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COMMUNICATIONS

Role of Al–O_2 chemistry in the laser-induced vaporization of Al films in air

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Evidence for the prominent role of atypical reactions, and enhanced vaporization arising from resonant optical absorption of the exciting beam, in the pulsed-laser heating of thin films is presented. Time-resolved emission of Al and the reaction product AlO are monitored in the laser vaporization of Al films in air. Optical emission is observed up to 200 microseconds after an 8 μs heating pulse, indicative of long chemical lifetimes. Furthermore, increased emission from both Al and AlO up to 100 μs after the heating pulse, are observed when the laser wavelength is tuned to resonance with AlO transitions. Since the electronic resonance with the reaction product AlO affects the subsequent emission of Al, these measurements underscore the importance of physical and chemical processes peculiar to laser-induced vaporization, and ablation. *© 1999 American Institute of Physics.*[S0021-9606(99)02026-7]

I. INTRODUCTION

Ablation and laser-induced vaporization involve complex processes[1] that have found many uses. Ablation is used routinely for elemental analysis and for probing materials at extreme temperatures or pressures. More recent applications include materials synthesis, notably in the synthesis of high Tc superconductors[2] and the artificial structuring of materials and coatings.[3] Chemical reactivity is traditionally ignored in ablation studies but may be very important, particularly when interactions with a background atmosphere are present.[4] Calculations show that inclusion of chemical reactions in models modifies predictions regarding the mean energies, angular distributions, and composition of desorbed particles.[5]

The objective of this letter is to present measurements of atypical physical and chemical processes that occur with laser-induced vaporization. The dynamic processes that occur when a thin film of Al is heated in air with a pulsed laser at ambient pressure were investigated using simultaneous time-and-wavelength-resolved emission spectroscopy. The temporal profiles of Al and AlO populations were obtained by monitoring emission in real time. The well-known reaction[6] Al+O_2 to produce AlO is insufficient to describe the observed emissions.

II. EXPERIMENTAL METHOD

The experimental configuration in which time-and-wavelength-resolved emission from products generated in laser-heated thin films is monitored, is shown in Fig. 1. A complete description of the method to obtain time-resolved spectra during a single laser pulse can be obtained elsewhere.[7,8] Aluminum sheets of 0.8 or 3 micron thickness and with 99.1% purity (Goodfellow) were used as received. Heating was provided by an 8 μs laser pulse from a tunable flashlamp-pumped dye laser (Cynosure) whose wavelength λ_L was tuned from 506 to 514 nm in 2 nm increments. The light was focused normally onto a 1 mm-diameter spot on the sample placed inside a $1\times1\times5$ cm cuvette, positioned on a translation stage. The incident laser energy was 135–180 mJ at the sample, or a fluence of 17–23 J-cm^{-2}. The fluence was above the 5–6 J-cm^{-2} threshold at which irradiated Al (90 nm-thick film) is observed to vaporize during a faster 5–15 ns laser pulse.[9] In our experiments, the laser energy creates a 1 mm-diameter hole in the film. For each individual experiment, the sample was translated to a fresh film area. Emitted light was then collected from the central region with diameter 0.2 mm, and dispersed in wavelength (Spex 270M) and in time (Hamamatsu streak camera). The signal was then digitized on a charge coupled device (CCD) detector (Hamamatsu). For this work, the spectral bandpass was 0.7 nm. The temporal resolution was set to either 2 or 20 μs, with time coverage of 64, or 640 μs, respectively.

III. RESULTS

Time-resolved emission from Al levels at 396 and 394 nm were obtained. Emission from these two lines was observed up to 200 μs after the laser pulse, with a slow monotonic decrease in intensities. Time-resolved emission from AlO, corresponding to the $B\,^2\Sigma^+ \rightarrow X\,^2\Sigma^+$ $\Delta v=-2$, 0, 1, 2, 3, 4, and 5 bands was also observed from 400 to 570 nm at similar times. Dramatic changes in the spectra were seen as the heating wavelength λ_L was tuned from 506 nm where there is no resonance with Al or AlO, to wavelengths of 508, 510, 512, and 514 nm corresponding to transitions to the $B\,^2\Sigma^+$ $v'=0$, 1, 2, and 3 levels, via the $\Delta v=-1$ $B\,^2\Sigma^+ \leftarrow X\,^2\Sigma^+$ band of AlO.[10]

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[a] Under contract with Nova Research Inc.

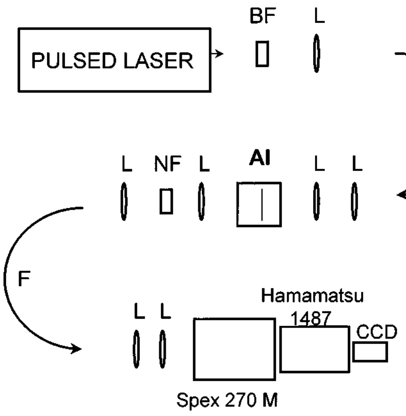

FIG. 1. Schematic diagram of the experimental method to measure time-and-wavelength-resolved emission from Al and AlO, produced from laser-induced vaporization of Al films in air. BF-bandpass filter, L-lens, F-optical fibers, Al-aluminum film sample in a cuvette mounted on a translation stage, NF-notch filter.

Typical time-and-wavelength-resolved emission spectra, with 2 μs resolution, are shown in Fig. 2 of the $\Delta v=0$ and $\Delta v=1$ bands of AlO. When the laser is on, strong emission from resonantly excited states is observed in the $\Delta v=0$ band. Only weak emission is observed in the $\Delta v=1$ band. With 2 nm increments in λ_L, profound changes in the spectra (intensities of wavelength-specific transitions are very strongly enhanced; these will be discussed in detail elsewhere) were observed. For the purpose of this paper, it is sufficient to recognize that resonant absorption is achieved with proper tuning of the laser wavelength to AlO transitions. When the laser turned off, ordinary emission from excited AlO is dominant. The spectra are characterized by clearly resolved bands degraded to the red.[10] These spectra are similar to those reported from AlO in experiments in which spectra were not temporally resolved.[11]

The time-dependence of the Al and AlO intensities when λ_L is off or on resonance with AlO bands is shown in Fig. 3. A typical 20 μs spectrum of the Al lines is shown in the inset, together with two Gaussian functional fits (ORIGIN, Microcal Software) of the peaks. The combined areas of the two fits represent the total Al intensity of the spectrum. The intensities of the different AlO bands behave similarly in time. Overlaid in Fig. 3 are the intensities of the $\Delta v=0$ band, represented by the areas under the spectra as shown in Fig. 2, and bounded by the wavelengths between 483 and 491 nm.

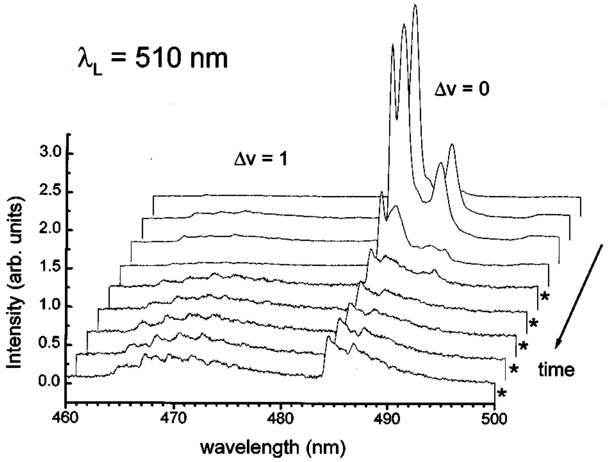

FIG. 2. Time-resolved emission (2 μs resolution) spectra of AlO bands when $\lambda_L=510$ nm, showing strong resonant emission in the $\Delta v=0$ band and only a slight perturbation in the $\Delta v=1$ band. The laser is on during the first four spectra. The intensities in spectra marked by* were multiplied by 5 for clarity.

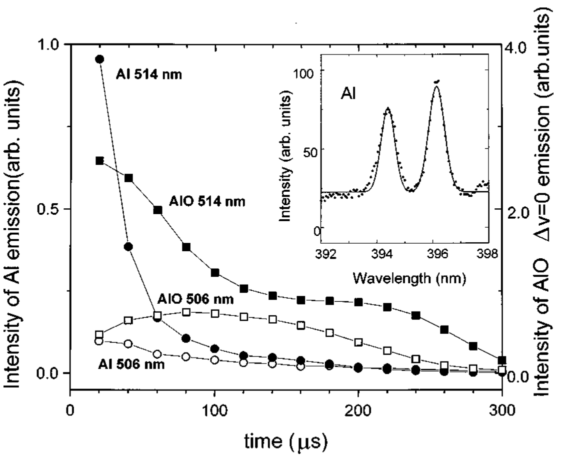

FIG. 3. Time dependence (20 μs resolution) of the Al emission intensities for the laser wavelengths $\lambda_L=506$ nm (empty circles), and 514 nm (filled circles), showing more intense early emission for resonant λ_L. The pulsed laser starts at $t=0.0$ μs, and the intensity for the first 20 μs is plotted at $t=20$ μs. Inset shows a characteristic spectrum of the Al lines at $t=220$ μs, and corresponding Gaussian function fit (ORIGIN, Microcal Software). The intensities plotted correspond to the areas under the fitted function of the two peaks. (The nonzero background in the inset arises from the $\Delta v=5$ emission band of AlO.) Overlaid are the intensities of the AlO $\Delta v=0$ (squares) for the same two laser wavelengths. The AlO intensities correspond to the area under the $\Delta v=0$ bands from 483 to 491 nm. All intensities plotted are corrected for instrumental response. The uncertainties in the intensity values given are 7%, which at $t=220$ ns are within the symbols used.

IV. DISCUSSION

The remainder of this communication will be a description of the origin of the emissions, the unusually long lifetimes, and the enhancement of both the Al and AlO intensities with $\lambda_L=514$ nm long after the extinction of the heat pulse.

The monotonic decrease of Al intensity in time and the observation of AlO emission shown in Fig. 3 is consistent with the production of AlO from Al reacting with air in the well-known reaction[6]

$$\mathrm{Al}+\mathrm{O}_2\rightarrow\mathrm{AlO}+\mathrm{O}. \qquad (1)$$

The persistence of Al and AlO emission at 200 μs after the laser pulse, however, is uncharacteristic of traditional atomic or molecular lifetimes.[12] The radiative lifetimes of the Al (Ref. 13) and AlO (Refs. 14,15) transitions are on the order of 7 ns, and 100–200 ns, respectively.

A simple mechanism in which the aluminum remains hot for several microseconds, and slowly cools off, is not likely to explain the long lifetimes. Separate experiments performed show that 2 μs after the laser onset, light is transmitted through the film. This is interpreted as due to fast expulsion of material, which is later observed as a hole in the film.

A possible mechanism by which the emissions can be prolonged invokes a chemistry-dependent model involving laser vaporization of solids in air,[16] and combustion of Al droplets.[17] The long time scales of Al emission observed can be attributed to the presence of air. It has been shown[4,16,18] that an increase to mbar pressures or introduction of oxygen drastically affects the vaporization process. An increase in emission lifetimes[18] and rapid decrease in velocities resulting in a more localized spatial extent of reaction products has been reported. Furthermore, evidence for the formation of fragments ejected from the surface that would eventually decompose have also been reported.[19,20] If Al fragments are indeed formed, and these vaporize as droplets, then long chemical lifetimes are expected. The combustion of Al droplets is a slow process.[17] It is hypothesized to occur through the peeling off of layers on the surface resulting in a decrease in diameter (d) through the equation

$$d^2 = d_0^2 - \beta t, \tag{2}$$

where d_0 is the initial diameter and β is the burning rate coefficient. In this process, vaporization is limited by the size of the droplets, and the thermal conductivity to transfer heat from the interior to the outside surface where radiative transitions can take place. The polynomial function involving the combustion of Al droplets in time is consistent with the slow decay curves of Al in Fig. 3. The Al curves are amenable to polynomial fits that arise upon proper consideration of the dependence of intensities on the droplet diameters. The functional form $I \propto \exp - t/\tau_c$, where τ_c is a chemical lifetime, conventional for gaseous reactions, falls too quickly in time to fit well the Al decay curves.

The temporal evolution of AlO emission intensity depends on several factors, such as the rate constant for the equilibrium reaction (1) and the subsequent reaction of AlO, the radiative lifetime of excited AlO, the population of Al described above, the population of O_2 in air, and the relative closeness of Al and O_2 for reaction (1) to occur. The rate constant for reaction (1) is measured[6] to be greater than the rate constant for the subsequent reaction[21] of AlO from 300 to 1400 K. Assuming these rate constants in the conditions of these experiments would result in a different dynamic behavior for the reactant Al compared with the intermediate AlO. The rate constants, together with the lifetime of excited AlO are, however, in the submicro and nanosecond time scales, much faster then the times measured in these experiments. What is observed therefore in emission reflects the nascent population of excited AlO being produced in time. Given the above model of Al emanating from droplets and the homogenous O_2 population in air, the plateau or maximum of the AlO intensities in time in Fig. 3 can now be explained in terms of diffusion and transport properties for reaction (1) to occur. AlO can be produced from Al vapor that emanates from the Al droplets reacting with the surrounding oxygen. Initially, the Al is concentrated near the original film position so that AlO formation is limited by the availability of O_2 around Al. Al then diffuses through the air, resulting in increased AlO production. As the Al or oxygen is consumed, and with subsequent cooling, the AlO intensity decreases in time.

The resonantly enhanced intensities exemplified in Fig. 2 provide evidence that additional energy is deposited on the AlO produced. It partly explains the behavior of the enhanced intensities for $\lambda_L = 514$ nm in Fig. 3. When $\lambda_L = 514$ nm, part of the intensity plotted at $t = 20\,\mu$s arises from the resonantly enhanced intensities described in Fig. 2. The AlO intensity is therefore enhanced compared with the AlO intensity when $\lambda_L = 506$ nm. When the laser is off at $t \geqslant 8\,\mu$s, the resonance no longer exists. However, it is seen in Fig. 3 that the AlO intensities are still higher. More strikingly, the Al intensities are drastically affected by the laser wavelength, even if the laser is resonant with the reaction product. Equation (1) is therefore insufficient to describe the enhanced intensities with resonant λ_L at extended times.

The interactions between the laser, the film, and the oxygen atmosphere are complicated. Increased collisions[16] due to the added energy, and energy also added from the resonant laser are expected to contribute in the emission increase in the following manner:

$$\mathrm{AlO}^* + \mathrm{Al} \rightarrow \mathrm{AlO} + \mathrm{Al}^*. \tag{3}$$

Reaction 3, which is facilitated by AlO* molecules in the $v' = 5$ state, can explain the early enhancement of the Al. This process, however, cannot thermodynamically persist for long times, up to 100 μs in Fig. 3. It is not likely to last because the radiative transitions for cooling are readily available for both Al and AlO vapors.

Chemical reactions peculiar to the extreme temperature attained may occur in laser vaporization measurements. The dissociation of AlO is not predicted to occur at ambient conditions. Its dissociation energy in the ground state is reported to be 5.24 eV.[22] At room temperature and assuming a Boltzmann $[\exp(-E/k_bT)]$ distribution of molecules, virtually no molecule (1 in 10^{88}) can dissociate. The reactions may however proceed in the conditions attained in these measurements. At 4500 K, the temperature inferred from reported AlO spectra,[11] one in 10^6 molecules has the energy to dissociate. The probability of dissociation further increases rapidly if it occurs in electronically excited surfaces with lower dissociation energy. Further studies on these excited states are necessary to make firmer conclusions.

V. CONCLUDING REMARKS

The importance of chemical reactions in laser ablation has been alluded to in various reports. With improved understanding of the ablation process and its importance in new applications, especially in those involving chemical bond formation/dissociation, its inclusion in models is necessary. On a fundamental basis, these dynamic measurements of the ablation process provide a window to investigate fast material response at extreme temperature conditions difficult to obtain otherwise.[11,23]

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