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LASER-INDUCED FLUORESCENCE STUDY OF $C_2$ FROM LASER SPUTTERING OF GRAPHITE AND POLYMERS

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Pulsed laser irradiation of graphite surfaces has been known for some time to lead to the ejection of $C$, $C_2$, $C_3$, etc. neutrals as well as related ions. Since most relevant thermodynamic quantities are known, graphite represents an ideal system for further study. The objectives of this work are two-fold: (1) to compare graphite laser etching results to simple thermal vaporization concepts, and (2) to compare the UV etching of polymers to the results from graphite. We observe that surface morphology and etching rates for graphite indicate a peak surface temperature of ~4000K and, hence, can be viewed as a classical vaporization process. The first objective then becomes a question of understanding the energies of molecules, e.g. $C_2$, in the etch plume in terms of an ~4000K surface temperature. The second investigation addresses the question of the specific mechanism facilitating far UV etching of polymers. Both photochemical (electronic rearrangement) and thermal degradation have been suggested in various studies.

Our experimental approach is to determine energies ("temperatures") of diatomic molecules in the etch plume by laser induced fluorescence, LIF. The kinetic energies are determined by time-of-flight (the detector being 0.5 to 3 cm from the target). The internal energies of $C_2$ dimers are determined from the rotational/vibrational population distributions in the $D^1\Sigma^+_g \rightarrow X^1\Sigma^+_g$ Mulliken bands. The present work appears to be the first observations utilizing laser probing of these simple, yet informative, transitions. About 200 rotational/vibrational transitions are observed with X-state energies up to ~14,000 cm$^{-1}$ above the lowest energy X-state.

For graphite etching, LIF measurements utilizing the Mulliken band indicate $C_2$ temperatures of 3500±100K when 1 monolayer/pulse is ejected. The similarity of this temperature to the estimated surface temperature agrees with the concept that internal temperatures of diatomic correctly reflect the true surface temperature. In contrast to the internal energies, the $C_2$ radicals have time-of-flight velocities which correspond to 4500K to 9000K. These high values are now understood on the basis of collisional effects within the initially dense vapor phase ("Knudsen layer" formation). The $C_2$ LIF spectra for UV etched polymers display rotational/vibrational energies which do not fit a simple Boltzmann distribution. For both PMMA and polyimide, the temperatures can nevertheless be approximated as 2100±700K. Temperatures in this range may or may not be the result of thermal decomposition followed by vaporization. What is pertinent to the argument is that, on the basis of the observed high kinetic energies (in the 2 to 3 eV range), polymer etching appears to be a photothermal process, similar to the case of sapphire. We are also quantifying the effects of gas molecules bound to the surface, which accelerates laser etching.

In summary, we have measured the energies of $C_2$ radicals generated by UV etching utilizing the Mulliken bands. In the case of graphite, the energies fit a straightforward thermal model. In the case of polymers, a photochemical decomposition apparently accounts for the rapid UV etching.