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ATOMIC OXYGEN EFFECTS ON BORON NITRIDE AND SILICON NITRIDE: A COMPARISON OF GROUND BASED AND SPACE FLIGHT DATA

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ABSTRACT

The effects of atomic oxygen on boron nitride (BN) and silicon nitride (Si₃N₄) have been evaluated in a low Earth orbit (LEO) flight experiment and in a ground based simulation facility at Los Alamos National Laboratory. In both the in-flight and ground based experiments, these materials were coated on thin ($\approx 250\text{\AA}$) silver films, and the electrical resistance of the silver was measured in situ to detect any penetration of atomic oxygen through the BN and Si₃N₄ materials. In the presence of atomic oxygen, silver oxidizes to form silver oxide, which has a much higher electrical resistance than pure silver. Permeation of atomic oxygen through BN, as indicated by an increase in the electrical resistance of the silver underneath, was observed in both the in-flight and ground based experiments. In contrast, no permeation of atomic oxygen through Si₃N₄ was observed in either the in-flight or ground based experiments. The ground based results show good qualitative correlation with the LEO flight results, indicating that ground based facilities such as the one at Los Alamos National Laboratory can reproduce space flight data from LEO.

INTRODUCTION

The low Earth orbit (LEO) environment, consisting primarily of atomic oxygen, reacts with and degrades many commonly used spacecraft materials.^{1,2} For spacecraft traveling at 8 km/sec, atomic oxygen strikes forward facing surfaces with a collision energy of about 5 eV. The effects of the LEO environment, especially atomic oxygen, on materials need to be understood in order to predict long term material behavior. Materials such as boron nitride (BN) and silicon nitride (Si₃N₄) are of interest to the space materials community because they are candidate optical coatings for spacecraft mirrors. For use on long duration missions, these materials must withstand the environment without undergoing significant changes in optical properties.

Due to the scarcity and high cost of space flight experiments, ground based simulation facilities provide an alternate means of evaluating space effects on materials. In order to validate ground based testing, however, correlation of ground based data with space flight data is necessary. In this paper, space flight and ground based results for BN and Si₃N₄ are presented. These materials were flown in a Space Materials Experiment (SME) funded by the Strategic Defense Initiative Organization (SDIO) through the U.S. Army Materials Technology Laboratory (AMTL) and integrated by Sparta, Inc.³ The SME was a LEO experiment flown as a part of the Delta Star mission, launched March 24, 1989. A variety of materials, including BN and Si₃N₄, were flown on an active panel which was instrumented so that telemetry to a ground station for evaluation was possible. Experiments on BN and Si₃N₄ were also conducted at the Los Alamos National Laboratory (LANL) simulation facility. The LANL facility is capable of exposing materials to hyperthermal atomic oxygen (1-5 eV) at real-time and accelerated fluxes (1-10³ X that of LEO).⁴

TECHNIQUE TO EVALUATE THIN FILMS

The technique used to evaluate the BN and Si₃N₄ films in both the Delta Star space flight and LANL ground based experiments consists of using silver oxidation as a sensor for atomic oxygen penetration through the films.⁵ A schematic of the sensors used is shown in Figure 1. The sensor has two strips of silver ($\approx 250\text{\AA}$) deposited on top of an alumina or sapphire substrate. Coatings of known thickness are deposited over the silver films, and the electrical resistance of the silver is measured in situ during exposure to detect atomic oxygen penetration through the coating. Silver oxidizes in the presence of atomic oxygen to form silver oxide, and the electrical resistance of the oxide is much higher than that of pure silver. The electrical resistance data for silver can be converted to electrical conductance (inverse of electrical resistance) to evaluate the layers of silver remaining since electrical conductance is proportional to the thickness of a conductor.

EXPERIMENTAL CONDITIONS

For the Delta Star SME, the spacecraft was flown in LEO at an altitude of 500km and inclination of -48° with an estimated flux of 1.8×10^{13} atoms/cm²-sec. During the orbiting of the spacecraft, sample temperatures varied between 10°C and 40°C. At the LANL facility, samples were exposed to atomic oxygen at kinetic energies of 1.0 eV and 2.2 eV. The estimated O-atom flux for the 1.0 eV exposures was 4.5×10^{16} atoms/cm²-sec, using an Ar/O₂ gas mixture for the beam. The estimated O-atom flux for the 2.2 eV exposures was 1.9×10^{16} atoms/cm²-sec, also using an Ar/O₂ gas mixture. In both the space flight and ground based experiments, electrical resistance of the silver was measured in situ during exposure to the atomic oxygen environment.

Auger electron spectroscopy (AES) and scanning electron microscopy (SEM) were performed at Photometrics Microanalytical Laboratories (Huntington Beach, California). Transmission electron microscopy (TEM) was performed at the University of California at Irvine.

SAMPLE PREPARATION

For the samples exposed at LANL, the sample substrates were made of sapphire, with surface roughness of $<0.05 \mu\text{m}$. Silver ($\approx 250\text{\AA}$) and either BN (750\AA) or Si_3N_4 (700\AA) were then deposited on the sensors. The Si_3N_4 thin films were sputter-deposited at the McDonnell Douglas Space Systems Company (MDSSC-HB) Microelectronics Center using an ion beam system. These films were reactively sputtered using a Si target in N_2 gas to a total thickness of about 700\AA . The BN thin films were sputter-deposited at Naval Weapons Center (China Lake, California) using rf diode reactive sputtering. These films were sputtered using a BN target in Ar/N_2 gas to a total thickness of about 750\AA .

For the samples flown on the Delta Star SME, the sample substrates were made of alumina, with surface roughness on the order of $2\text{-}3\mu\text{m}$. The Si_3N_4 samples were coated by Battelle Northwest Laboratories and provided through the Air Force Weapons Laboratory. Si_3N_4 of $0.35\mu\text{m}$ and $0.70\mu\text{m}$ thicknesses was coated on the flight samples. The BN samples were coated by Spire Corporation and provided through the Army Materials Technology Laboratory. The thickness of the BN coated on flight samples was $1.0\mu\text{m}$.

RESULTS

To evaluate the data from the oxygen sensors, the silver films were assumed to be of uniform thickness across the surface, and the electrical resistance of the silver was converted to electrical conductance to evaluate the rate of decrease in silver film thickness as a function of atomic oxygen fluence. In both the space flight results from the Delta Star mission and the ground based results from LANL, no permeation of atomic oxygen through Si_3N_4 was observed. The data from the Delta Star flight experiment is presented in Figure 2, which shows the conductance of silver underneath the Si_3N_4 films plotted as a function of atomic oxygen fluence. Data for both the $0.35\mu\text{m}$ and $0.70\mu\text{m}$ Si_3N_4 indicated no silver oxidation. Similar results were obtained from LANL. Data taken at LANL for Si_3N_4 (700\AA) during exposure to an atomic oxygen beam at 1.0 eV energy (Figure 3) and at 2.2 eV energy (Figure 4) also indicated no silver oxidation or permeation of atomic oxygen through Si_3N_4 .

Auger analysis of a sample with 700\AA Si_3N_4 coated over Ag ($\approx 250\text{\AA}$) on a Si wafer substrate showed that after atomic oxygen exposure at LANL (2.2 eV , 210°C , total fluence of $4.7 \times 10^{20} \text{ atoms/cm}^2$), the oxygen concentration at the surface increased from 23 atomic % to 42 atomic %, while the nitrogen concentration at the surface decreased from 24 atomic % to 12 atomic %. Auger depth profile of the exposed sample indicated that oxygen was present only within 50\AA of the surface. Optical microscopy up to 100X magnification and SEM up to 10,000X magnification of Si_3N_4 coated oxygen sensors did not reveal microcracking of the Si_3N_4 films after exposure at LANL. TEM was used to study Si_3N_4 films which had been deposited on sodium chloride (NaCl) crystals before and after atomic oxygen exposure at LANL. This technique permitted easy removal of the film for TEM; the NaCl was dissolved in water and the Si_3N_4 films were then collected on copper grids. The films showed

some microcracking which appeared to be primarily in areas where there were irregularities on the NaCl surface. Electron diffraction was also done on the Si₃N₄ films, and it indicated that the film was amorphous before and after atomic oxygen exposure.

Permeation of atomic oxygen through BN was observed in both the space flight results from the Delta Star mission and the ground based results from LANL. The data from both the flight experiment and LANL clearly indicated that there was transport of atomic oxygen through BN. Data from the Delta Star flight experiment for a sensor with two strips of Ag (~250Å) coated with 1.0µm BN are presented in Figure 5. Data from the LANL simulation facility taken with a 1.0eV atomic oxygen beam (Figure 6) and with a 2.2 eV atomic oxygen beam (Figure 7) for sensors coated with 750Å BN are presented in Figures 6 and 7. In both sets of results, the conductance data indicated a steadily decreasing silver thickness (oxidation of silver to silver oxide) underneath the BN films with increasing atomic oxygen fluence.

For samples exposed at LANL, Auger depth profiles of a sample with 750Å BN coated over Ag (~250Å) on a Si wafer substrate showed that there was oxygen and carbon, in addition to boron and nitrogen, through the entire thickness of samples both before and after atomic oxygen exposure (2.2 eV, 45°C, total fluence of 1.7×10^{20} atoms/cm²-sec). Because a pure BN standard was not available, absolute atomic compositions of the elements present were not calculated using Auger analysis since the sensitivity factors required were unknown. The carbon concentration in both the exposed and unexposed samples was estimated to vary between 5 and 15 atomic % through the thickness of the films. The oxygen concentration in both the exposed and unexposed samples was estimated to vary between 5 and 20 atomic % through the thickness of the films. A 25% decrease in the thickness of the BN film after exposure at LANL was detected in the Auger depth profile and confirmed using ellipsometry. Optical microscopy up to 100X magnification and SEM up to 10,000X magnification of BN coated sensors after exposure at LANL did not reveal microcracking in the film.

Data on BN from the Delta Star SME, however, did not indicate erosion of this material from exposure to the LEO environment. A BN (0.1 µm) coated quartz crystal microbalance (QCM) was included in the SME, and results showed a slight mass gain of 0.75 µg/cm² after 150 days of mission elapsed time. It is unclear at this time whether the mass gain was due to contamination of the surface or due to oxygen incorporation into the BN.

DISCUSSION

The experimental data from the LANL ground based facility shows good agreement with space flight data from the LEO Delta Star mission in that the same trends were observed for Si₃N₄ and BN. Both space flight and ground based data for Si₃N₄ showed that this material did not allow oxygen transport through it. The stability of Si₃N₄ to atomic oxygen may be attributed to the conversion of Si₃N₄ to SiO₂ during exposure. The conversion of Si₃N₄ to SiO₂ has been observed in both thermal atomic oxygen⁶ and hyperthermal atomic oxygen systems.⁷

The space flight and ground based data for BN, however, showed that there was oxygen transport through this material. In both the space flight and ground based experiments, oxidation of silver underneath BN was observed. Direct correlation of the rate of oxygen transport through the BN (rate of oxidation of the silver) from the space flight and ground based data was not attempted because of the differences in the preparation techniques and thickness of the BN films as well as the differences in the substrate surface roughness on the sensors. Even though the LANL results showed a thickness loss in the BN, the remaining thickness of this material during atomic oxygen exposure was sufficient to completely cover the silver surface. There was oxidation of silver underneath, and therefore, oxygen transport through the remaining BN overlayer.

The loss of BN material under ground based exposure conditions needs to be studied further. The ground based exposures were performed under atomic oxygen fluxes which were $>10^3$ greater than the orbital conditions. Atomic oxygen surface catalyzed recombination may have heated the surface to drive off volatile oxide intermediates⁸ into the gas phase thereby producing surface recession. Under the relatively low fluxes at the Delta Star altitude, surface catalyzed recombination would have been greatly reduced. Results from the Delta Star SME showing oxidation of silver underneath BN but no mass loss in BN with LEO environment exposure confirmed that there was oxygen transport through this material, even under low atomic oxygen flux conditions. Since the characteristics of the BN (purity, density) probably play an important role in the behavior of these films in an atomic oxygen environment, a quantitative comparison of the silver reaction rates between the ground based and space flight data was not attempted.

In summary, the ground based experimental results from LANL show good qualitative agreement with space flight results from the Delta Star mission. The ability to reproduce LEO space flight results in a ground based simulation facility using the same technique (oxygen sensors) indicates that ground based facilities are able to simulate the LEO atomic oxygen environment. In the future, additional experiments to quantitatively correlate ground based data and space flight data using identical samples and techniques are needed.

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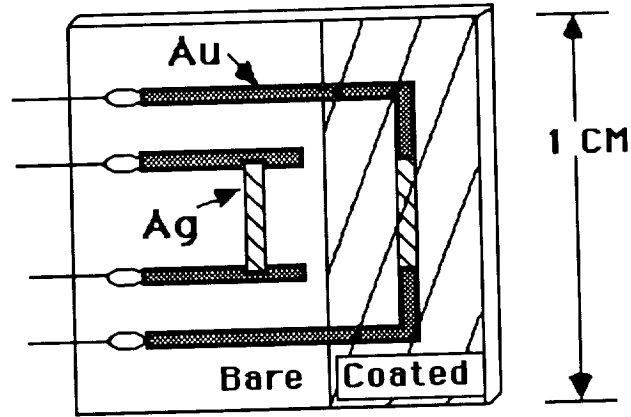


Figure 1: A schematic of the atomic oxygen sensor. The thickness of the silver is $\approx 250\text{\AA}$, and substrates are made of sapphire or alumina.

Conductance of Ag vs. Atomic Oxygen Fluence
Si₃N₄ Coated Sensor
 Flown on Delta Star Flight Experiment

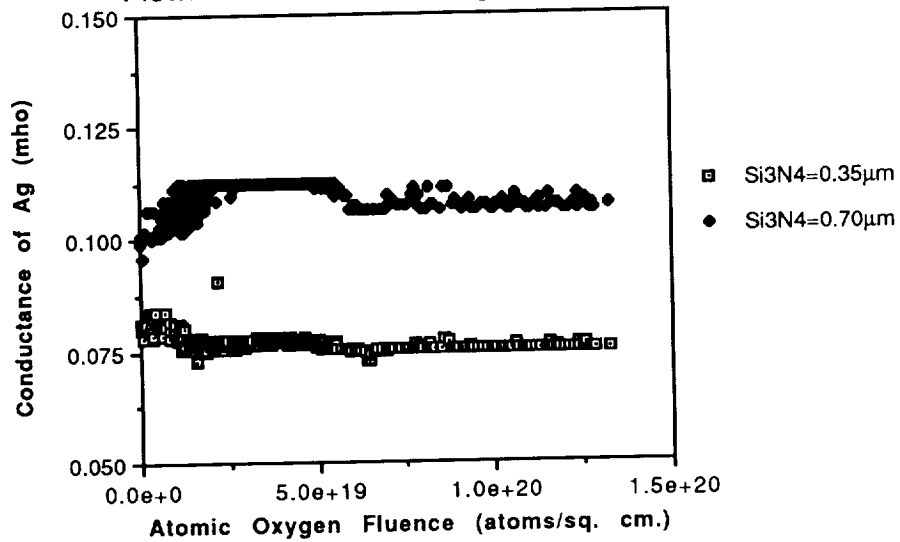


Figure 2: Plot of conductance of silver underneath films of Si₃N₄ as a function of atomic oxygen fluence for a sensor flown on the Delta Star Space Materials Experiment. The data indicates no silver oxidation; there was no atomic oxygen transport through the Si₃N₄ films.

Conductance of Ag vs. Atomic Oxygen Fluence
Si₃N₄ (700Å) Coated Sensor
Exposed at LANL Atomic Oxygen Facility

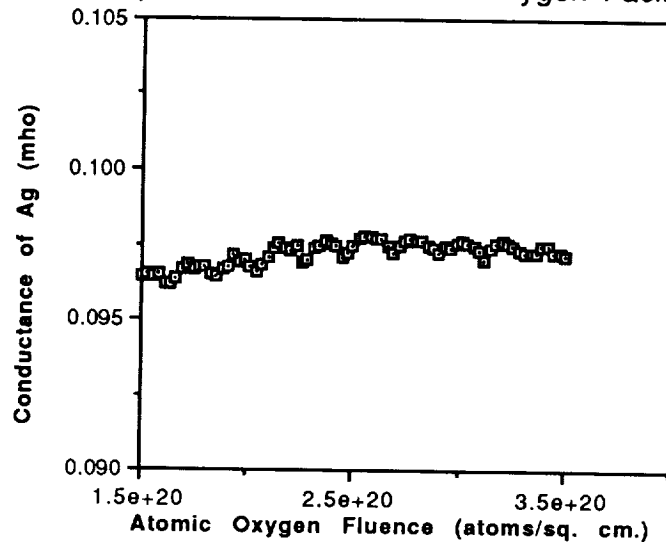


Figure 3: Plot of conductance of silver underneath a 700Å film of Si₃N₄ as a function of atomic oxygen fluence. The sensor was exposed at Los Alamos National Laboratory to an atomic oxygen beam of 1.0 eV energy and at a sample temperature of about 45°C. The data indicates no atomic oxygen transport through the Si₃N₄, as was observed in the Space Materials Experiment.

Conductance of Ag vs. Atomic Oxygen Fluence
Si₃N₄ (700Å) Coated Sensor
Exposed at LANL Atomic Oxygen Facility

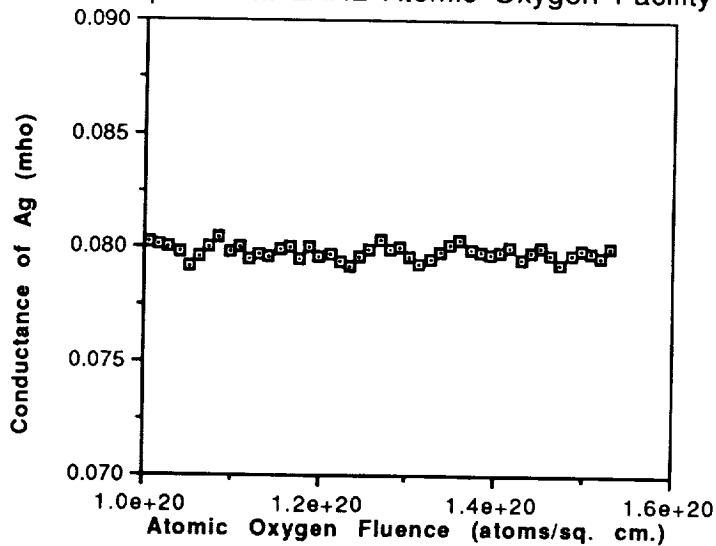


Figure 4: Plot of conductance of silver underneath a 700Å film of Si₃N₄ as a function of atomic oxygen fluence. The sensor was exposed at Los Alamos National Laboratory to an atomic oxygen beam of 2.2 eV energy and at a sample temperature of about 60°C. The data indicates no atomic oxygen transport through the Si₃N₄, as was observed in the Space Materials Experiment.

Conductance of Ag vs. Atomic Oxygen Fluence
BN (1.0 μ m) Coated Sensor
Flown on Delta Star Flight Experiment

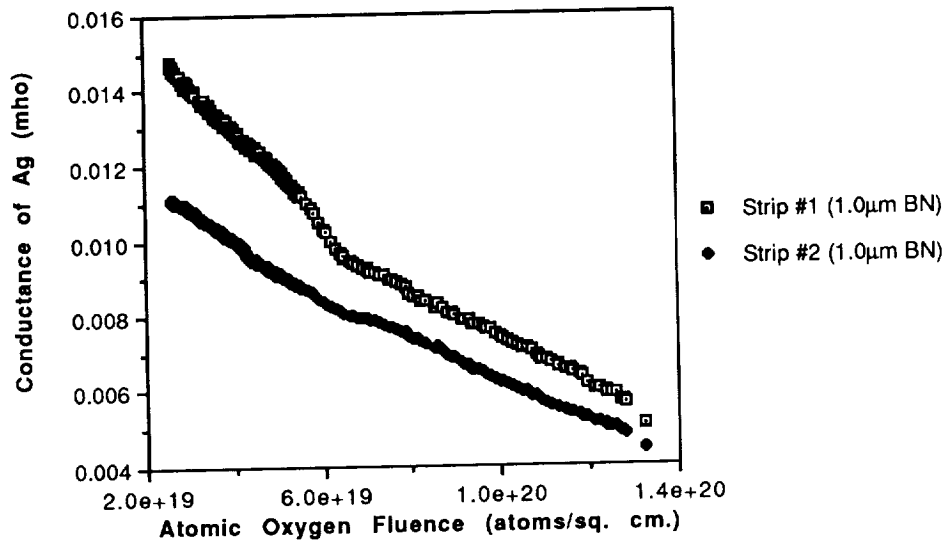


Figure 5: Plot of conductance of silver underneath 1.0 μ m films of BN as a function of atomic oxygen fluence for a sensor flown on the Delta Star Space Materials Experiment. The data shows steadily decreasing conductance (layers of remaining silver) as the silver is oxidized to silver oxide, indicating atomic oxygen transport through the BN.

Conductance of Ag vs. Atomic Oxygen Fluence
BN (750 \AA) Coated Sensor
Exposed at LANL Atomic Oxygen Facility

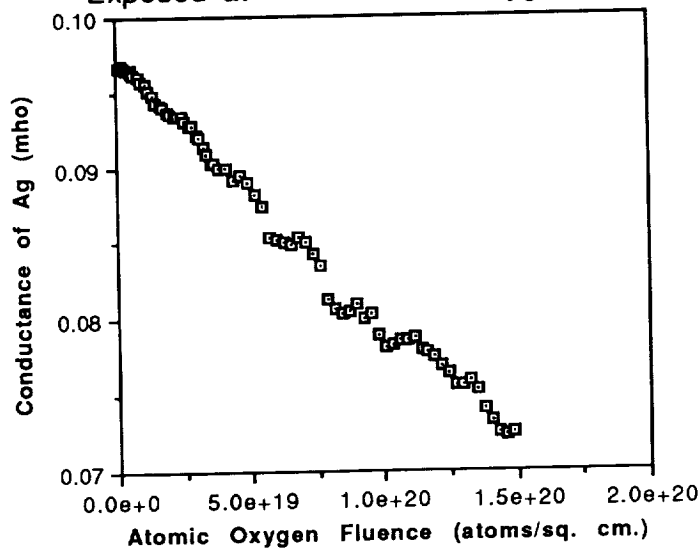


Figure 6: Plot of conductance of silver underneath a 750 \AA film of BN as a function of atomic oxygen fluence. The sensor was exposed at Los Alamos National Laboratory to an atomic oxygen beam of 1.0 eV energy and at a sample temperature of about 70 $^{\circ}$ C. Atomic oxygen transport through the BN was observed, as was also observed in the Space Materials Experiment.

Conductance of Ag vs. Atomic Oxygen Fluence
BN (750Å) Coated Sensor
Exposed at LANL Atomic Oxygen Facility

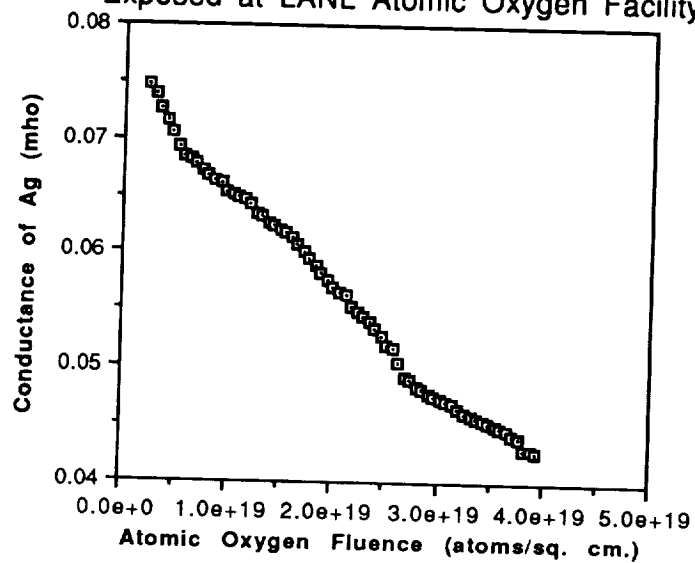


Figure 7: Plot of conductance of silver underneath a 750Å film of BN as a function of atomic oxygen fluence. The sensor was exposed at Los Alamos National Laboratory to an atomic oxygen beam of 2.2 eV energy and at a sample temperature of about 40°C. Atomic oxygen transport through the BN was observed, as was also observed in the Space Materials Experiment.