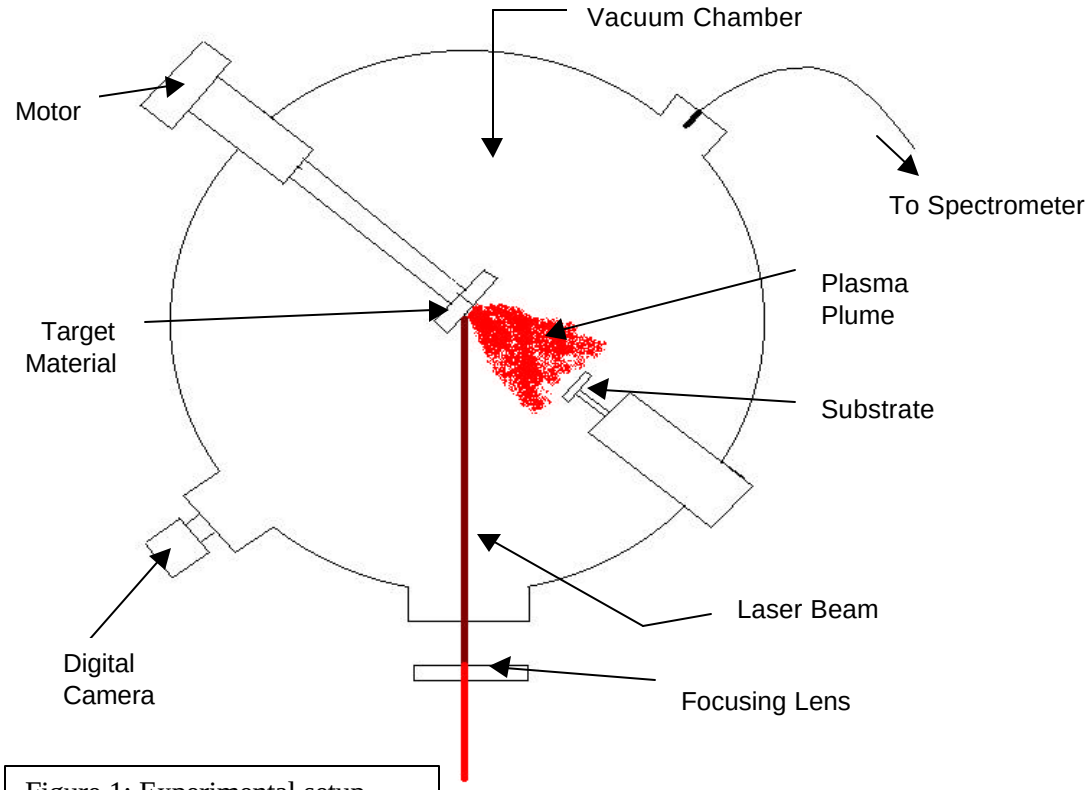

Figure 1: Experimental setup

The FEL laser beam gets focused onto a point on the rotating target, and creates a plasma plume, in some cases. This plume strikes the substrate, and thin films are deposited. While this is occurring, we have two measurement devices trained on the procedure. One is a digital camera, which we used to image the process and the other is a spectrometer. We used an Ocean Optics S2000 Miniature Fiber Optic Spectrometer, shown in Figure 2, a simple CCD-based spectrometer. It uses a crossed Czerny-Turner spectroscopic grating to disperse the light, and a Sony ILX511 linear silicon CCD array as its detector. The S2000 features of fiber-optic input cable that we either placed in the chamber, as shown in Figure 1 above, or in the case of open-air ablation experiments, right up next to the plume. The spectrometer was run with a PC running OOIBase v1.5 software.

Figure 2: Ocean Optics S2000 spectrometer, exterior

V. Results & Discussion

With the simple spectrometer, we were able to monitor emission of plumes and see significant blackbody radiation and, in some cases, individual plasma emission lines.

A. *Detecting Blackbody Radiation*

During ablation, we are able to see a plume of vapor/plasma shooting out of the target, as shown in Figure 3. The plume appears mostly white.

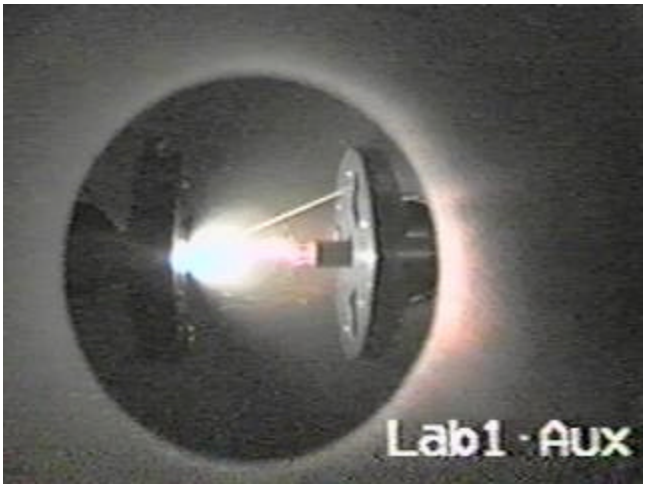

Figure 3: Laser ablation taking place inside vacuum chamber. Notice the white plume from the target on the left.

Emission spectroscopy reveals a large blackbody component. In order to be able to confirm, with our spectrometer, that this really is a blackbody curve, and to see if we could measure temperature, we took a spectrum of a known blackbody source – a 2800 K tungsten lamp (Ocean Optics LS-1 Tungsten Halogen Light Source). This spectrum and fit are shown in Figure 4:

$$S = I_B f \tag{6}$$

Where I_B is the blackbody function in Equation (5), and f is a function that accounts for spectrometer efficiency (grating, fiber, CCD). This correction function is shown in Figure 5.

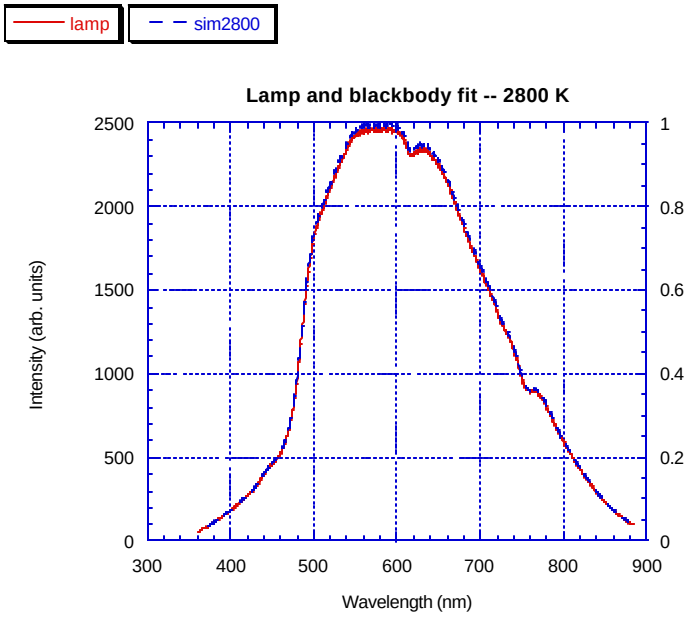

Figure 4: Spectrum (red solid) and fit to Eq. (6) (blue dashed) for a 2800-K lamp.

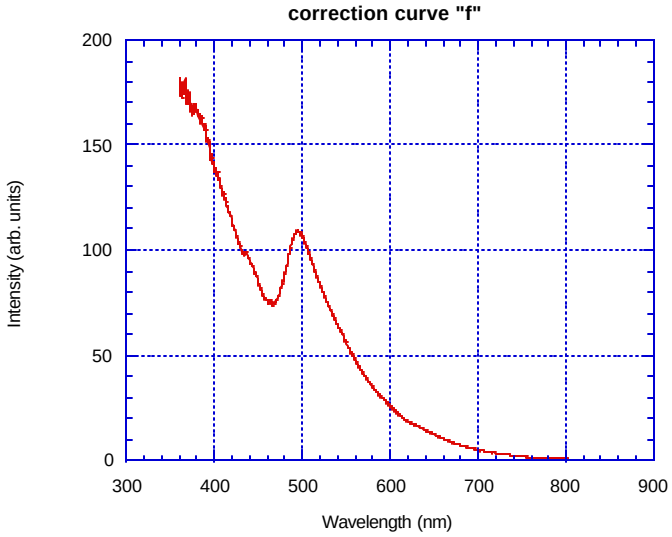

Figure 5: Correction function f from Eq. (6) taken from fit of 2800 K lamp spectrum.

With this f, we can then try to find the closest blackbody fit to other curves, and from this

estimate the temperature. For instance, Figure 6 shows a carbon target being ablated by the FEL at a power of 500 W and a repetition rate of 75 MHz, with a fit according to Equation (6), using the function *f* found from the 2800 K lamp spectrum. The curve is fit well, with a blackbody temperature of 3100 K. This temperature is close to what we calculated in section III, as well as that observed by others.[5]

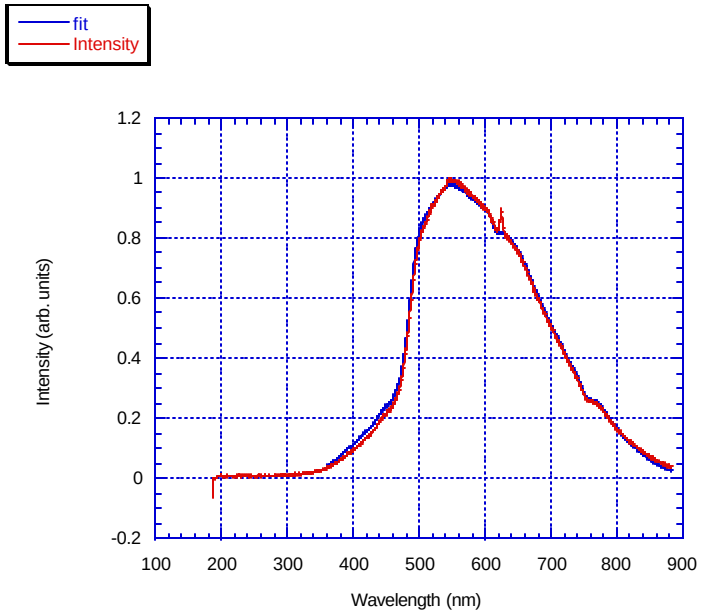

Figure 6: Carbon target ablated by FEL at 500 W (red), and corrected blackbody curve for T=3100 K (blue). Intensity has been normalized to 1.

B. *Blackbody emission as a function of laser power*

Once we had verified that we could indeed detect blackbody radiation in the plume, we were curious what effect the laser parameters – power and repetition rate – had on the ablation process. Our first test involved varying the laser power from 50 W to 500 W while keeping the repetition rate constant and using the same graphite target. The results are shown in Figures 7 and 8. A rapid increase in peak intensity of emission,

which is supported by other experiments[6], is demonstrated in Figure 7. There is also no noticeable change in peak wavelength, and thus no change in plume temperature, as laser power increases, as shown in Figure 8.

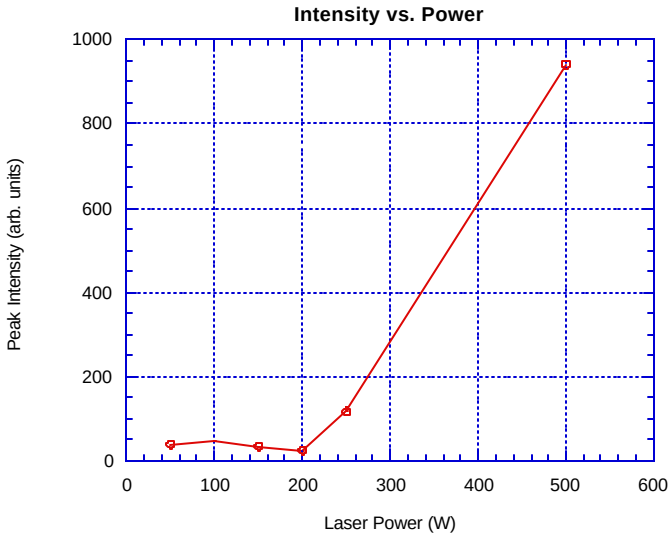

Figure 7: Peak intensity versus laser power for carbon target ablation.

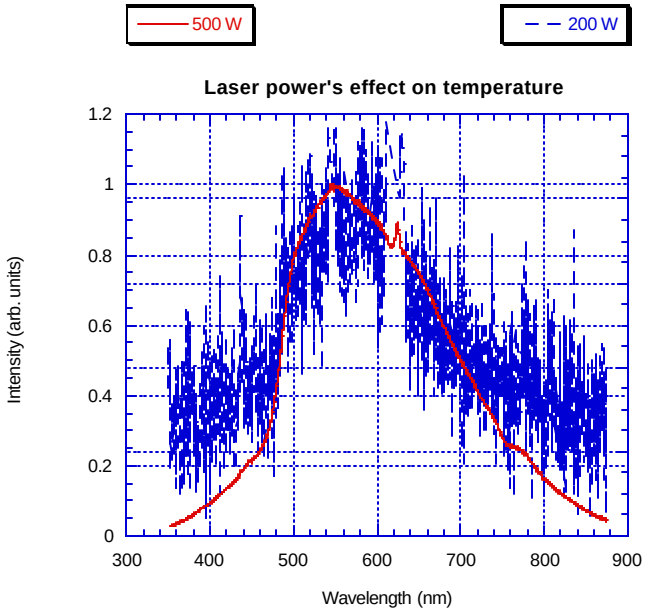

Figure 8: Effect of laser power on temperature. Approximate blackbody curves shown. Sharp peaks in 200 W curve are reflections of the FEL harmonics. Both curves have been normalized in intensity to the same maximum value.

C. *Blackbody emission as a function of laser repetition rate*

Our second experiment in testing the effect of laser parameters on the ablation process involved varying the repetition rate while keeping the power constant and using the same graphite target. The results are shown in Figures 9 and 10. There is a dramatic increase in intensity between the 74.85 MHz and 18.7 MHz repetition rates, as shown in Figure 9. The increase is by a factor of 2.5, the 74.7 MHz intensity being the higher value. The ratio of 74.7 to 18.7 MHz is 3.75, so this factor of 2.5 is within expectations. Since the curves are not shifted, there is no change in target temperature, as demonstrated in Figure 10. This result is intriguing, for the theoretical model predicts a temperature increase on the order of a factor of two as repetition rate increases from 20 MHz to 75 MHz. This could point to flaws in the theoretical model.

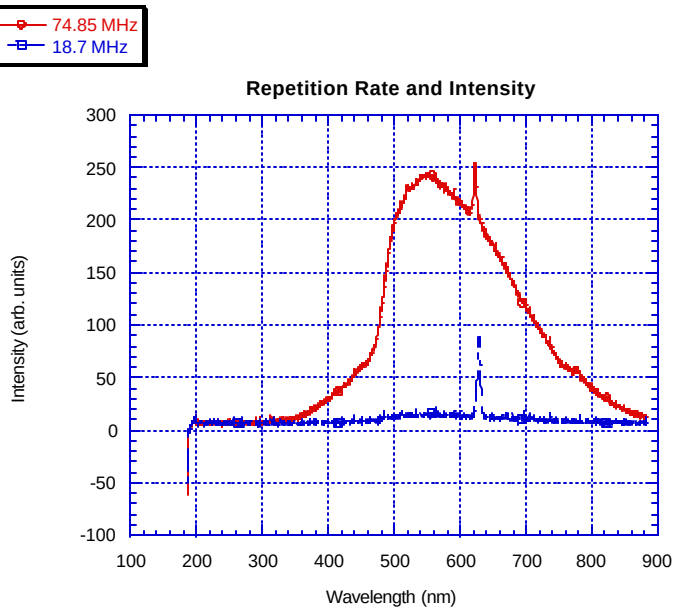

Figure 9: Effects of repetition rate on intensity.

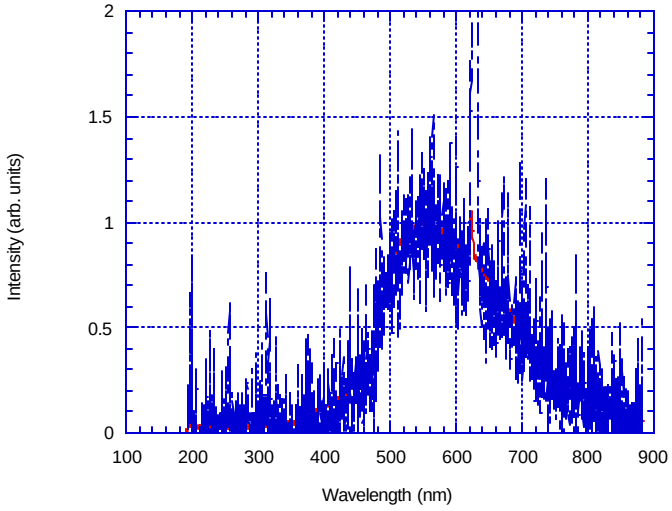

Figure 10: Effects of repetition rate on temperature. Red curve taken at repetition rate of 74.85 MHz, blue curve 18.7 MHz. Both curves have been normalized in intensity.

D. *Blackbody emission as a function of material*

Having ascertained the effects of laser parameters – power and repetition rated – on the ablation process, we next tested the effects of differing target materials on the process. The results are shown in Figure 11. The temperatures we extract are 2700 K for the Al_2O_3 target, as shown in Figure 12, and 3100 K for the carbon target from Figure 6.

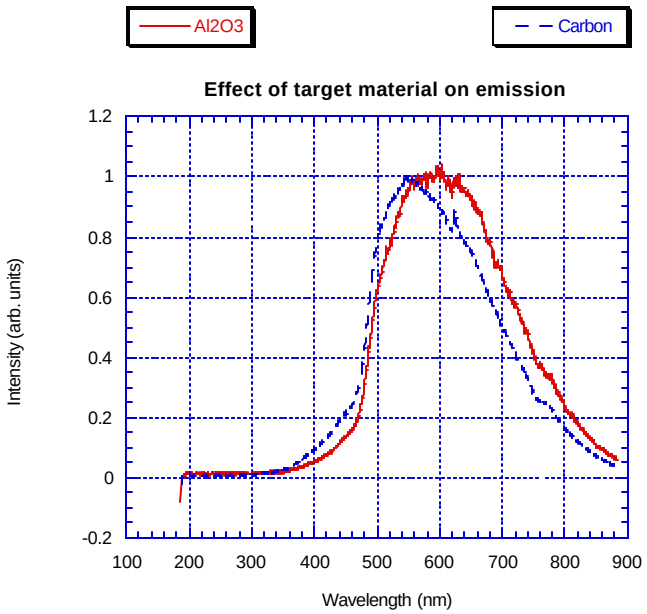

Figure 11: Effect of target material on plasma emission. Intensity has been normalized to same maximum value

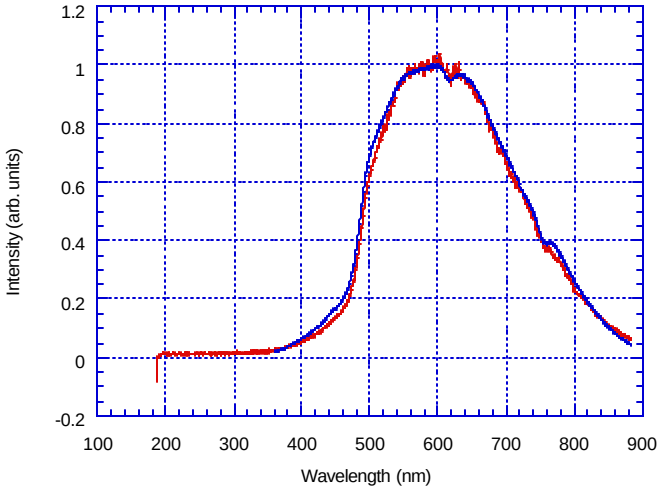

Figure 12: Emission spectrum (red) and fit from Eq. (6) (blue) for Al_2O_3 target in Figure 11.

E. *Individual spectral line emission*

When the laser interacts with the plasma plume, some of its energy is absorbed by the atoms, exciting them. Electrons are pushed into higher energy states, only to later fall back down to lower states. When this transition occurs, radiation is emitted at a specific frequency. This is atomic emission. Using optical spectroscopy, we hoped to observe some of these atomic emission lines in the plasma. Unfortunately, this proved to be quite difficult, as the spectral lines are hard to see. Most of the strong emission lines for the elements that made up the plasmas lie in the ultraviolet region of the electromagnetic spectrum – outside the frequency range of our spectrometer (we are able to detect wavelengths down to 200 nm). More of a problem, however, is that we are using infrared radiation for excitation, rather than the usual ultraviolet used for PLD. For instance, Figure 13 shows the emission spectrum from an iron target, with iron spectral lines overlaid. Though the spikes in the emission spectrum are evidently due to the presence of atomic spectral lines, it is not evident which line dominates. Clearly, there is broadening in the spikes. This broadening is due to both systematic causes, namely the spectrometer having only a 1-nm resolution, and physical causes, such as a “Doppler shift” due to atomic movement and the effect of atomic collisions in the target and plume. This is evidence for the contribution of any number of emission lines.

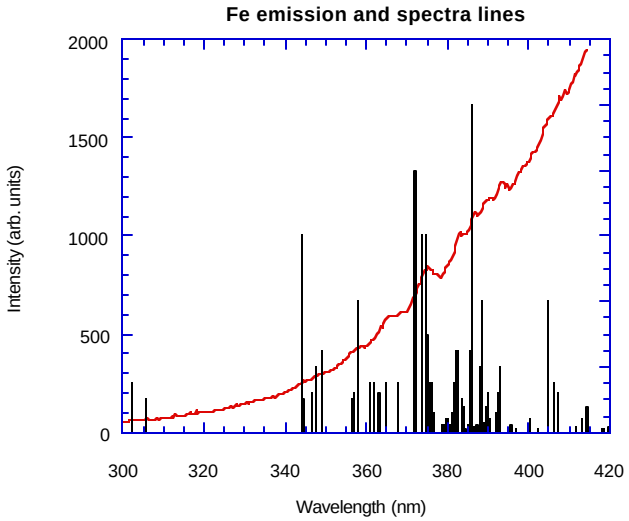

Figure 13: Emission spectrum from Fe target (red) with spectral lines due to emission from Fe neutrals and singly ionized states overlaid (black).

This is not the case with FeMn, however. Due to the manganese (Mn), we can see clear evidence of specific spectral line contribution. This is primarily due to the transition strength being so high. The emission spectrum from an FeMn target with the spectral lines overlaid is shown in Figure 14. Detail from Figure 14 showing the emission spike at approximately 405 nm is shown in Figure 15. The overlaid spectral lines demonstrate a clear correlation between atomic emission lines and the spike in the FeMn emission spectrum.

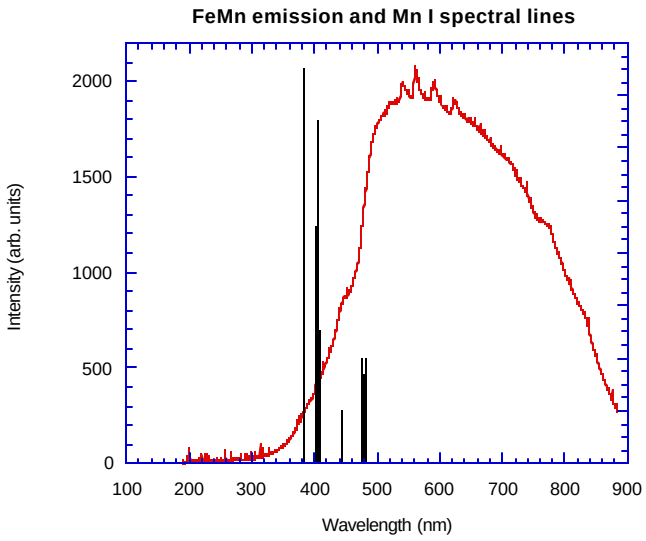

Figure 14: Emission spectrum from an FeMn target (red) with Mn neutral emission spectral lines overlaid (black).

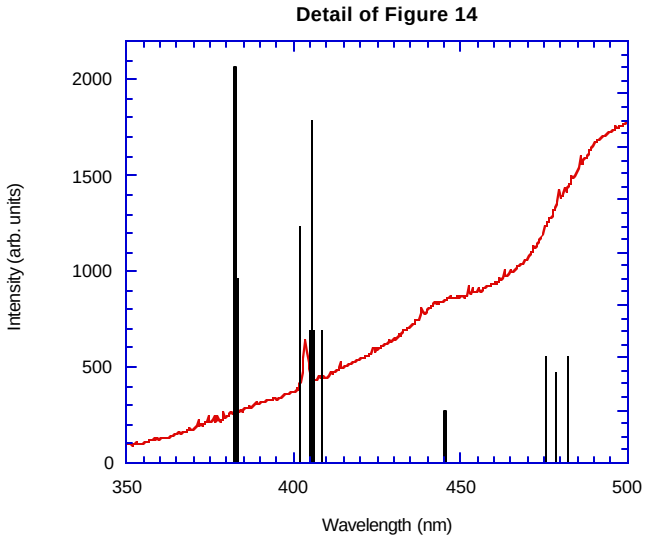

Figure 15: Detail of Figure 14 showing emission spike at ~405 nm for FeMn emission curve (red).

VI. Conclusions

Our work has shown what one can expect with basic optical spectroscopy: temperature measurement from blackbody emission, and superimposed atomic spectral lines. Optical spectroscopy is much more difficult because we have an ablating laser that is in the infrared region of the electromagnetic spectrum. The target materials we used have atomic emission spectra that are most visible in the ultraviolet range, which is the range in which lie most other laser sources used for PLD. Our experiment confirmed our ability to detect blackbody emission and from this calculate the temperature of the plasma plume. Tests of the effects of laser parameters on the ablation process yielded some surprising results, such as the absence of any temperature change when increasing the repetition rate. These results are intriguing, but limited by systematic problems with our optical spectrometer.

However, with better detection schemes, we may improve on our results. For example, CCDs are not as sensitive as photomultiplier tubes (PMTs) in detecting radiation. Using a scanning monochromator with a PMT may improve our ability to detect individual emission lines.

In addition, there may be a problem with the theoretical model used in these experiments. The model makes the assumption that the pulse length, t_p, is greater than 4 ps. The FEL operates with pulse lengths less than 4 ps, thus may not be in a heat diffusion regime. This could explain our seemingly analogous results.

VII. Further Research

The hope for emission spectroscopy is that we may be able to identify ions in the gas. But that task may be difficult to accomplish in the infrared region of the electromagnetic spectrum. The FEL may soon be tunable down to 1 μm and eventually through the ultraviolet region, which will make emission spectroscopy easier. Another experiment to be conducted is to time-resolve the emission from the plasma to see the effect of each individual laser pulse and the temperature buildup.

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