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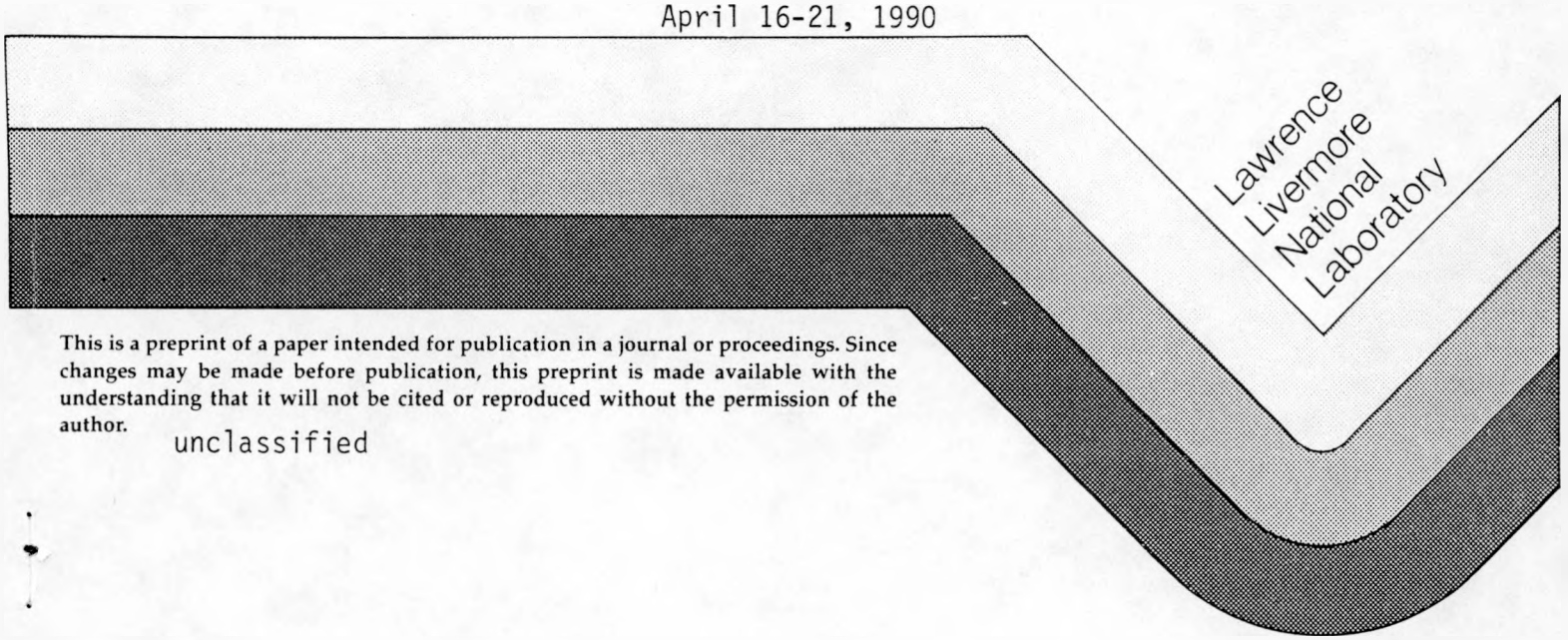

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CLUSTER FORMATION IN LASER-INDUCED ABLATION AND EVAPORATION OF SOLIDS OBSERVED BY LASER IONIZATION TIME-OF-FLIGHT MASS-SPECTROMETRY AND SCANNING TUNNELING MICROSCOPY.

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ABSTRACT

Laser ionization time-of-flight mass analysis (LIMA) used pulses (5ns) of a frequency- quadrupled Nd-YAG laser (266 nm) focused onto spots of 4 - 100 μm diameter to ablate material, and a reflectron time of flight tube to mass-analyze the plume. The observed mass spectra for Si, Pt, SiC, and UO_2 varied in the distribution of ablation products among atoms, molecules and clusters, depending on laser power density and target material.

Cleaved surfaces of highly oriented pyrolytic graphite (HOPG) positioned at room temperature either 10 cm away from materials ablated at 10^{-5} Torr by 1-3 excimer laser (308 nm) pulses of 20 ns duration or 1 m away from materials vaporized at 10^{-8} Torr by 10 Nd-Glass laser pulses of 1 ms duration were analyzed by Scanning Tunneling Microscopy (STM) in air with Ångstrom resolution. Clusters up to 30 Å in diameter were observed.

INTRODUCTION

Ablation and vaporization of solids by laser pulses of nanosecond resp. millisecond duration have recently become important techniques for removal and deposition of materials. In ablation, laser irradiation removes solid by explosive ejection of material while evaporation is a thermally activated process. High temperature superconducting [1] and silicon carbide [2] films have been obtained with nearly perfect stoichio-metry using these techniques. Millisecond laser heating can also be used for fundamental studies of the vaporization process [3].

It has been speculated [4] that the observed stoichimetry of films deposited by laser ablation is due to large clusters being emitted in the ablation process. In laser vaporization studies of UO_2 using mass spectrometric methods, Olander [5] has attributed the fact that at surface temperatures exceeding 2400 K the observed UO_2^+ signal deviates from that expected for equilibrium vaporization to nucleation and growth of polymeric clusters in the vapor plume.

In the present work we have investigated cluster formation using laser ionization time-of-flight mass analysis (LIMA) by adjusting its power density to match that used in laser ablation for film deposition.

In addition, we have deposited a fraction of a monolayer onto the basal plane of pyrolytic graphite by either laser ablation or laser vaporization at power levels where cluster formation is expected, and used scanning tunneling microscopy (STM) to identify clusters on a graphite surface.

EXPERIMENTAL

In the LIMA system a frequency quadrupled Nd-Yag laser (wavelength =266 nm) with 5 ns pulse width ablates a target and ionizes the material ablated. The ions generated are detected by a reflectron time-of-flight (1.5 m) mass spectrometer. Only ion species can be detected by this method. The laser beam can be focused so that the peak power density is comparable to that of the excimer laser employed for film deposition (about $4x10^8$ W/cm^2).

A home-made [6] and a commercial [7] STM , both operating with Ångstrom resolution, were used to analyze materials deposited onto graphite. Standard operating conditions for the microscopes were a bias voltage of 100 mV and a tunneling current of 1nA.

RESULTS

Silicon carbide.

Fig.1 shows the mass spectrum of silicon carbide for a laser peak power density of $4x10^8$W/cm^2, exhibiting monomers, dimers, trimers of SiC and various fragments thereof. Since no C^+ was detected, the Si^+ was more likely due to fragmentation of carbide in the plume rather than direct ejection from the surface. At a laser peak power density of $2x10^{12}$ W/cm^2 only elemental carbon and silicon were detected.

A SiC target was ablated by an excimer laser pulse (wavelenth = 308 nm and peak power density of $4x10^8$ W/cm^2) and the ablated material deposited onto a highly oriented pyrolytic graphite (HOPG) substrate. Fig.2 shows an STM image of deposited silicon carbide partially covering a HOPG substrate. Clusters as large as 3 nm can be clearly identified.

It is not obvious why we should observe fewer multimers with increasing laser power, in contrast to the trend postulated by Olander et al. for UO_2 at lower power. It is possible that in LIMA clusters existing in the plume are dissociated into monomers at high laser power.

Uranium Dioxide

The effect of laser power density on the number of clusters *observed* by LIMA is pronounced for uranium dioxide. UO_2 clusters as large as tetramers can easily be detected by LIMA (Fig. 3) for a maximum laser power density of about $2x10^8$ W/cm^2. For a power

density of $2x10^9$ W/cm^2 the largest multimers detectable were dimers and only elemental ions were observable beyond 10^{11} W/cm^2.

Our LIMA cannot be used to determine the lower limit of the power density necessary to generate clusters, because the same laser pulse is used for evaporation and (multiphoton) ionization. At low power densities the ionization probability is so small that no signal is observed. Yagnik and Olander [8] have studied the vaporization of UO_2 using millisecond laser pulse with the power density range between $0.75x10^4$ and $4.5x10^4$ W/cm^2 using a quadrupole mass spectrometer. The number of ions in the plume was negligible compared to neutrals emitted from the surface. Up to a peak power density of about $2x10^4$ W/cm^2 the measurements conform to equilibrium vacuum vaporization. At higher power density, however, the UO_2 signal levels off and practically ceases to increase with laser pulse energy. Their explanation of this phenomenon was that UO_2 monomers collide in the plume and grow into clusters. This could not be tested, however, since even the UO_2 dimer was beyond the mass range of their instrument.

We deposited UO_2 on HOPG using 1 ms pulses onto a UO_2 target with a power density of $5.4x10^4$ W/cm^2. At a distance of 1 m between the UO_2 target and the graphite substrate, 10 pulses should have resulted in a coverage of about 4% of UO_2 *monomers* if one extrapolates the vapor pressure data from the literature. The existence of clusters of UO_2 on that graphite substrate (Fig. 4) can clearly be seen by STM. No individual molecule of UO_2 was detected in the areas scanned. This is in accord with the hypothesis that the deviation of the UO_2^+ signal by three orders of magnitude from the expected value at the highest power density is due to almost complete coalescence of UO_2 monomers into clusters.

Silicon and Platinum

LIMA data for silicon showed only monomer and dimer ions while the platinum spectra showed only monomer ions. From this result we would not expect to see any deposited clusters with the STM. However, we did see clusters from both these materials when they were deposited onto the surface of graphite. We found clusters up to 3 nm in diameter. There are two possible explanations for this. First, if Si and Pt atoms can easily diffuse on graphite, clusters can grow on the surface by Pt or Si atoms colliding with each other (and with clusters) and sticking together. Another possibility is that impinging Si and Pt atoms stick only to selected sites on the graphite surface or to a Si or Pt atoms already at such a site so that growth would exclusively happen at these locations.

SUMMARY AND CONCLUSION

The combination of LIMA and STM is a promising method for studying laser vaporization and ablation of materials. For power densities of the order of 10^8 to 10^9 W/cm^2 and nanosecond pulse duration used for the production of thin films of refractory materials for use in integrated circuits and high-Tc ceramic superconductors, the ejected particles are mainly molecules and clusters. At higher power densities the elements are the major constituents detected by LIMA in the vapor plume. To resolve whether this is due to photon induced dissociation, we will use in future experiments post-ionization of the ablated/evaporated plume by a second, indepently controlled, laser pulse.

A possible explanation for the formation of clusters is collision of monomers and nucleation and growth of polymeric $(SiC)_n$ and $(UO_2)_n$ from the molecular units in the highly-supersaturated vapor plume leaving the target. As for Si and Pt, cluster growth occurs most likely on the surface of the graphite substrate.

By using the combination of LIMA (with post-ionization) and STM the different growth mechanisms can be studied. The ejection of molecules or clusters of molecules rather than elements from the surface could be a major factor for the success of film deposition of SiC and high T_c ceramics by laser techniques.

ACKNOWLEDGEMENT

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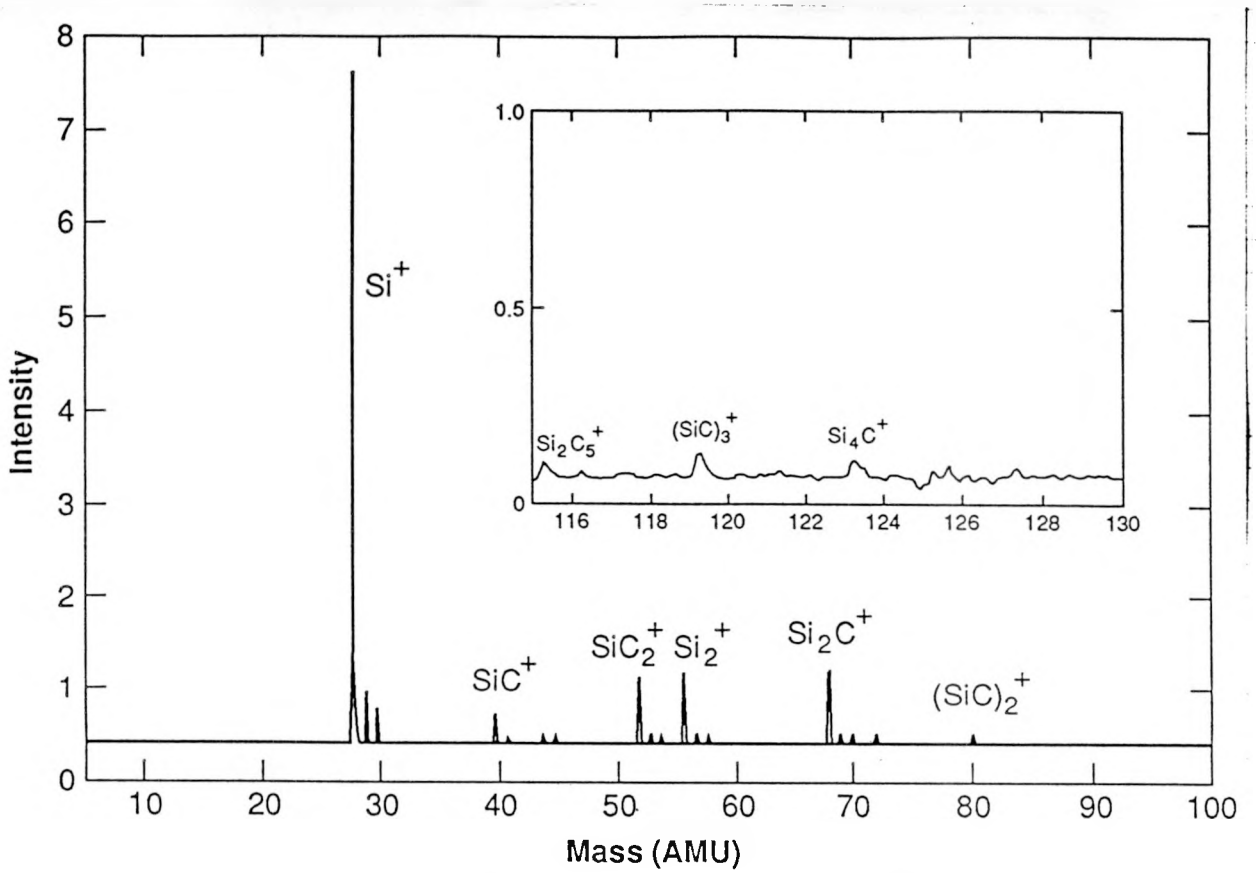

Figure 1. LIMA mass spectrum for SiC ablated at 4 x 10^8 W/cm^2.

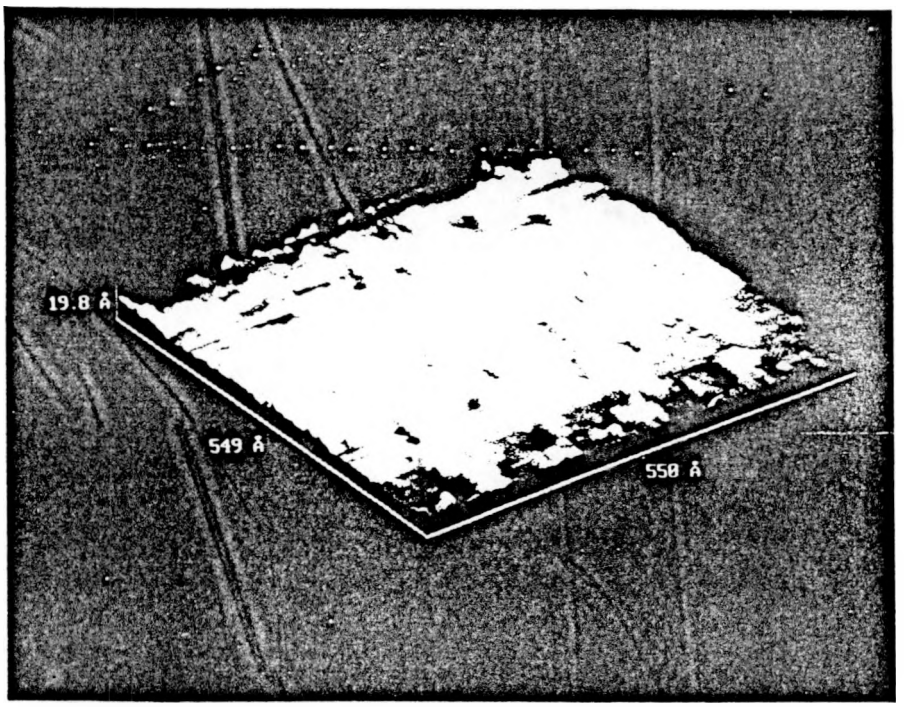

Figure 2. Scanning tunneling micrograph of SiC clusters partially covering the surface of highly oriented pyrolytic graphite.

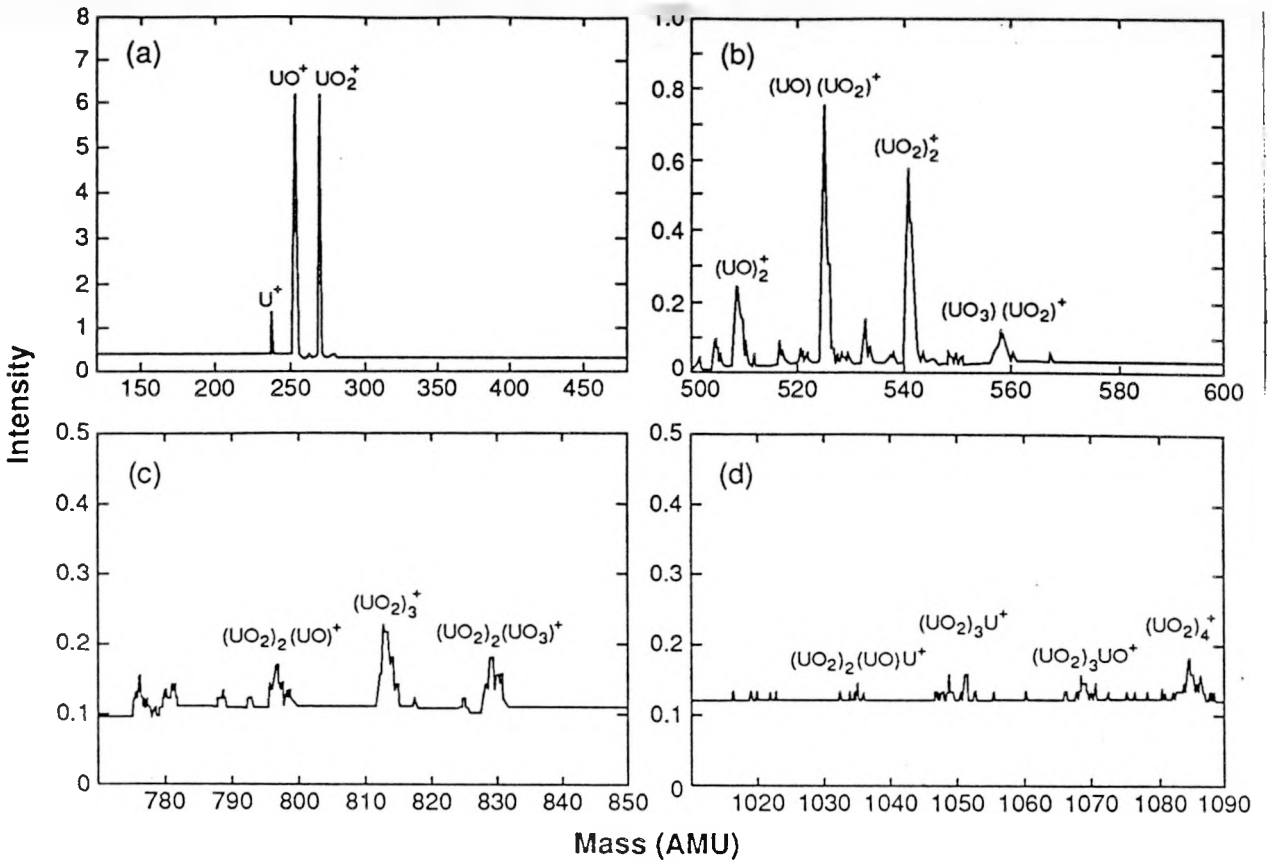

Figure 3. LIMA mass spectrum for UO_2 ablated at 2 x 10^8 W/cm^2.

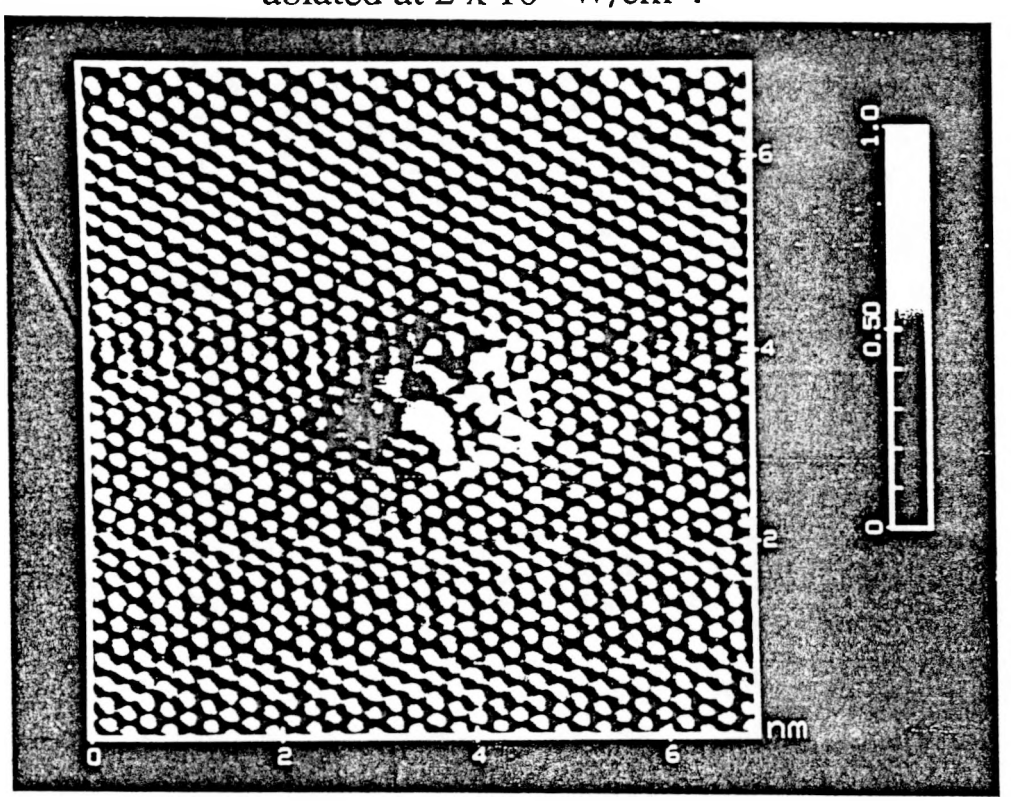

Figure 4. Scanning tunneling micrograph of UO_2 clusters on the surface of highly oriented pyrolytic graphite.

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