A Sputtering Derived Atomic Oxygen Source for Studying Fast Atom Reactions

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ABSTRACT

A novel technique for generation of fast atomic oxygen has been developed. These atoms are created by ion beam sputtering from metal oxide surfaces. Mass resolved ion beams at energies up to 60 KeV are produced for this purpose using a 150 cm Isotope Separator. Studies have shown that particles sputtered with 40 KeV Ar^+ on Ta_2O_5 were dominantly neutral and exclusively atomic. The atomic oxygen also resided exclusively in its ^3P ground-state. The translational energy distribution for these atoms peaked at ca 7 eV (the metal-oxygen bond energy). Additional measurements on V_2O_5 yielded a bimodal distribution with the lower energy peak at ca 5 eV coinciding reasonably well with the metal-oxygen bond energy. The 7 eV source was used to investigate fast oxygen atom reactions with the 2-butene stereoisomers. Relative excitation functions for H-abstraction and π-bond reaction were measured with trans-2-butene. The abstraction channel, although of minor relative importance at thermal energy, becomes comparable to the addition channel at 0.9 eV and dominates the high-energy regime. Structural effects on the specific channels were also found to be important at high energy.

INTRODUCTION

In recent years the Space Shuttle program has enabled scientists to make observations and gather data on the effects of the earth's environment on materials exposed at low orbit attitudes and at orbiting velocities of 8×10^5 cm/s. Such tests have shown materials to undergo extensive degradation which result in surface modification and even mass loss (1-4). Since the earth's atmosphere is dominantly comprised of atomic oxygen at these altitudes, it was thought that the most probable cause for these effects was due to chemistry initiated by the high velocity impact with these atoms. This prompted a recent surge of effort aimed at developing atomic oxygen sources for the purpose of investigating these energetic phenomena under controlled laboratory conditions. Studies of this nature are undoubtedly crucial to the development of new materials that would be more impervious to these effects not only from the standpoint of satisfying immediate interests in obtaining more suitable protective materials for the Shuttle's ram direction surfaces, but also from the standpoint that such long term degradative effects could have a severe impact on the longevity and performance of any future orbiting stations (5).

The present report describes a source of fast atomic oxygen that is derived from ion beam sputtering. This report also describes an application of this source to the investigation of high energy atomic oxygen

chemistry in the gas-phase. It is felt that investigations of this kind provide a sounder foundation through which the chemistry occurring on surfaces can be better understood.

EXPERIMENTAL APPARATUS

The complete system for O-atom generation and reaction is shown schematically in Figure 1. The system utilized a 150 cm isotope separator for the purpose of generating and mass resolving kilovolt ion beams. Ions were generated within a dual plasmatron source then extracted through a 4.45 mm diameter aperture. The source housing along with the aperture plate were electrically floated at the desired acceleration voltage. Acceleration voltages between 5 and 60 KeV were possible. Positive ions were accelerated toward an extraction lens that was biased with +200 v and focused slightly. A strong vertical focussing was also provided by an Einzel lens system while the other two plates were at ground potential. The beam was then subjected to a uniform magnetic field applied by a 90°, 150 cm magnet for momentum analysis. The system has the resolving power of 400. For the majority of the test studies described in this report, a 40 KeV argon ion beam was employed at intensities ranging between 15 and 25 µA after mass resolution and focussing.

The sputtering chamber comprised of a set of focussing lenses, differentially pumped aperture, and reaction chamber. As the ion beam emerged from the magnetic sector, it was focussed through 4.8 mm diameter differential aperture using cylindrical electrostatic lenses. The aperture was cut from a brass disk and vacuum sealed onto a larger aluminum flange that made a vacuum seal between the target chamber and the forechamber holding the focussing lenses. Both chambers were constructed of 15.2 cm inside diameter pyrex pipe. The reaction chamber was 20 cm long. The back-end was also vacuum sealed to a second aluminum flange that provided access to the chamber. All beam monitoring connections fed through this flange were of the type of sealed BNC connectors. A polished brass sleeve, 15.0 cm x 12.7 cm diameter was mounted inside the chamber using teflon rings for electrical isolation. This sleeve was biased with a positive potential in order to draw secondary electrons out of the reaction zone. Holes were cut in the sleeve and aligned with ports on the pyrex chamber to provide access for gas inlets, vacuum monitoring devices, a quadrupole mass analyzer equipped with a differential sampler, and a product collector. Background pressures were typically below 1×10^{-6} torr. Reactant gases were differentially pumped through the target chamber at pressures ranging from 1×10^{-5} to 3×10^{-2} torr.

The sputtering source comprised of a 12.1 cm diameter brass disk mounted on a vacuum sealed rotatable rod. Metal oxide foils, prepared in an anodizing cell (6), were mounted on this disk at a fixed angle incident to the impinging ion beam path. The source could be moved to any distance from the front aperture, and rotated 360°.

The product collector comprised of a 92 cm x 7.6 cm diameter pyrex impact trap that was mounted 90° to the gas flow. The inner surface of

this trap was liquid nitrogen cooled during a run. The entire trap could also be baked-out at about 200°C. During a run, products and substrate gas were condensed onto the inner surface of this trap for later analysis via gas chromatography - mass spectrometry. Non-condensible products, however, were monitored via on-line mass spectrometry. Collected products were processed through a manifold consisting of various solid adsorbents used to concentrate reaction products relative to the substrate gas. The techniques used in this process are similar to those employed in bulk gas processing for atmospheric analysis (7).

Source Characteristics

A principal concern in designing the above system was to minimize the effects of secondary electrons on the resultant atom-molecule chemistry. These electrons were emitted as a result of primary ion collisions with the oxide surface, and also as a result of ion interaction with substrate gases. From tests designed to monitor electron impact effects on gaseous constituents present in the target chamber, it was determined that a sleeve surrounding the reaction zone and biased with a + 90 v potential would minimize these effects.

A study was also carried out to provide information related to the question whether metastable atomic oxygen states are generated through ion beam sputtering. It is well documented that metastable $O(^1D)$ atoms undergo reaction with saturated hydrocarbons via C-H insertion to yield the respective alcohol (8). On the other hand, ground-state $O(^3P)$ atoms only abstract H-atoms to yield water. It was possible to measure the metastable state distribution by measuring the yields of alcohol and water arising from sputtered O-atom reaction with a saturated hydrocarbon molecule. Normal butane gas was used in this test. The following results were obtained: a Ta_2O_5 target showed only a trace amount of alcohol that was below detection limits for quantification; a V_2O_5 target yielded levels corresponding to 1 metastable in 150 atoms. It was concluded that the present conditions for sputtering yielded relatively clean sources of $O(^3P)$ atoms.

The O-atom sputtering yield (atoms/ion) was also determined from the water product yields in the above tests. Results indicated O-atom sputtering yields as high as 76 atoms/ion and 190 atoms/ion for fresh Ta_2O_5 and V_2O_5 surfaces, respectively. This afforded dynamic concentrations of ca 1 x 10^9 and 2.6 x 10^9 atoms/$cm^3 \cdot \mu A$, respectively. It may be possible to attain even higher concentrations by increasing the mass, energy, or intensity of the ion beam. Studies have shown that the sputtering yield generally increases as the mass and energy of the impinging ion beam increases (9).

Preliminary measurements were taken on the O-atom translational energy distribution using a quadrupole mass analyzer modified with an energy filter. The energy filter was made from a brass disk with a 6.35 mm aperture that matched the focussing lens to the mass filter. A gold plated tungsten wire mesh (80% transmission) was spot welded across the aperture.

This lens was mounted in the mass filter assembly between the ionizer and focussing lens, and was biased with up to 70 volts using a floated power supply. The entire assembly was mounted at 90° to the axis of the ion beam. The metal oxide target was also fixed in an orientation 60° incident to the axis of the ion beam, but could be rotated on axis to allow for energy distribution measurements to be taken at both forward (150° ± 10) and backward (30° ± 15) scattering angles. In operation, neutral atoms were ionized, energy filtered, then mass filtered. The m/e signal at 16 was recorded as a differential response to increases in the applied energy discrimination potential.

Comparisons were made between the m/e signals at 16 from neutral and ionic particles sputtered from the surface in vacuo by running the ionizer in both the on and off modes. Results showed that the positive ions occupied only a very small fraction (< 1%) of the sputtered material. It was also noted that the m/e signal ratio 16:181 was stoichiometric for Ta_2O_5 suggesting that the sputtered material is also dominantly atomic.

Results from these preliminary energy distribution measurements on neutral O-atoms sputtered from Ta_2O_5 are shown in the histograms in Figures 2a-c. Figures 2a and 2b represent distributions measured in the forward scattered and backscattered directions. While the distribution appears poorer in the later case, the integrated signal in this direction was about a factor of 6 lower than the forward direction. Peak energies in both cases seemed to coincide with the Ta-O bond energy (10). Increasing the mass of the primary ion beam, as seen in Figure 2c, did little to alter the peak energy and distribution. Parallel measurements were taken on V_2O_5. A bimodal distribution was observed for this oxide where the peak energy of the lower energy component roughly corresponded to the V-O bond energy. The higher energy component, ca 12 eV, may be representative of the oxide surface undergoing a stoichiometric change during ion bombardment (6).

GAS-PHASE STUDIES

Since a number of materials of aerospace interest contain carbon-based chemical bonds, and the impact velocities in low earth orbits provide ca 5 eV of collision energy for reaction, it would seem logical that studies on the gas-phase reactions using the fast atomic oxygen source with molecules containing such bonds, could facilitate understanding certain cases of material degradation.

In a recent preliminary study, the 7 eV source was used to measure the effective competition between π-bond reaction and H-abstraction on trans-2-butene. While it is generally accepted that thermal $O(^3P)$ atoms react preferentially, if not exclusively, with the π-bonds of unsaturated hydrocarbon molecules (8), it is not known under what conditions H-abstraction may effectively complete against this channel. Recent studies using substituted alkenes have shown H-abstraction thresholds at ca 1 kcal/mol with rising excitation functions attributing to the significance of this channel at higher energies.

In the present study, collision energies ranging between 7 eV and room temperature were obtained by buffering the target chamber with various pressures of neon. The average energy lost per collision with this buffer was calculated using equations derived from the Estrup-Wolfgang theory (11). Results indicate that the abstraction channel was of minor relative importance at thermal energy, but <u>dominates</u> the high-energy regime. A structural effect between cis- and trans-2-butenes was also observed in this high energy regime. The trans isomer was more susceptible to H-abstraction (relative to π-bond reaction) than the cis isomer. Two explanations are offered for this observation: a true structural effect may indeed be exerted at the point of the atom's approach to the molecule, thereby altering the effectiveness of one channel over the other; a pseudo abstraction channel may also be operative, where H-migration across the C-O bond of the addition complex followed by dissociation yields the same result as direct abstraction. In the later, a structural effect may be exhibited after the fact through varying intermediate stabilities.

SUMMARY

In summary, a system has been described for the generation and reaction of energetic O-atoms through ion beam sputtering. This process produces a clean source of ground-state $O(^3P)$ atoms with translational energies in the range of aerospace interest. High concentrations of atomic oxygen are also available through sputtering. Levels at 2.5×10^{10} and 6.6×10^{10} atoms/cm^3 were obtained using a 25 μA Ar^+ beam on Ta_2O_5 and V_2O_5, respectively. Achieving higher levels should also be possible by increasing the intensity, mass, or energy of the ion beam.

An application of this source was demonstrated in the studies on fast atomic oxygen reactions with unsaturated hydrocarbons. Results not only have shown that the nature of the chemistry is extremely dependent on the collision energy, but suggest that the entrance channels for specific reactions could be sensitive to geometry factors as well.

ACKNOWLEDGEMENT

REFERENCES

1. L. J. Leger, I. K. Spiker, J. F. Kuminecz and T. J. Visentine, "STS Flight 5 LEO Effects Experiments - Background Description and Thin Film Results," AIAA Paper 83-2631-CP, October 1983.

2. L. J. Leger, J. T. Visentine and J. F. Kuminecz, "Low Earth Orbit Atomic Oxygen Effects on Surfaces," AIAA Paper 84-0548, Presented at the 22nd Aerospace Sciences Meeting, Reno, NV, January 1984.

3. J. T. Visentine, L. J. Leger, J. F. Kuminecz and I. K. Spiker, "STS-8 Atomic Oxygen Effects Experiment," AIAA Paper 85-0415, Presented at the 23rd Aerospace Sciences Meeting, Reno, NV, January 1985.

4. B. D. Green, G.E. Caledonia and T. D. Wilkerson, "The Shuttle Environment: Gases, Particulates and Glow," J. Spacecraft and Rockets, October 1985.

5. L. J. Leger, J. T. Visentine and J. A. Schlensing, "A Consideration of Atomic Oxygen Interactions with Space Station," AIAA Paper 85-0476, Presented at the 23rd Aerospace Sciences Meeting, Reno, NV, January 1985.

6. R. Kelly and N. Q. Lam, Radiation Effects 19, 39 (1973).

7. A. C. Stein (editor) "Air Pollution" (Academic Press, New York 1968) Vol. 3, p. 497.

8. R. J. Cventanovic, "Advances in Photochemistry" (Interscience Publishers, John Wiley and Sons, New York 1963) W. A. Noyer, Jr., G. S. Hammond and J. N. Pittls, Jr. (editors), pp. 117-149.

9. H. F. Winters, "Radiation Effects on Solid Surfaces" ACS Advances in Chemistry Series, Monograph 158 (Am. Chem. Soc., Washington, DC, 1976) pp. 1-29.

10. O. Kubaschewski, E. L. Evans and C. B. Alcock, Metallurgical Thermochemistry (Pergamon Press, Oxford, 1967), p. 303.

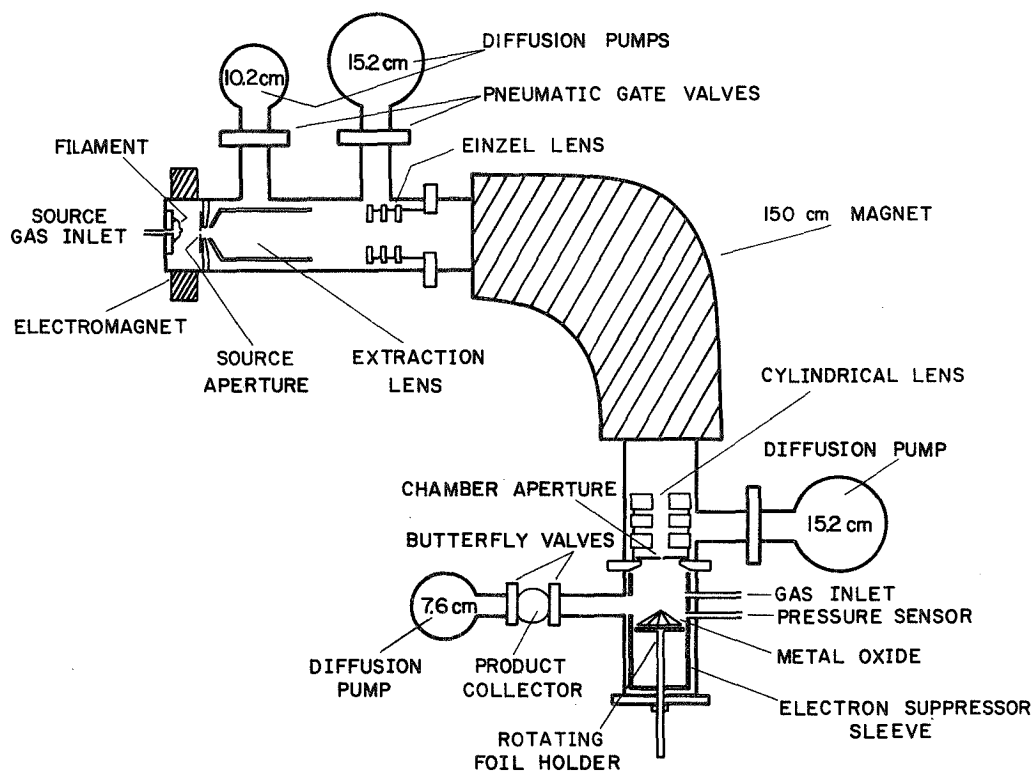11. R. Wolfgang, J. Chem. Phys. 39(11), 2983, 1963.

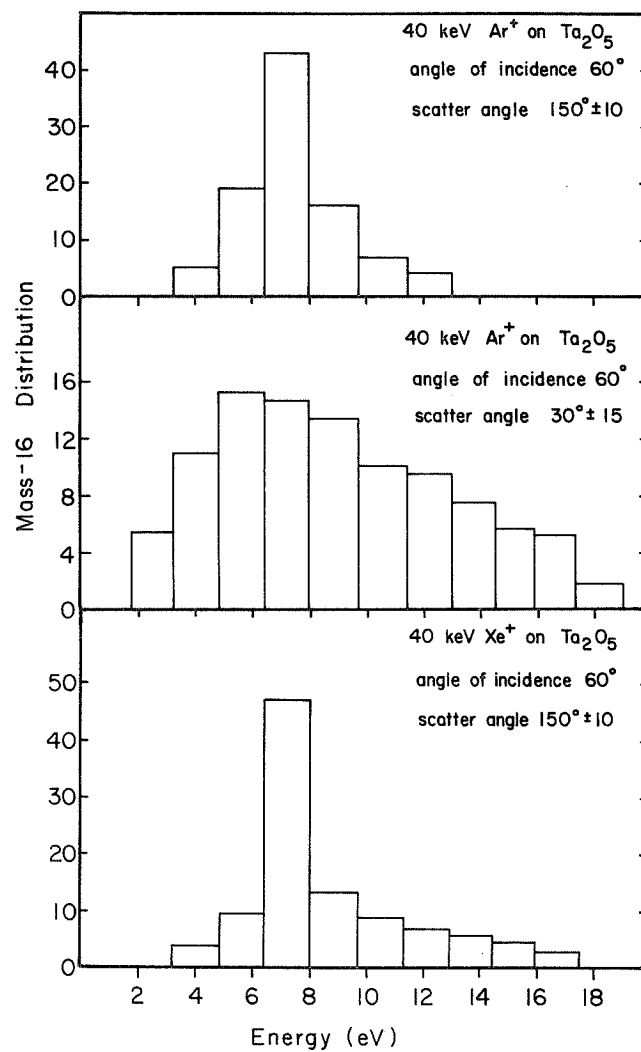Fig. 1   Schematic view of isotope separator and sputtering chamber.

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Fig. 2 Translation energy distribution of O-atoms sputtered from Ta_2O_5