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IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

We have used laser-induced fluorescence to measure the energy distributions of Al atoms and AlO molecules produced by excimer laser ablation of Al_2O_3. Excimer laser fluences close to the threshold for ablation were used to minimize the effects of gas phase collisions. The kinetic energies of both species were high, ~ 4 eV for Al and ~ 1 eV for AlO, but the AlO rotational and vibrational energies were quite low, corresponding to a temperature of ~ 600 K. These results rule out thermal vaporization and provide indirect support for an electronic ablation mechanism.

Excimer laser ablation of insulators is important in a variety of microelectronic fabrication processes. In addition, there are a number of unresolved questions regarding the ablation mechanism. Processes that can contribute to material removal by UV laser pulses include thermal vaporization, electronic excitation to repulsive or weakly bound states, droplet expulsion, and exfoliation.[1] Al_2O_3 provides a particularly interesting substrate because previous morphological studies[1,2] have eliminated droplet expulsion and exfoliation, so that only thermal and electronic processes need to be considered. In the present work we use the technique of laser-induced fluorescence to examine the energy distributions of Al atoms and AlO molecules produced by excimer laser ablation of Al_2O_3. These measurements will be seen to rule out thermal vaporization and to provide indirect support for an electronic mechanism for material removal.

It is important in ablation or sputtering studies involving insulators to clearly distinguish between thermal and electronic processes for particle ejection. We consider the laser etching mechanism to be thermal if the material removed per pulse is determined by the equilibrium vapor pressure integrated over the time history of the surface temperature:

$$\text{mass loss per unit area} = \sum_j \int dt \, m_j \alpha_j P_j (2\pi m_j kT)^{-1/2},$$

$$(1)$$

where m_j is the mass of species j, α_j is a vaporization coefficient, P_j is the vapor pressure, and T is the temperature. For Al_2O_3, the species which evaporate from a heated surface include Al atoms, O atoms, AlO molecules, and Al_2O molecules; and the vaporization coefficients are $\alpha_j \simeq 0.3$ for all of these species[3] for both a solid and liquid surface.[4] Note also that for thermal vaporization from bulk materials, the vaporized species generally have energy distributions which are well characterized as Maxwell–Boltzmann at the surface temperature, provided that gas phase collisions are negligible.[5] For vaporization of a high density of material, collisional effects may alter the energy distributions of the particles as they expand into vacuum.[6] In contrast to thermal processes, an electronic mechanism for material removal is based on the idea that UV absorption by the substrate results in excitations to either weakly bound or repulsive electronic

states. Excitation to repulsive states can directly result in desorption. Weakened bonding can either be a long-term effect such as modification of the surface stoichiometry,[7] or a short-term effect such as extensive removal of electrons from the valence band resulting in reduced cohesion of the solid.[8] In the case of weakened bonding, vaporization could in principle occur at temperatures well below those predicted from the equilibrium vapor pressure, but we would consider such a case to be essentially an electronic mechanism.

The apparatus used in our experiments consisted of a 248-nm KrF excimer laser which produced 20 ns pulses and was used for ablation of Al_2O_3, and a tunable pulsed dye laser used to probe the ablated species Al and AlO as shown in Fig. 1. The excimer laser was focused to a ~ 0.5 mm $\times 2$ mm spot on the Al_2O_3 target. The dye laser illuminated a 3-mm-diam $\times$ 12-mm-long volume at a distance of 10–20 mm above the target. Approximate flight time distributions were determined by using laser-induced fluorescence (LIF) to measure the density of a selected species in the observation volume as a function of time delay between the excimer laser and dye laser pulses. The Al_2O_3 targets were either $(2\bar{1}\bar{1}0)$ oriented sapphire wafers or oxidized polycrystalline metal. In the latter case, amorphous Al_2O_3 was formed by dosing Al metal with O_2 gas.[9] The substrates were mounted in a turbo pumped vacuum chamber, and the ablation experiments were carried out at a pressure of $\sim 10^{-5}$ Torr. The substrates were translated at a rate of ~ 0.5 mm/min to bring fresh material into the excimer laser beam. The excimer laser repetition rate was 5 Hz. The majority of the excimer laser beam was incident on material that had received a dose of 10^2–10^3 UV pulses. Thus the results presented here correspond to the case of steady-state ablation rather than ablation of a virgin surface. The excimer laser fluence at the sample was varied in the range of 0.1–10 J cm^{-2} per pulse.

Ablation of Al_2O_3 occurred for laser fluences > 0.6 J cm^{-2}. Al atoms in the plume of ablated material were detected by LIF, exciting the ground-state atoms via the $3^2P_{1/2}$–$4^2S_{1/2}$ transition at 394.4 nm and detecting 396.2 nm emission, i.e., the $3^2P_{3/2}$–$4^2S_{1/2}$ transition. AlO molecules were detected via the $B^2\Sigma^+$–$X^2\Sigma^+$ transition. Two types of energy distributions were measured: velocity distributions
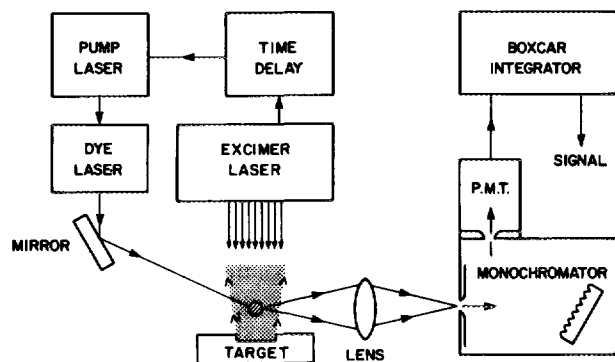
FIG. 1. Experimental apparatus. The dye-laser pulse is delayed by a variable time (typically a few μs) after the excimer-laser pulse to provide time-of-flight measurements.

by time-of-flight and, for AlO, internal energy distributions by measuring the intensity distribution of rotational transitions in the molecular bands. Fluences near threshold for ablation were used to minimize the effects of gas phase collisions.

Typical results for time-of-flight velocity distributions for Al and AlO are shown in Fig. 2. The velocity distributions are not Maxwellian, and rather high kinetic energies are observed. For laser fluences near threshold, the velocity distributions peak at kinetic energies of ~ 4 eV for Al atoms, and ~ 1 eV for AlO molecules. The velocity distributions were observed to depend strongly on the excimer laser fluence. The Al kinetic energy *increases* from ~ 4 eV near threshold (~ 0.6 J cm^{-2}) to ~ 20 eV at 3 J cm^{-2}. In contrast, the AlO kinetic energy *decreases* from ~ 1 eV near threshold to ~ 0.3 eV at 3 J cm^{-2}. The dependence on fluence is due to gas phase collisions in the laser-produced plasma formed during the ablation process.[10] The precise mechanisms for the observed changes are not known. How-
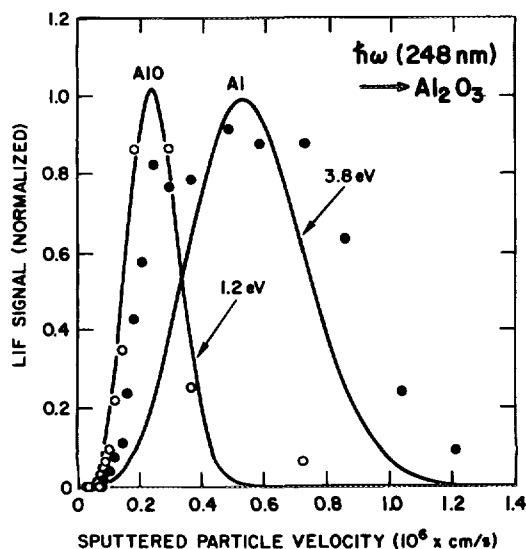
ever, one can conclude that the measured velocity distributions do not reflect the surface temperature achieved by absorption of the intense UV pulse. This is clear from the high velocities which would correspond to temperatures much greater than the critical temperature,[11] from the disparity between Al and AlO kinetic energies, and from the opposite trends of kinetic energy versus fluence observed for these two species.

In contrast to the kinetic energy distributions, the internal energy distributions of AlO were observed to be only weakly dependent on the excimer laser fluence. A systematic trend was observed indicating that the degree of rotational excitation is larger for molecules with larger velocities. For a given velocity (i.e., flight time) the rotational distribution was approximately Maxwell–Boltzmann with temperatures in the range 500–2000 K. The rotational temperatures were ~ 600 K for molecules near the peak of the flight time distribution, whereas temperatures as high as 2000 K were observed for the very few molecules with velocities much greater than average. A typical spectrum showing individual rotational transitions is illustrated in Fig. 3. Very similar results were obtained for the vibrational distributions of AlO in the $v = 0$, 1, and 2 levels. The vibrational distributions were approximately Boltzmann, with a temperature ~ 600 K for molecules near the peak of the flight time distribution, and the effective vibrational temperatures showed only a small variation with excimer laser fluence.

The basic question to answer is whether the surface temperature rose sufficiently for thermal vaporization to explain the etching observed. Measured etch rates were ~ 0.4 nm per pulse at a fluence of ~ 1.5 J cm^{-2}. For a thermal vaporization mechanism, this would require surface temperatures of ~ 4500 K for a duration of ~ 5 ns. This temperature is a factor of ~ 5 greater than the typical rotational and vibrational temperatures observed for AlO, and it is a factor of ~ 2 greater than the maximum rotational temperature observed. The typical rotational temperatures (~ 600 K) were obtained for molecules with a kinetic energy of ~ 1 eV by time-of-flight. Thus it appears to be unlikely that these "typical" molecules could have relaxed by collisions. Although some rotational cooling could occur in the expanding gas,[6]

FIG. 2. Time-of-flight velocity distributions are shown for Al atoms and AlO molecules. The excimer-laser fluence was ~ 0.7 J cm^{-2}. The solid lines show Maxwell–Boltzmann distributions for comparison.
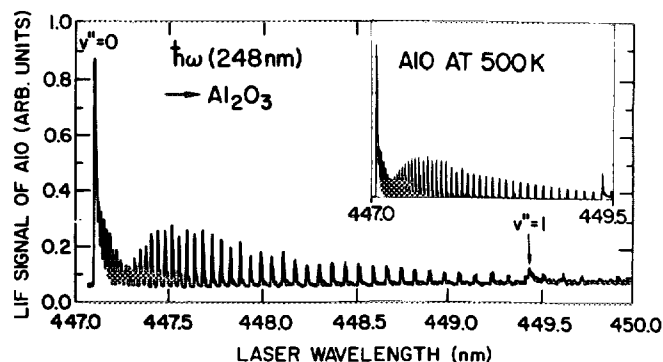

FIG. 3. Laser-induced fluorescence spectrum of AlO produced by ablation of Al$_2$O$_3$ is shown. The rotational distribution is approximately Boltzmann with $T \simeq 500$ K, as shown by comparison with the calculated spectrum in the inset.

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we do not believe that such an effect could account for the large discrepancy between the measured AlO internal temperatures and the surface temperature required for thermal vaporization. This conclusion is supported by the observations that: (1) the internal temperatures are essentially independent of fluence, i.e., independent of the density of material in the expanding plume, and (2) the kinetic energy distributions remain very broad, indicating minimal conversion of random motion into directed motion of the expanding gas. In fact, because of the broad distribution of high kinetic energy particles in the plume, we expect that the rotational and vibrational temperatures observed should probably be greater than the surface temperature at the time of ejection. Thus the low internal temperatures observed strongly suggest that the surface temperature never reached a value large enough (>4500 K) for the rate of thermal vaporization to account for the etching.

Additional support for this argument was obtained by monitoring AlO formed by ablation of a very thin oxide film on aluminum metal. In this case, the oxide thickness was ~ 3 nm. This is sufficiently small that the surface temperature rise can be estimated using the known optical and thermal properties of bulk aluminum. For an excimer laser fluence of 1 J cm^{-2}, the estimated peak surface temperature was ~ 500 K. This low temperature is due in part to the high reflectivity of aluminum ($R \simeq 0.925$). Note that the thermal and optical properties of bulk Al differ substantially from those of bulk Al$_2$O$_3$. Nevertheless, the energy distributions of AlO molecules observed for these two substrates were very similar. This suggests a common nonthermal mechanism for ablation of bulk Al$_2$O$_3$ and the thin oxide film on Al metal.

Since a thermal mechanism is not supported by the experimental data, the observations indirectly suggest that the ablation mechanism must be an electronic process. To complete the argument, it would be desirable to show that the results explicitly support such a process. This is difficult, however, since the details of the nonlinear coupling of UV radiation to the solid are not known at this time. Nevertheless, the experimental observations are consistent with electronic mechanisms for material removal in a general sense because (1) the kinetic energies are in the eV range, i.e., comparable to short-range repulsive interactions, (2) the low rotational energies of AlO could result from fragmentation along the bond axis, and (3) low vibrational energies are expected if expulsion takes place on a time scale slower than or comparable to the vibrational period.[12]

In summary, kinetic and internal energy distributions of Al atoms and AlO molecules formed by excimer laser ablation of Al$_2$O$_3$ have been determined by laser-induced fluorescence. The results lead to the conclusion that thermal vaporization cannot account for the ablation of Al$_2$O$_3$. Instead, the data provide indirect evidence for an electronic mechanism for material removal.

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