PRODUCTION OF PULSED ATOMIC OXYGEN BEAMS VIA LASER VAPORIZATION METHODS

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Abstract

Energetic pulsed atomic oxygen beams have been generated by laser-driven evaporation of cryogenically frozen ozone/oxygen films and thin films of indium-tin oxide (ITO). Mass and energy characterization of beams from the ozone/oxygen films have been carried out by mass spectrometry. The peak flux, found to occur at 10 eV, is estimated from the data to be $3 \times 10^{20} m^{-2} S^{-1}$. Analysis of the time-of-flight data indicates a number of processes contribute to the formation of the atomic oxygen beam. The absence of metastable states such as the $2p^3 3s^1(^5S)$ level of atomic oxygen blown-off from ITO films is supported by the failure to observe emission at 777.3 nm from the $2p^3 3p^1(^5P_J)$ levels. Reactive scattering experiments with polymer film targets for atomic oxygen bombardment are planned using a 35" universal crossed molecular beams apparatus.

1. INTRODUCTION

Atomic oxygen-induced degradation of various materials in low earth orbit (LEO) is a problem of current concern for engineers involved with selection of materials for Space Station and other LEO missions[1]. Flight experiments carried out onboard a number of space shuttle flights have attempted to characterize the interaction of atomic oxygen bombarding organic polymeric[2-4], paint[3-4], and metal[5] surfaces with a relative energy of 5 eV and a flux of about $10^{19} m^{-2} S^{-1}$. These flight experiments have provided an engineering database of erosion rates for a wide variety of materials[6], but do not provide much insight into the mechanisms of the gas-surface chemistry involved in the material degradation processes. For the DuPont polyimide Kapton, a thermal blanketing material, preferential attack at the phenyl ring positions by oxygen is indicated from comparison of resonance Raman spectra of exposed and control specimens[2]. A future flight experiment, entitled Evaluation of Oxygen Interaction with Materials (EOIM-3)[7], will attempt to directly detect products of atomic oxygen interaction with selected materials using the AFGL ion-neutral mass spectrometer. Uncertainty in NASA mission planning for the STS in the near future, though, has placed new emphasis on the development of ground-based capability to study the atomic oxygen degradation problem in a detailed fashion.

A number of approaches have shown considerable promise in simulating the effects of atomic oxygen bombardment on materials. A dc arc discharge source has been employed to study the interaction of atomic oxygen with Kapton[8] and amorphous carbon[9-10] at energies up to 1 eV. The results from these studies are encouraging, as the rates of erosion of the materials were found to be in good agreement with those found on the shuttle. The possibility has not been ruled out that a synergism between atomic oxygen bombardment and ultraviolet radiation from the arc, or metastable contamination of the beam may have strongly influenced the measured erosion rates. A source using a CO_2 laser-sustained plasma, under development at Los Alamos[11], has yielded beams of higher kinetic energy but suffers from the

same problem of uv and/or metastable interference. A pulsed source utilizing a CO_2 TEA laser focussed in pure O_2 to initiate a blast wave in the throat of a conical nozzle[12] has been demonstrated to produce $> 10^{18}$ oxygen atoms per pulse at velocities in excess of 11 km S^{-1}. The velocity distribution from this source was determined via monitoring of the 777.3 nm emission from the ^5P level of atomic oxygen, a direct indication of the presence of high-energy metastable atoms in the beam. The spark from the focussed laser also produces intense ultraviolet radiation which may affect the surface chemistry unless the sample is protected from exposure during the laser pulse. Other sources, utilizing charge exchange[13] or electron detachment of ion beams[14], are currently under consideration, but such sources suffer from low fluxes and have therefore not been utilized in material degradation studies.

An alternative scheme for production of energetic atomic oxygen beams involves a technique known as laser blow off. This method has been successfully used to generate pulsed metal atom beams in the 1 – 20 eV energy range[15]. A thin coating of metal on a transparent substrate mounted in vacuum is irradiated by a focussed high energy laser directed at the target film from the substrate side. The metal film is vaporized and an intense pulse of energetic metal atoms is produced. The ion content of beams produced from rear surface irradiated films is greatly reduced compared to that of beams produced by front surface laser evaporation of materials.

This paper describes the extension of the laser blow off technique to produce beams of atomic oxygen from films of frozen ozone/oxygen mixtures or indium-tin oxide. Analysis of the time-of-flight data for the atomic oxygen beams is performed and a physical interpretation of the processes occurring in the ozone/oxygen film is suggested. In a separate experiment, spectroscopic evidence indicating the formation of metastable atomic states of oxygen could not be observed for the laser blow off of ITO films. The utility of the source for future mechanistic studies of the interaction of energetic oxygen atoms is explored.

2. EXPERIMENTAL DETAILS

A schematic representation of the apparatus used for generation of the atomic oxygen beams is shown in Figure 1. An excimer laser (Lumonics Model 861-S), operated with the KrF lasing mixture (248 nm, 100 mJ/pulse), is focussed into the target by a 20 cm focal length quartz lens mounted in tandem with a 45° angle of incidence dielectric turning mirror (CVI, Inc.) on a x-y translation stage. A 1-inch diameter Supracil 1 window transmits the laser radiation into the vacuum apparatus. The vacuum apparatus consists of $2\frac{3}{4}$-inch Conflat flanged fittings attached to a 4-inch diameter chamber containing the quadrupole mass analyzer. A liquid nitrogen trapped 2-inch diffusion pump provides pumping in the region of the cold window. A 50 ℓ S^{-1} ion pump is used in the quadrupole analyzer region to maintain vacuum in the low 10^{-8} torr range.

The target substrate is a $\frac{1}{2}$-inch diameter sapphire window (ESCO Optics, Inc.) supported by a copper mount in thermal contact with the 10K stage of a cryogenic refrigeration unit (CTI Model 21). An Au-Fe/Chromel thermocouple mounted near the cold window permits determination of the temperature of the window during the course of the experiment. The temperature typically will reach 20-25K at the window mount with appropriate shielding of the cold stage. Thin films of ozone/oxygen mixtures are prepared by permitting pre-mixed gaseous ozone and oxygen to flow through the nozzle of a movable doser onto the cold sapphire window. Ozone is collected on silica gel at −78° C after formation in a corona discharge of flowing oxygen (Matheson, Ultra-High Purity). The composition of the film is established by admitting the appropriate partial pressures of ozone and oxygen into a calibrated volume.

The thickness of the film is determined by the quantity of gas allowed to flow through the nozzle of the doser. No independent determination of film thickness is made during the course of the experiment.

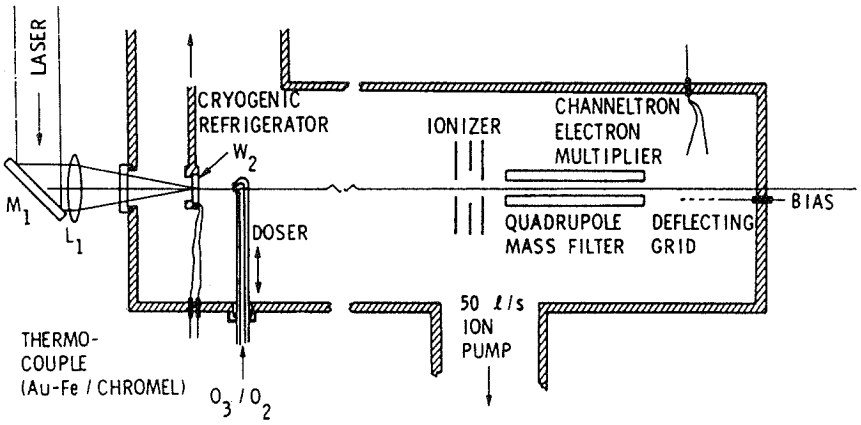

Figure 1. Schematic representation of the apparatus for laser blow off time-of-flight measurements from cryogenic films.

Measurements of the time-of-flight of the individual constituents in the beam are made on a single shot basis. The laser focussing lens is positioned to allow the beam to strike a new spot on the film for each shot. The quadrupole mass analyser (EAI 300), with the ionizer located 30 cm from the target, is tuned to the desired m/e to be transmitted. The transmitted ions are deflected by a biased grid into a channeltron electron multiplier (Galileo Electro-optics CEM 4700) placed off-axis to prevent interference from the laser pulse or fast neutral species unaffected by the quadrupole mass analyzer. A 100 MHz transient waveform recorder (Biomation 8100), triggered by a photodiode monitoring the laser, captures the amplified output of the channeltron electron multiplier. The signal is then output to an X-Y recorder. The recorded time-of-flight traces were digitized at 3 microsecond timebase intervals and the data stored on magnetic disk for subsequent analysis.

For the attempts to observe metastable oxygen emission, a 1-micron thick ITO film deposited on glass (Applied Films, Inc.) was mounted on an x-y translation stage in a 10-inch vacuum cross. A Nd:YAG laser (Quanta-Ray DCR2A-20) operating on the third harmonic (355 nm, 50 mJ/pulse) and focussed by a 40-cm focal length lens was directed into the rear surface of the film through a Supracil 1 window on the chamber. An IP-28 photomultiplier tube (RCA) viewed a region 20-cm downstream from the target film through a 630 nm cut-off filter (Schott) and window on a perpendicular arm of the vacuum cross. The output of the PMT was viewed on an oscilloscope synchronized to the laser pulse.

3. RESULTS

Time-of-flight traces for KrF laser blow-off of an approximately 0.3 micron thick film composed of 20% ozone in solid oxygen are shown in Figure 2. The m/e=16 trace corresponds to signal due to O^+ ion transmitted through the mass filter on a single laser shot. The m/e=32 trace is due to molecular

O_2^+ on a subsequent laser shot. Both traces in the figure have been corrected for transit time through the mass spectrometer according to:

$$(v_1^2 + v_0^2)^{1/2}(tv_1 - d_1) - d_2 v_1 = 0 \tag{1}$$

where v_1 is the initial velocity of the particle prior to ionization, v_0 is the velocity of an ion initially at rest after acceleration by the ion energy potential V (11 eV), t is the total transit time from target to detector, d_1 is the distance from the target to the ionizer (30 cm) and d_2 is the distance from the ionizer to the detector (20 cm). Equation (1) is solved numerically for v_1 at each time-channel in the raw data to obtain the corresponding arrival time at the ionizer. The time-of-flight data is then mapped onto a uniform timebase by linear interpolation of the intensities on the corrected timebase.

The signal detected for m/e=32 indicates some molecular oxygen is present in the beam. Since molecular oxygen undergoes dissociative ionization, there will be a contribution due to molecular oxygen in the m/e=16 time-of-flight trace. The electron-impact ionization processes and corresponding probabilities for molecular oxygen are:

$$O_2 \longrightarrow O_2^+ + e^- \qquad P_{O_2^+} = 0.7 \tag{2}$$

and

$$O_2 \longrightarrow O^+ + O + e^- \qquad P_{O^+} = 0.3 \tag{3}.$$

The contribution of the O_2 dissociative ionization component in the m/e=16 time-of-flight signal may be removed by subtracting m/e=32 data corrected for m/e=16 transit time and scaled by the appropriate factor. This scaling factor is given by the ratio of probabilities for dissociative ionization to simple ionization:

$$\frac{P_{O^+}}{P_{O_2^+}} = 0.43 \tag{4}.$$

The effect of this correction to the m/e=16 data is shown in the lower trace of Figure 3.

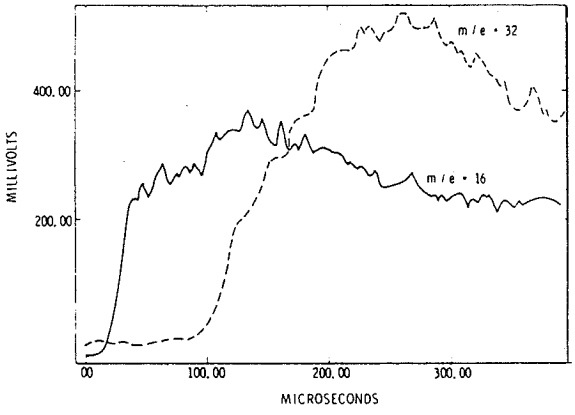

Figure 2. Time-of-flight traces of $m/e = 16$ and $m/e = 32$ for laser blow off from a 0.3 micron film of frozen ozone/oxygen.

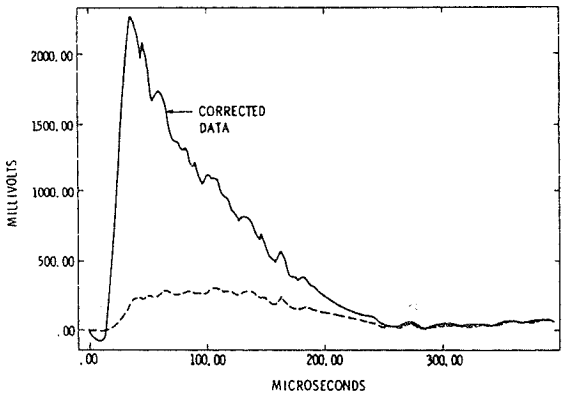

Figure 3. The dashed line corresponds to the $m/e = 16$ signal corrected for dissociative ionization of O_2. The solid line represents the $m/e = 16$ data corrected for finite residence time in the ionizer.

The corrected data now represents a signal proportional to the number density of atomic oxygen in the ionizer as a function of time after the laser pulse. It is desirable to extract from this data the flux of atomic oxygen arriving at the ionizer from this data. This procedure must take into account the dependence of ionization probability upon the residence time in the ionization region of the mass analyzer. The probability of ionization as a function of time would be expected to follow the typical survival equation:

$$P(t) = 1 - \exp(-t/\tau) \tag{5}$$

where τ is some characteristic time of the particular ionizer. Since the efficiency of standard electron-impact ionizers is on the order of 10^{-5}, the series expansion of equation (5) may be cut off at the linear term. In other words, the probability of ionization is inversely proportional to the velocity of the incident neutral. The number density data is converted to an intensity proportional to the flux by multiplying the data by a scale factor proportional to velocity which is set to unity at sufficiently long time ($\approx$ 400 microseconds). Below a minimum cut-off time ($\approx$ 20 microseconds), the scale factor is kept constant to avoid excessive amplification of noise at short times. The result of the conversion of the data is illustrated in Figure 3.

An estimate of the absolute flux of atomic oxygen arriving at the ionizer was made in the following manner. A sensitivity factor for the mass spectrometer was obtained by addition of known pressures of molecular oxygen to the system and summing the signal strengths of the m/e=16 and m/e=32 features for operating conditions identical to those for the time-of- flight measurements. The sensitivity factor is then scaled by the ratio of cross-sections for ionization of atomic oxygen to molecular oxygen. The larger ionization volume for static gas measurements compared to that for beam measurements is also taken into account. Figure 4 illustrates the atomic oxygen intensity plotted against translational energy. The peak flux occurring at 10 eV is estimated (within a factor of five) to be $3 \times 10^{20} m^{-2} S^{-1}$. This flux is comparable to values observed for laser blow-off of metal films [15].

The optical measurements for laser blow off from ITO films showed no indication of emission at the 777.3 nm line of oxygen. A small quantity of nitric oxide (NO) gas was metered into the vacuum chamber to establish the presence of atomic oxygen via recombination glow of the excited NO_2 product:

$$NO + O \longrightarrow NO_2^* \longrightarrow NO_2 + h\nu \tag{6}.$$

The recombination glow was observed downstream from the target after the laser pulse, indicating the production of atomic oxygen in the blow off process.

4. DISCUSSION

The technique of laser blow-off using films of ozone and oxygen is shown to produce intense, energetic beams of atomic oxygen. The energy spectrum of the beam, as graphically illustrated in Figure 4, indicates that the source would be useful in mechanistic studies where effects of varying the translational energy of the incident atomic oxygen on material surfaces are investigated. A simple rotating chopper, synchronized to the laser triggering, would permit the study of the effect of incident energy variation of atomic oxygen across the sample surface. The chopper would obstruct laser light used by the blow off source from striking the portion of the surface under atomic oxygen bombardment. Molecular oxygen would also be prevented from striking a portion of the sample surface since, as can be witnessed in Figure 2, its velocity is considerably less than that of atomic oxygen.

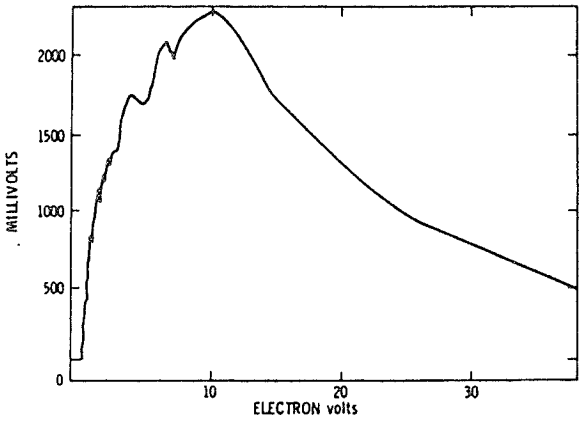

Figure 4. Flux of atomic oxygen plotted against translational energy for laser blow off from an ozone/oxygen film.

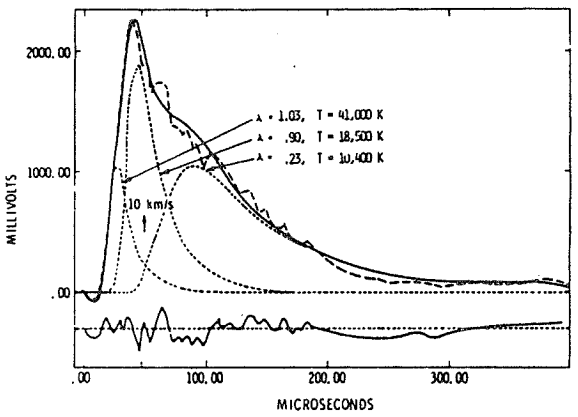

Figure 5. Results of fitting the sum of three components in the form of equation(8) to data observed for blown-off atomic oxygen from a solid ozone/oxygen film.

The observation that molecular oxygen appears to "straggle" behind the arrival of atomic oxygen is somewhat curious. The laser blow off source, as developed by Friichtenicht [15], generates a bubble of expanding gas moving with a center-of-mass flow velocity. As in seeded nozzle beams, little slippage in the velocity of heavier components in the beam is expected. In order to attempt to understand what may be occurring in the blown-off ozone/oxygen films, the time-of-flight data for m/e=16 flux was analyzed according to the model developed by Utterback, *et al.*[16].

The basis for the laser blow off model is a gas bubble expanding spherically in the center-of-mass frame according to a Boltzmann velocity distribution. In the model, the center-of-mass velocity is simply related to the root mean square velocity of this Boltzmann distribution by a multiplier λ:

$$v_{com} = \lambda v_{rms} \tag{7}$$

For on-axis detection, the equation relating the flux arriving at a detector a distance d from the target as a function of time t is:

$$\phi(t) = \frac{N_0}{4\pi}\left(\frac{m}{kT}\right)^{3/2}\left(\frac{2}{\pi}\right)^{1/2} d/t^4 \exp\left\{-\left(\frac{m}{kT}\right)t^{-2}\left[d - \lambda t\left(\frac{3kT}{m}\right)^{1/2}\right]^2\right\} \tag{8}$$

where m is the mass of the species and T is the temperature of the expanding gas bubble. Note that for $\lambda = 0$, equation (8) describes the particle flux from a pulsed source with a Maxwell-Boltzmann velocity distribution. For the molybdenum atom source analyzed by Utterback *et al.*[16] the value of λ was 1.1, indicating a rather well-developed center of mass flow. A non-linear least squares program was written to fit the observed data to equation (8). The equation was found to fit the data poorly. The program was modified to allow the fitting function to be described by a sum of up to three components of the form shown above. The resulting fit to the data is shown in Figure 5. The use of three components to model the data is not intended to represent a unique description of the time-of-flight data; clearly the fit could be improved by including additional components in the model. The point is that the process occuring in the frozen ozone/oxygen film is not well-described by the simple laser blow off model.

Laser blow off of metal films has been characterized by formation of a confined hot plasma which ingests material until the outer surface of the film is breached. There is evidence [15] that the edge of the film is lifted from the substrate somewhat as the gas bubble breaks out into the vacuum. In essence a miniature nozzle is formed which aids in directing the gas flow along the normal to the surface. A frozen ozone/oxygen film would not be expected to behave in such a manner. Solid ozone and ozone/oxygen mixtures will detonate when triggered by mechanical shocks, electrical sparks, etc. Several processes can therefore be envisioned as taking place in the laser driven ozone/oxygen film. The process leading to the initial escape of film material, which should be somewhat analogous to the blow off process in the metal films, is characterized by the highest temperature (41,000 K) and largest λ (1.03). Subsequent loss of film material would be expected to be due to local detonation of the film material followed by evaporation of the mixture over a larger area due to heating of the substrate. This sequence is qualitatively supported by the m/e=16 and m/e=32 time-of-flight traces in Figure 2, as well as the fitted values for the λ's shown in Figure 5.

Other film materials for generation of atomic oxygen beams via laser blow-off are currently under investigation. The initial selection of the ozone/oxygen system was based on the desire to exclude elements other than oxygen and to produce a film which is highly absorbing at the KrF laser wavelength. The disadvantages of this system include the risks associated with the handling of ozone and the fact that cryogenically frozen films suffer from the tendency to condense water, nitrogen and other background components in the vacuum system. The *in situ* prepared films are rather non-uniform as deduced by shot-to-shot flucuations observed in the intensities of the time-of-flight traces. Materials which are stable under ambient conditions, i.e. certain heavy metal oxides, I_2O_5, etc., are strong candidates for film materials. An important factor in material selection seems to be the tendency not to form ionically-bound species. A laser evaporation study of uranium oxide indicated that the vapor was composed chiefly of UO_2 and UO with very little atomic oxygen or uranium detected[17]. Mass spectrometeric characterization of the blow off from ITO and I_2O_5 films will be performed in the near future. If a more suitable film material than cryogenic ozone/oxygen is found, the laser blow off technique should provide an ideal source of fast atomic oxygen for mechanistic studies of material interactions in the low earth orbit environment.

The recent acquisition of a 35" crossed molecular beams apparatus of the design by Y. T. Lee[18], will permit a wide variety of experiments to be performed in support of understanding the gas-surface chemistry occurring in low earth orbit. The rotatable mass spectrometric detector will allow the measurement of energy and angular distributions for products from bombarded surfaces. More fundamental chemistry of fast atomic oxygen reactions with simpler model compounds (i.e. alkanes, substituted benzenes, etc.) may be explored in great detail to permit extrapolation to the initial encounter of atomic oxygen with polymer molecules on a surface. A thorough understanding of the mechanisms for atomic oxygen interaction may prove crucial in the molecular design of highly resistant new materials.

5. ACKNOWLEDGEMENTS

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