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Plasma spectroscopy of titanium monoxide for characterization of laser ablation

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Abstract. Ablation of titanium wafers in air is accomplished with 60 μs pulsed, 2.94 μm laser radiation. Titanium monoxide spectra are measured in the wavelength range of 500 nm to 750 nm, and molecular signatures include bands of the $C^3\Delta \rightarrow X^3\Delta$ α, $B^3\Pi \rightarrow X^3\Delta$ γ′, and $A^3\Phi \rightarrow X^3\Delta$ γ transitions. The spatially and temporally averaged spectra appear to be in qualitative agreement with previous temporally resolved studies that employed shorter wavelengths and shorter pulse durations than utilized in this work. The background signals in the current study are possibly due to particulate content in the plume. A chemical kinetic model of the plume is being developed that will be coupled to a diatomic emission model in order to extract a molecular temperature from the observed spectra.

1. Introduction

Titanium monoxide (TiO) emissions have long been of interest in astronomy [1, 2, 3, 4, 5], and recently been studied in numerous laser-induced breakdown spectroscopy (LIBS) experiments [7, 6, 10]. Computed line strengths are utilized to fit experimental TiO γ′ emission spectra [7] and discern a temperature of 3600 ± 700 K and 4200 ± 800 K at delays of 52 μs and 72 μs, respectively, after ablation in air using a Q-switched Nd:YAG laser with 1064 nm wavelength and 13 ns pulse duration. Using the same experimental setup [6], fitting of recorded $\Delta v = -1$ sequence data of the γ band yields a temperature of approximately 5000 K at time delays of 1-2 μs, and a reduced temperature of approximately 2500 K at a time delay of 50 μs. However, the fitted temperature depends on background contributions. In that same study, application of spectroscopic fitting routines to published TiO emission spectra [10] indicates a temperature of 2170 ± 60 K.

The present study investigates TiO emissions during long-pulse mid-infrared ablation of titanium wafers in air. Spatial and temporal averaging due to long spectrometer integration times and large viewing volumes cause the measured signal to be dominated by the most intense phase of the plume. For mid-infrared ablation of aluminum in air, it was found that the

plume was dominated by AlO emission rather than atomic or ionic emissions due to the rapid thermalization of the plume under weak laser-plume coupling at longer wavelengths [8]. It is unknown if the titanium ablation plume will undergo a similar rapid thermalization, since it has a much more complex molecular structure than AlO with numerous excitation and relaxation channels [9]. The purpose of this study is to perform laser ablation of titanium under the same conditions as [8] and semi-quantitatively compare the observed plume emissions to that study as well as previous works at shorter wavelengths and pulse durations.

2. Apparatus

A flashlamp-pumped Er:YAG laser device (Megawatt Lasers) operating at 2.94 μm with variable pulse duration between 50 and 400 μs, up to 1 J pulse energy, and a 10 Hz repetition rate is sent through a long-pass 2 μm filter to remove residual flashlamp radiation. The beam propagation was characterized with a minimum spot radius of 0.307 ± 0.02 mm and an M-squared-value of $M^2 = 17$. The temporal waveform with full-width, half-max (FWHM) of 60.23 μs has a steeper leading edge than a Gaussian temporal pulse, and includes significant ringing. With the spot size and pulse duration characterized, the maximum fluence was found to be 250 J/cm^2. The peak irradiance amounted to 4.15 MW/cm^2 when focused into a cryostat containing ambient laboratory air. Pulse-to-pulse energy jitter was typically less than 1%. The visible emission spectra are collected with an f/4 lens (perpendicular to the laser path and parallel to the wafer surface) and fiber-coupled to a spectrometer (Ocean Optics HR4000 Custom) that shows an optimized detection range of 350-800 nm. The instrument lineshape of the spectrometer is a slightly asymmetric Lorentzian shape with a 0.2-nm full-width at half-maximum. The relative spectral response was calibrated using a 1500 K blackbody source. With a single 10 μs integration time, the signal-to-noise ratio was 5. With a 100 ms integration time and five-pulse average, the signal-to-noise ratio exceeded 125.

The wafers were 99.9% pure titanium (MTI Corporation), single-side polished. The samples were stored in a desiccator, to reduce but not eliminate surface oxidation. The nominal titanium density of 4.5 g/cm^3, thermal diffusivity of 0.072 cm^2/s and heat of vaporization of 8.88 MJ/kg are assumed. The cryostat was mounted on a translation stage and was moved every 2-3 shots to avoid the formation of craters. Damage sites on the wafer were measured with a white light interferometer (Zygo ZeGage) with 0.1-nm depth resolution.

3. Results

In the experiments, single pulse effects show no splatter and very little melt flow. The occurrence of a raised center is likely due to the thermocapillary effect [11]. The features for two shots at 10Hz repetition rate are similar to the single shot case, but more pronounced in depth and height of the protrusion relative to the crater depth. Figure 1(a-i) depicts the effects of laser ablation of Ti wafers in ambient laboratory air. Using energy balance, the ablation threshold of titanium can be calculated as $I_{th} = \rho L_v \sqrt{\kappa t}$ where ρ is the density, L_v the latent heat of vaporization, κ is the thermal diffusivity, and t is the pulse duration. This definition yields a peak irradiance threshold of 1.42 MW/cm^2. With a pulse energy of 740 mJ, a pulse duration of 60.23 μs, and a spot size of 307 μm, the peak irradiance on the titanium wafer was 4.15 MW/cm^2. The thermal diffusion length can be taken as $L \approx \sqrt{4\kappa t} \approx 40$ μm using the pulse duration of the laser. For a beam diameter of 614 μm, there is not much transverse heat conduction. Figure 1(a) shows that melt features are relatively confined to an area approximately equal to the beam area.

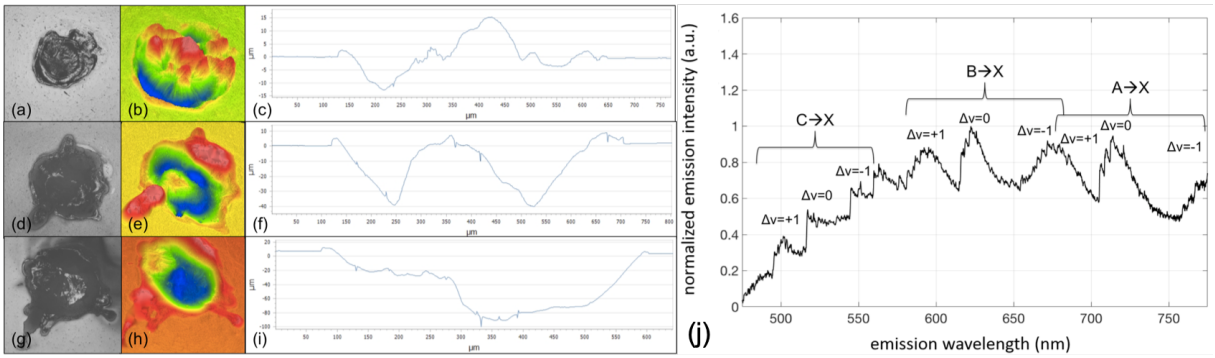

Figure 1. Single 250 J/cm^2, 60 μs pulse on Ti wafer optical image (a), white light interferometric image (b), and depth profile (c). Two pulses at 10 Hz repetition rate (d,e,f). Three pulses at 10 Hz repetition rate (g,h,i). Spatially and temporally averaged emission spectra (j).

Figure 1(j) displays spatially and temporally averaged emission spectra from various TiO bands [12] resulting from mid-infrared laser ablation of Ti wafers in air. The spatial and temporal averaging complicates the interpretation of a temperature, since the temperature evolves non-linearly over the lifespan of the plume. At the shortest integration time of 10 µs, which is long compared to atomic and molecular interactions but still shorter than the lifetime of the plume, no atomic or ionic emissions were observed at any delay time relative to the laser pulse. Thus, Figure 1(j) shows that the plume is likely dominated by TiO molecular emissions rather than atomic or ionic emissions.

4. Discussion and Conclusion

Longer wavelength and longer pulse duration lead to lower peak irradiance than that for time-resolved experiments [7, 6, 10], and lower signal-to-noise and lower signal-to-background in the recorded data, as well. Spatially and temporally averaged spectra appear qualitatively similar to temporally-resolved spectra recorded in other studies at time delays of several tens of µs after ablation with shorter wavelength and higher peak irradiance. The lack of atomic or ionic emissions could indicate that the shock front is comparatively weak and the plume thermalizes rapidly [8]. The spectra in the current study show significant background signals, potentially indicating particulate content in the plume. Relative populations of the A, B, and C states will be investigated using a chemical kinetics model and included in the diatomic emission intensity model [13, 14] for further investigations of recorded molecular titanium-monoxide signatures.

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