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AUTHOR(S): J. B. Cross, E. H. Lan, C. A. Smith, W. J. Whatley, and S. L. Koontz

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A COMPARISON OF GROUND-BASED AND SPACE FLIGHT DATA: ATOMIC OXYGEN REACTIONS WITH BORON NITRIDE AND SILICON NITRIDE

J. B. Cross
Los Alamos National Laboratory

E. H. Lan and C. A. Smith
McDonnell Douglas Space Systems Company

W. J. Whatley
Sparta, Inc.

S. L. Koontz
National Aeronautics and Space Administration
Johnson Space Center
Houston, TX 77058

ABSTRACT

The effects of atomic oxygen on boron nitride (BN) and silicon nitride (Si_3N_4) have been studied in low Earth orbit (LEO) flight experiments and in a ground-based simulation facility at Los Alamos National Laboratory. Both the in-flight and ground-based experiments employed the materials coated over thin (≈250Å) silver films whose electrical resistance was measured in situ to detect penetration of atomic oxygen through the BN and Si_3N_4 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 Si_3N_4 was observed in either the in-flight or ground-based experiments. The ground-based results show good qualitative correlation with the LEO flight results, thus validating the simulation fidelity of the ground-based facility in terms of reproducing LEO flight results.

INTRODUCTION

The low Earth orbit (LEO) environment, consisting primarily of atomic oxygen, reacts with and degrades many commonly used spacecraft materials.[1,2] Spacecraft traveling at 8 km/sec experience bombardment by atomic oxygen on forward facing surfaces (ram surfaces) with a collision energy of about ≈5 eV and a flux of $\approx 10^{15}$ AO/s-cm^2 or one monolayer/second. Since access to LEO is limited and expensive and there is a need for accelerated testing, ground-based testing methodology of materials needs to be developed. 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 Si_3N_4 thin films are presented. Materials such as boron nitride (BN) and silicon nitride (Si_3N_4) are of interest to the space materials community because they are candidate optical coatings for spacecraft mirrors to be used on long duration missions and must withstand the environment without undergoing significant changes in properties. These materials were flown in a Space Materials Experiment (SME) sponsored 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 Si_3N_4, were flown on an active panel which was instrumented so that data telemetry to a ground station was possible. A set of passive samples were also flown on STS 41 and exposed on the STS manipulator arm to ram AO for ~40 hours resulting in a fluence of ~10^{20} AO/cm^2 which is comparable fluence obtained on SME. Experiments on BN and Si_3N_4 were also conducted at the Los Alamos National Laboratory (LANL) simulation facility which is capable of exposing materials to hyperthermal atomic oxygen (1-5 eV) over a flux range of 1-10^3 X that of LEO flux.[4]

TECHNIQUE AND EXPERIMENTAL CONDITIONS

The technique used to evaluate the BN and Si_3N_4 films in both the Delta Star and STS 41 space flight and LANL ground-based experiments consists of using silver oxidation as a sensor for atomic oxygen penetration through the films.[5] The sensor has two strips of silver (~250Å) deposited on top of an alumina or sapphire substrate (Figure 1). 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 with near 100% efficiency 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 is converted to electrical conductance (inverse of electrical resistance) to evaluate the thickness of silver remaining since electrical conductance is proportional to the thickness of a conductor.

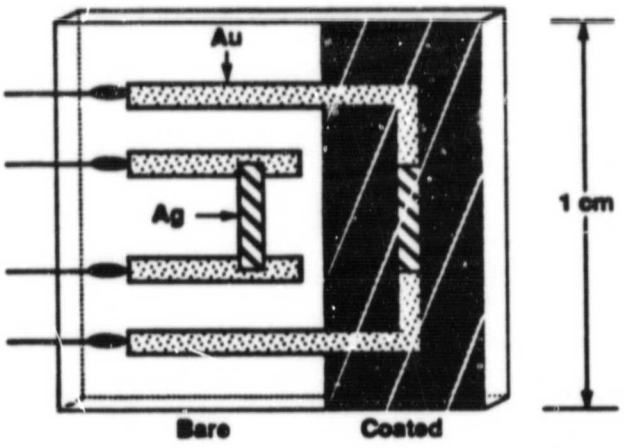

Figure 1. Atomic oxygen sensor. Thick (10-20 microns) gold lead-in wires are deposited on insulating substrate. Thin (250Å) silver film is deposited and overcoated with film of interest.

The Delta Star SME spacecraft was flown in LEO at an altitude of 500 km and inclination of -48° with an estimated flux of 1.8 x 10^{13} atoms/cm^2-sec for approximately nine months with active data acquisition. While in orbit sample temperatures varied between 10°C and 40°C. The STS 41 exposure was performed on the STS manipulator arm at a flux level of ~7 x 10^{14} atoms/s-cm^2 and a substrate temperature ranging between -10 to 50°C for a 40-hour time period (fluence ~10^{20} atoms/cm^2). Ground-based LEO simulation facility exposures were performed at atomic oxygen kinetic energies of 1.0 eV and 2.2 eV and fluxes of 4.5 x 10^{16} atoms/cm^2-sec and 1.9 x 10^{16} atoms/s-cm^2 respectively.

SAMPLE PREPARATION

The sample substrates employed in ground based and STS exposures were made of sapphire, with surface roughness of <0.05 μm. Silver (≈250Å) and either BN (750Å) or Si_3N_4 (700Å) were then deposited over the silver 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 700Å. In addition to the sapphire substrates, silicon wafer substrates were coated with 250Å of silver and then overcoated with Si_3N_4 for use in XPS and Auger analysis. 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 750Å. Silicon substrates were also coated with silver and then BN. The samples flown on the Delta Star SME were made of alumina with surface roughness on the order of 2-3 μm with 250Å of silver deposited on the substrate. Si_3N_4 films of 0.35 μm and 0.70 μm thicknesses was coated on the flight samples by Battelle Northwest Laboratories and provided through the Air Force Weapons Laboratory. The BN samples were coated (1.0 μm) by Spire Corporation and provided through the Army Materials Technology Laboratory.

RESULTS

No permeation of atomic oxygen through Si_3N_4 was observed in either the space flight results (Delta Star and STS 41) or the ground based results. The Delta Star flight results are presented in Figure 2A which shows the conductance of silver beneath the Si_3N_4 films plotted as a function of atomic oxygen fluence. The ground based results for Si_3N_4 (700Å) during exposure to an atomic oxygen beam at 1.0 eV and at 2.2 eV energy (Figure 2B) also indicated no permeation of atomic oxygen through the Si_3N_4 film.

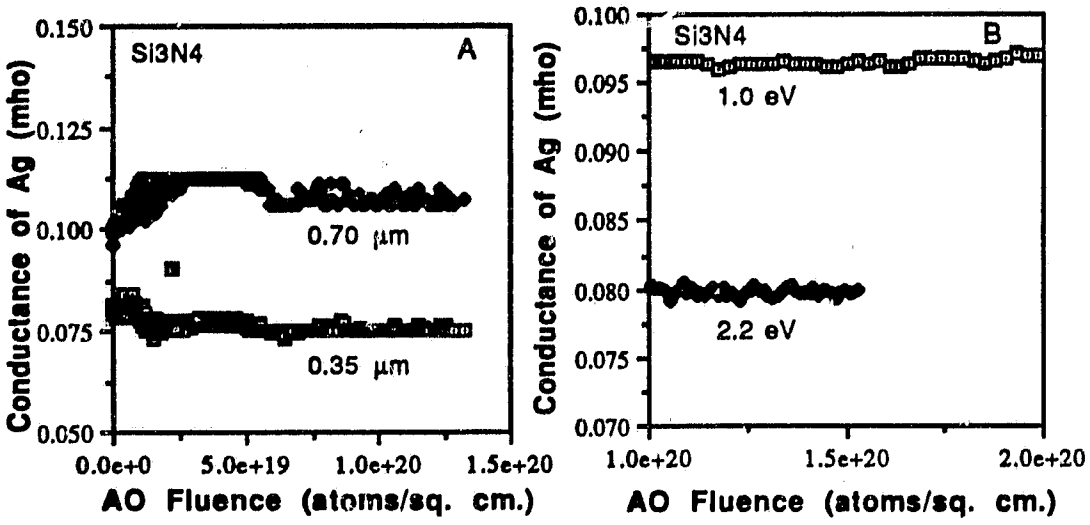

Figure 2. Panel A shows Delta Star SME flight results for Si_3N_4 films 0.7 and 0.35 μm thick on a rough alumina substrate. Panel B shows laboratory results for a 700 Å thick Si_3N_4 film on a smooth sapphire substrate.

Auger analysis of a sample with 700Å Si_3N_4 coated over Ag (≈250Å) on a Si wafer substrate showed that after atomic oxygen exposure at LANL (2.2 eV, 210°C, total fluence of 4.7 x 10^{20} 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 50Å 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 performed on the Si_3N_4 films and indicated that the film was amorphous before and after atomic oxygen exposure.

Permeation of atomic oxygen through BN was observed in both space flights (Delta Star and STS 41) and the ground based results. Figure 3A shows the Delta Star flight data while Figure 3B shows the ground test results and the STS 41 data. All boron nitride samples show the conductance steadily decreasing when exposed to increasing atomic oxygen fluence.

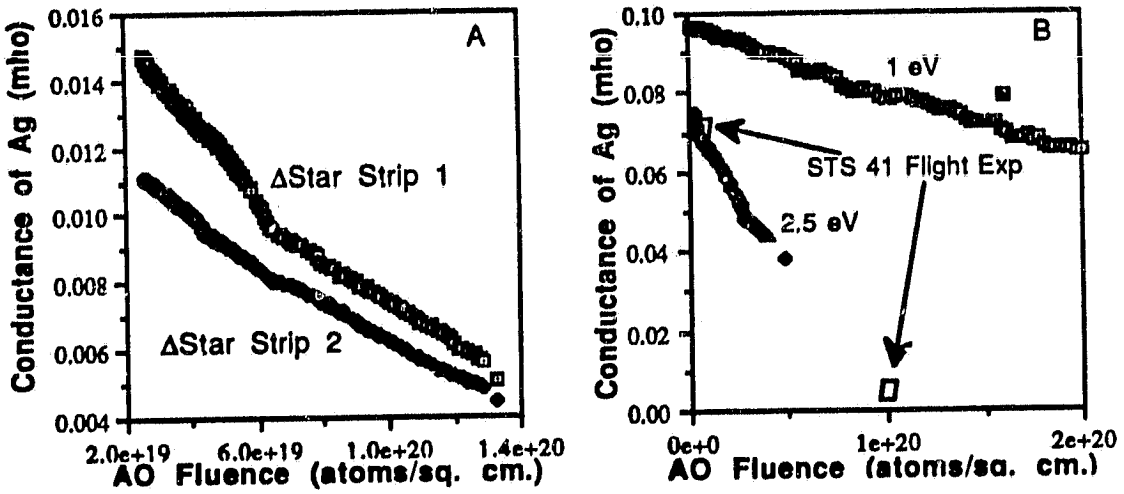

Figure 3. Panel A shows Delta Star SME flight results using 1 μm thick BN films over 250Å Ag film on rough alumina substrates. Panel B shows STS 41 flight and laboratory results for 750Å thick BN films on smooth sapphire substrates.

Auger depth profiles of 750Å BN coating over Ag (≈250Å) on a Si wafer substrate exposed in the ground based facility showed 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 x 10^{20} atoms/cm^2-sec). 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 $\mu g/cm^2$ rather than loss 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

Ground-based facility results shows good agreement with space flight data for both Si_3N_4 and BN. Atomic oxygen removes nitrogen from Si_3N_4 through ,most likely, the formation of nitrogen oxides (NO,NO_2) which are volatile and then forms SiO_2 which has a very low diffusion rate for AO and protects the underlying nitride from further reaction. The conversion of Si_3N_4 to SiO_2 has been observed in both thermal atomic oxygen[6] and hyperthermal atomic oxygen reactions.[7]

The space flight and ground based data for BN, however, showed that there was oxygen transport through this material resulting in oxidation of silver underneath the BN. Direct correlation of the rate of oxygen transport through the BN (rate of oxidation of the silver) from the space flight (SME) 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 ground based results showed a thickness loss in the BN, the remaining thickness of this material during atomic oxygen exposure was sufficient to cover completely the silver surface. There was oxidation of silver underneath, and therefore, oxygen transport through the remaining BN overlayer. The BN thickness decrease found in the laboratory exposure results is attributed to hydrated boron oxide leaching caused by water attack on the boron oxides when the sample was exposed to laboratory air environment during sample transfer to the surface analysis apparatus. Immediately after removing the BN AO exposed sample from the ground-based facility a well defined AO beam image was observed which subsequently disappeared after a one week exposure to laboratory air during shipment from Los Alamos to McDonnell Douglas Corporation. The SME flight experiment BN coated QCM however showed a small mass gain rather than loss since water is not present in LEO to form the volatile hydrated boron oxides and therefore oxygen would remain incorporated in the film. Ground-based QCM mass change measurements are planned in the future to confirm this hypothesis.

The results shown in Figure 3B indicate a possible translational energy dependance on AO permeation through BN and even the STS 41 flight results seem to agree with the higher translational energy ground based results. A more detailed study than the one presented here is needed before definite conclusions can be drawn on the effect of translational energy. However there exist calculations[9] which indicated that surface barriers larger than the bulk diffusion barriers can exist for material which would imply that translational energy may be effective in surmounting the surface barrier which would be the rate limiting step in oxygen permeation. The magnitude to these surface barriers are related to the elastic constants of the material in question, i., e., soft materials, which BN is, have in general lower barriers to oxygen penetration than hard materials such as SiO_2. A general conclusion that can be drawn from these results is that soft optical coatings should be avoided or at least be thoroughly investigated if long term exposure to the LEO environment is contiplated.

It is evident from these results that orbital exposure results alone are not sufficient to fully characterize the interaction of the LEO environment with materials. LEO exposure experiments are needed to validate ground-based results but only through the use of ground-based LEO simulation facilities can complete evaluation and characterization of materials before, during and after exposure be obtained and accelerated testing be performed. With a complete understanding of the LEO environmental effects on material, full-life material certification tests can then be undertaken in ground-based simulation facilities.

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