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TITLE INVESTIGATION OF OPTICAL DAMAGE VIA RESONANCE IONIZATION
MASS SPECTROMETRY

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Investigation of Optical Damage via Resonance Ionization Mass Spectrometry

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Resonance ionization mass spectrometry (RIMS) has been used as a diagnostic for interrogating optical damage events. RIMS involves multistep laser photoionization, generally through real intermediate states, followed by mass separation and detection. It is a sensitive and selective means of detection, and has the potential for detection of ultratrace inclusions in substrates and/or coatings.

In initial experiments, damage on uncoated CaF_2 substrates was initiated by pulses of 1.06- μm light from a Q-switched $\text{Nd}^{3+}:\text{YAG}$ laser. Interruption of the spalled plume revealed CaF radicals only when damage events occurred. No Ca atoms were observed, and no attempt was made to detect F atoms or CaF_2 . In subsequent experiments conducted at laser intensities below the damage threshold, we observed the presence of surface adsorbents and a correlation between the presence of the adsorbents and the occurrence of optical damage.

Key words: damage; RIMS; diagnostics

1. Introduction

Laser-induced desorption and laser-based detection of ablated or sputtered species are both becoming widely used techniques in a variety of studies, including surface chemistry, sputtering, and optical damage. Much work has concerned laser-desorption of adsorbed species from substrate surfaces as detected by a variety of mass spectroscopic techniques [1-10]. Other experiments have concentrated on probing the basic processes related to laser-ablation of the substrate material itself [11-16]. Laser detection of desorbed particles via fluorescence or ionization is also becoming a widely used technique in more traditional particle-induced sputtering experiments [17-20].

Few investigations have, however, coupled the advantages found in laser-induced desorption to those of the sensitive and specific laser-based schemes now available for the detection of the desorbed material [21-24]. We report here, the use of resonance ionization mass spectrometry (RIMS) as a diagnostic for interrogating laser-induced optical damage events. RIMS is a sensitive and selective means of detection, and has the potential for detection of ultratrace inclusions in substrates and/or coatings, as well as the detection of active sites on the surface where subsequent damage is likely to occur.

2. 1. Oriental

The damage/description experiments described below took place in the source region of a time-of-flight mass spectrometer described in detail previously [25]. Figure 1a depicts a schematic of this region, while figure 1b describes a typical timing sequence used. Briefly, the Q-switch output from the Nd:YAG damage/description laser (Quanta Ray/Spectra Physics Model Q-SW 150) was sent to the timing sequence. The laser output, initially from a fiber-optic probe, was focused onto the substrate surface with the aid of two lenses (approx. 100 mm and 100 mm focal length). Once alignment was completed, the frequency tripler was detuned, the output light reflected with a dichroic mirror, leading only (1934) the laser output to the target. The laser pulses from this laser typically arrived at the substrate 10 ns after the Q-switch output trigger. Beam size at the substrate was approximately 0.47×0.75 mm², and the average fluence used producing fractures was 3 J cm^{-2} . These values are to be regarded as approximate, since the "spot size" depends on the laser beam profile, which is not necessarily Gaussian. As often occurs in this type of experiment, the only way to determine the spot size

Figure 1. Schematic of the experimental apparatus. The 1.06- μm damage pulse is typically focused to a beam diameter of 0.7 mm at the substrate surface. The delay time to the dye laser probe pulse was $\sim 30\text{--}50\ \mu\text{s}$.

The CaF_2 substrates (Janos Optical) were polished flats, 1.9 cm in diameter and 3 mm thick. Each was cemented to a 15-cm stainless steel rod for mounting within the mass spectrometer source region. The substrates could be translated and rotated while in the source region via a high vacuum feedthrough (Varian Model 1371). The rotation axis of the substrate was parallel but not coincident with the 1.06- μm laser beam axis. A displacement of 5 mm between these two axes allowed the interrogation of different substrate sites via substrate rotation. Rotation rates varied from revolution/15 minutes to 1 revolution/60 minutes. The long substrate mounting rods were required to prevent metal ion formation near the source region from the focused 1.06- μm laser striking the surfaces of the vacuum chamber.

A gas inlet system facilitated gas-phase RIMS studies and provided a means of introducing adsorbents onto the surface of the substrate. A stainless steel nozzle opposite the surface being interrogated directed the adsorbents to this surface. The inlet system was also constructed in such a manner as to allow adsorbent purification via distillation prior to deposition. All adsorbents were triply distilled prior to use.

Pulses from an excimer-pumped dye laser (Lambda Physik, Models 101/2002) were used to effect ionization. Ions were generated from ground electronic states of the detected species in a variety of multiphoton transition sequences. The excimer laser typically produced 100-mJ, 15-ns pulses and was triggered after a variable delay. Dye laser pulses (2 mJ, 10 ns) were spatially filtered and loosely focused (0.07 cm diam) through the ionization region. The laser beam propagated parallel to the substrate surface, at a distance of 2.5 cm. The extraction field was approximately 110 V/cm, perpendicular to the paths of both laser beams. This was followed by a drift tube at $\sim 1000\text{ V}$; the flight path was 0.4 m. A pair of deflection plates between the extractor and flight tube restricted the transmission of ions to the detector and minimized any transmission variation due to ion velocity components perpendicular to the flight tube. Detection electronics consisted of a channel electron multiplier, a preamplifier, an amplifier, and a boxcar averager whose gate delay was set to the flight time of the ions of interest. The boxcar gate width was adjusted so as to encompass only a few mass units about that of the detected species. An oscilloscope was used to observe simultaneously the arrival of the damage/desorption laser pulses, the ion signal, and the boxcar gate.

3. Results and Discussion

In most experiments, the exposed, polished substrate was initially at a low bias of the sample electrode. Electric breakdown was observed at thresholds fundamentally consistent with previous observations on CaF_2 [25]. However, the breakdown threshold was surface-site dependent, possibly due to defects or surface contamination. Neither Ca atoms nor Ca radicals could be detected prior to breakdown. After breakdown, however, Ca radicals were easily detected via a two-photon transition to the $4d^1$ excited state (2548 cm^{-1}) from the $4s^2$ ground state. Absorption of a second photon of the dye laser promoted ionization (ionization potential 6.0 eV) [27]. Figure 2 shows the ionization of Ca radicals by the dye laser. The ionization of Ca radicals by the dye laser was observed at a delay of $\sim 10\ \mu\text{s}$ in contrast to the major features of the 2548 cm^{-1} transition, which occurred within a few nanoseconds of the laser pulse.

Figure 2. Optical MPI spectrum of desorbed CaF, obtained at a 50- μ s delay after the desorption pulse. Bandhead positions are indicated for the $\Delta v = 0$ sequences for the electronic transitions observed.

Time-of-flight spectra of the CaF radicals could not be recorded due to a large nonresonant signal from ions of many different masses at shorter flight times. The source of this contaminating signal is the intense UV-light pulse generated at the substrate surface during breakdown. The source of the interference was confirmed by placing electron/ion deflectors in the flight path of the spalled material. All attempts to reduce this signal by particle deflection failed, although ions are certainly generated in such a breakdown event. The breakdown-generated light pulse was easily visible to the naked eye and sometimes generated overloads in the electronics due to the formation of many ions as it struck the optic elements of the ion spectrometer. Such light-generated signals have been observed previously [2]. Direct inversion of spectral intensities to state populations is not currently possible (as in much laser-induced fluorescence work) due to the lack of knowledge of the two-photon line strengths of the transitions involved [28]. However, it is clear that several low-lying vibrational states of the ground electronic state have been populated in the damage event. No Ca atoms could be detected after the onset of breakdown, even though detection sensitivity for desorbed alkaline earth atoms is high [29]. This suggests that the mechanism for breakdown at 1.06 μ m is thermal, or hydrodynamic in nature, since previous observations [20,30] suggest that an electronic or photophysical interaction leads to the production of free metal atoms. No attempt was made to observe either Ca atoms or CaF₂.

In an attempt to correlate surface contamination with low breakdown threshold, a series of adsorption/desorption experiments were performed. In previous work [5,9], water aggregation appeared correlated to low damage thresholds at a particular site. However, water is not a good KIMS candidate due to its high ionization potential and sparse electronic structure. Only recently has the multiphoton ionization spectrum of water been obtained at the relatively high pressure of 10⁻⁴ Torr [31]. In the experiments reported below, nitrogen dioxide (NO₂) was chosen for the adsorbate for several reasons. First, at wavelengths at and below 300 nm, NO₂ is more efficiently ionized than O₂, the NO₂ being easily detected via multiphoton ionization due to its low ionization potential [32]. Second, if the NO₂ reacts with surface water, several of the possible reaction products, like HNO₃, have dissociating UV absorptions at the NO resonance wavelengths. Thirdly, NO₂, like water, is polar and seeks the most high potential sites where damage is likely to occur [33]. In addition, at the wavelength chosen for this preliminary study, 355 nm (corresponding to the $\bar{v} = 0 \rightarrow 1$ transition in CaF), the $\bar{v} = 1 \rightarrow 0$ transition in NO₂ is $\bar{v} = 1 \rightarrow 0$ in CaF, i.e., the $\bar{v} = 1 \rightarrow 0$ transition, and efficiency, have been measured. This technique of detection of the ionization of the adsorbate has been used previously in several experiments [34,35].

Following the substrate mounting, samples were placed within the mass spectrometer and evacuated to 10^{-7} torr for several hours. The substrates were then exposed to NO_2 at low pressure (10^{-6} torr) for sufficient time to form several monolayers. Substrates were then again returned to 10^{-7} torr. The RIMS sensitivity for detecting NO from NO_2 is very high, requiring another several-hour period of pumping to eliminate background nitric oxide RIMS signals prior to a desorption experiment.

Each area on the substrate was then sequentially exposed to low intensity and high intensity laser pulses. At $1.06\text{-}\mu\text{m}$ intensities below the damage threshold (typically $0.4\text{--}0.6\text{ J cm}^{-2}$) the ion signal at the bandhead wavelength of the NO δ (1,0) was recorded as a function of substrate rotation angle. Such records are shown for two samples in figure 3b. On a second pass, at intensities near or above the damage threshold (approximately 5 J cm^{-2}), a signal due to breakdown was recorded as a function of substrate rotation angle. These spectra are shown for the same two samples in figure 3a. Only a single pass below the damage threshold was made, since laser annealing was observed for sites receiving multiple exposures below these thresholds. This annealing effect and the low signal-to-noise ratio in these experiments prevented time-of-flight spectra from being recorded for the adsorbent. The NO signals of figure 3 were recorded at a $50\text{-}\mu\text{s}$ flight time between desorption and ionization. The correlations observed between damage and desorbent concentration for the two samples are representative of the correlations observed for all samples interrogated. Not all sites showing higher concentrations of adsorbent produce breakdown; however, most all breakdown sites exhibited higher adsorbent concentrations.

FIG. 3. Ion signal as a function of substrate rotation for two different laser intensities (10^{-6} torr NO_2 , 10^{-7} torr). (a) $I = 1 \times 10^9\text{ W cm}^{-2}$ (b) $I = 5 \times 10^8\text{ W cm}^{-2}$

The efficiency of detecting the active sites by adsorbent aggregation could be improved over that observed above by using a desorbing wavelength in resonance with the adsorbent [5,9]. This is not the case for the experiments described above. From our static gas phase NO_2 experiments, we estimate (incorporating observed signal-to-noise, detection volume, etc.) a lower detection limit of $\sim 6 \times 10^5$ molecules of NO_2 . Using this number, a rough calculation of our desorption efficiency yields $\sim 10\%$, assuming a temporal and spatial overlap of 10^{-3} , a partition function of 10^{-2} , and a dissociation and ionization efficiency of 10^{-1} . Although this desorption efficiency certainly represents an upper bound for this nonresonant process, it could be dramatically improved via vibrational resonant frequencies. RIMS is inherently more sensitive for such studies than the traditional residual gas analyzers due to its order of magnitude better ionization efficiency over electron bombardment. Further improvement in the present apparatus can be made by providing a line-of-sight path between substrate surface and detectors. Such improvements will be incorporated into future instrumentation.

Since the neutral/ion production ratio ranges from 10^{-2} to 10^{-3} in laser desorption of adsorbents and substrates [11,16,21,22], efficient detection of the neutral major product channel is imperative to our understanding of such processes. RIMS provides such a sensitive, specific detection scheme. It shows potential for monitoring ultratrace inclusions in substrates and/or coatings, as well as for nondestructively locating active surface sites where subsequent damage is probable.

4. References

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