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Low Earth Simulation and Materials Characterization

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Oxygen plasma ashers and an electron cyclotron resonance (ECR) sources are currently being used for low Earth orbit (LEO) simulation. The suitability of each of these simulation techniques is considered. Thin film coatings are characterized by optical techniques, including variable-angle spectroscopic ellipsometry, optical spectrophotometry, and laser light scatterometry. Atomic force microscopy (AFM) has been used to characterize the surface morphology of thin aluminum films as a function of substrate temperature during deposition. Results on diamondlike carbon (DLC) films show that DLC degrades with simulated atomic oxygen (AO) exposure at a rate comparable to Kapton polyimide. Since DLC is not as susceptible as Kapton to environmental factors such as moisture absorption, it could potentially provide more accurate measurements of AO fluence on short space flights.

Introduction

THE low Earth orbit (LEO) space environment presents new challenges for materials research in the development of oxidation-resistant thin-film coatings. The University of Nebraska-Lincoln Center for Microelectronic and Optical Materials Research has been investigating both experimental techniques for LEO environment simulation, as well as macroscopic and microscopic properties of proposed materials for space power systems. The LEO environment is simulated by using either semiconductor plasma reactors or an electron-cyclotron resonance (ECR) source. Optical characterization of materials is done by variable-angle of incidence spectroscopic ellipsometry (VASE), transmission and reflectance spectrophotometry, and laser light scattering. Atomic force micro-scopy (AFM) allows imaging of surface topography down to the nanometer scale, giving accurate measurements of surface roughness that can be compared with laser scatterometry and VASE. Recent experimental results on thin films of diamondlike carbon will be presented to demonstrate the usefulness of these methods.

Low Earth Orbit Atomic Oxygen Simulation

The LEO environment is commonly simulated in laboratory situations by using a standard semiconductor plasma reactor with an atmosphere of either air or pure oxygen gas. We use a Structure Probe Incorporated Plasma Prep II plasma reactor with oxygen as the source gas. The Plasma Prep II creates a 100-W rf discharge at 13.56 Mhz with a chamber pressure of 50 to 100 mTorr. Typical oxygen flux in the chamber is approximately 3×10^{19} oxygen atoms/cm^2/h as determined by mass loss of Kapton polyimide, manufactured by DuPont.

These small, barrel-type plasma "ashers" have become standard for simulation of the LEO environment due to their simplicity, cost, and high plasma density, although they are far from ideal. The average energy per particle is less than 0.5 eV, which is far lower than the 4.5 eV encountered in LEO. Also, the particles in the plasma are omnidirectional, with particles striking the sample surface from all directions, while incident particles are extremely directional in LEO. Finally, the presence of many excited species in the plasma makes the asher environment far more complex than that of LEO. The result is that rather than having a true simulation, one uses the simple rule of thumb that if a material will survive asher exposure representative of a short fraction of operational lifetime (commonly 10^{20} to 10^{21} atoms/cm^2), it will also be able to withstand the atomic oxygen environment of low Earth orbit. This simple assumption will obviously not be true in all cases; true interactions of atomic oxygen with space materials can be far different from what happens in ashers. Thus, new or improved techniques of LEO simulation are of great interest.

One possible new LEO simulation technique under investigation at the University of Nebraska is the use of an electron-cyclotron resonance source.[1,2] ECR sources have the potential to overcome many of the drawbacks of plasma ashers. The ECR gun is a low-energy ion source that provides a highly directed beam of excited atomic or molecular species at low energies. Figure 1 shows the major parts of an ECR system. A waveguide is used to supply 2.45-GHz microwaves to the discharge chamber. However, to minimize the input microwave power, a static magnetic field is applied, causing the electrons to spiral around inside the chamber. By adjusting the magnitude of the magnetic field, the frequency of the electrons can be adjusted to match the input microwave frequency (875 Gauss required for a microwave frequency of 2.45 GHz). The spiral paths followed by electrons and ions in the discharge chamber minimize diffusion to the chamber walls, resulting in a high density plasma. ECR sources work in the pressure range of 10^{-5} to 10^{-1} Torr and can provide beam fluxes of 10^{19} to 10^{20} atoms/cm^2/h, which is within an order of magnitude of fluxes in plasma ashers. ECR sources do not contain acceleration grids and

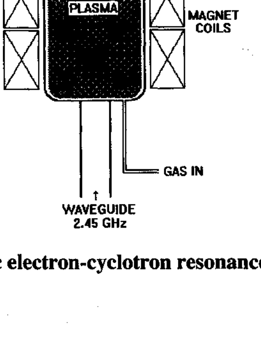

Fig. 1 Basic electron-cyclotron resonance source.

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Table 1 Twenty samples prepared for spaceflight aboard STS-46 showing types of data taken on the samples

Sample	1	2	3	4	5	6	7
700 Å Al/quartz	x	x	x	x	x		
1000 Å Al/quartz	x	x	x	x	x		
1500 Å Al/quartz	x	x	x	x	x		
700 Å Al/quartz	x	x	x	x	x		
1000 Å Al/quartz	x	x	x	x	x		
1500 Å Al/quartz	x	x	x	x	x		
5000 Å DLC/quartz		x		x	x		
1000 Å DLC/quartz		x	x	x	x		
5000 Å DLC/Si	x	x	x	x	x		
1 μm DLC/Si	x	x	x	x	x		
Diamond		x		x	x		x
Diamond		x		x	x		x
Solar concentrator multilayer stack	x	x		x	x		
Solar concentrator multilayer stack	x	x		x	x		
PG		x		x	x	x	
HOPG	x	x		x	x	x	
40% C/BN		x		x	x	x	
60% C/BN	x	x		x	x	x	
Graphite C/C composite		x		x	x	x	
Graphite C/C composite		x		x	x	x	

1 = variable-angle spectroscopic ellipsometry
2 = photography
3 = atomic force microscopy
4 = spectrophotometry
5 = mass measurement
6 = scanning electron microscopy
7 = Raman scattering

are therefore very "clean" ion sources. Also, the use of ECR sources on high vacuum systems allows for lower base pressures in the system. The lower base pressure, along with the presence of a smaller variety of excited species in the ECR plasma, makes the ECR a desirable source of atomic oxygen.

The University of Nebraska–Lincoln has prepared 20 samples of candidate power system materials to be launched aboard Space Shuttle mission STS-46. Analysis of these samples after space exposure will serve to further improve LEO atomic oxygen simulation techniques. Upon return from the spaceflight, comparison of these samples with identical samples exposed to simulated LEO environments will allow for critical comparison of laboratory-based simulation techniques with the LEO environment. Table 1 shows the list of samples to be exposed to the LEO environment for a total of 40 h, as well as the experimental methods used to characterize the samples. These materials include thin films of aluminum, diamondlike carbon, and diamond, and also, bulk samples of potential thermal radiator materials made from graphite, pyrolytic graphite/boron nitride, and carbon fiber/carbon composites.

Experimental Materials Analysis Techniques

The technique of variable-angle spectroscopic ellipsometry (VASE) uses collimated linearly polarized light that is specularly reflected from a material surface to determine layer thickness, as well as surface and interfacial roughness, on a scale less than a nanometer in the vertical dimension.[3–5] This technique serves as an extremely accurate monitor of layer degradation, even for extremely thin layers. When these layers consist of microscopic mixtures of materials, VASE can determine constituents. For example, the oxygen-to-nitrogen ratio in SiO_xN_y can be determined even for films on the order of 10 nm thick.

Light incident on rough surfaces reflects with both specular and diffuse components. The dependence of light intensity on the angle from the specular direction contains information about the surface microstructure. Thus, a scatterometer measures the intensity of light as a function of angle. Analysis is not trivial, but when done properly yields values for the root-mean-square surface roughness, which can be compared with surface roughness measured by VASE or atomic force microscopy.

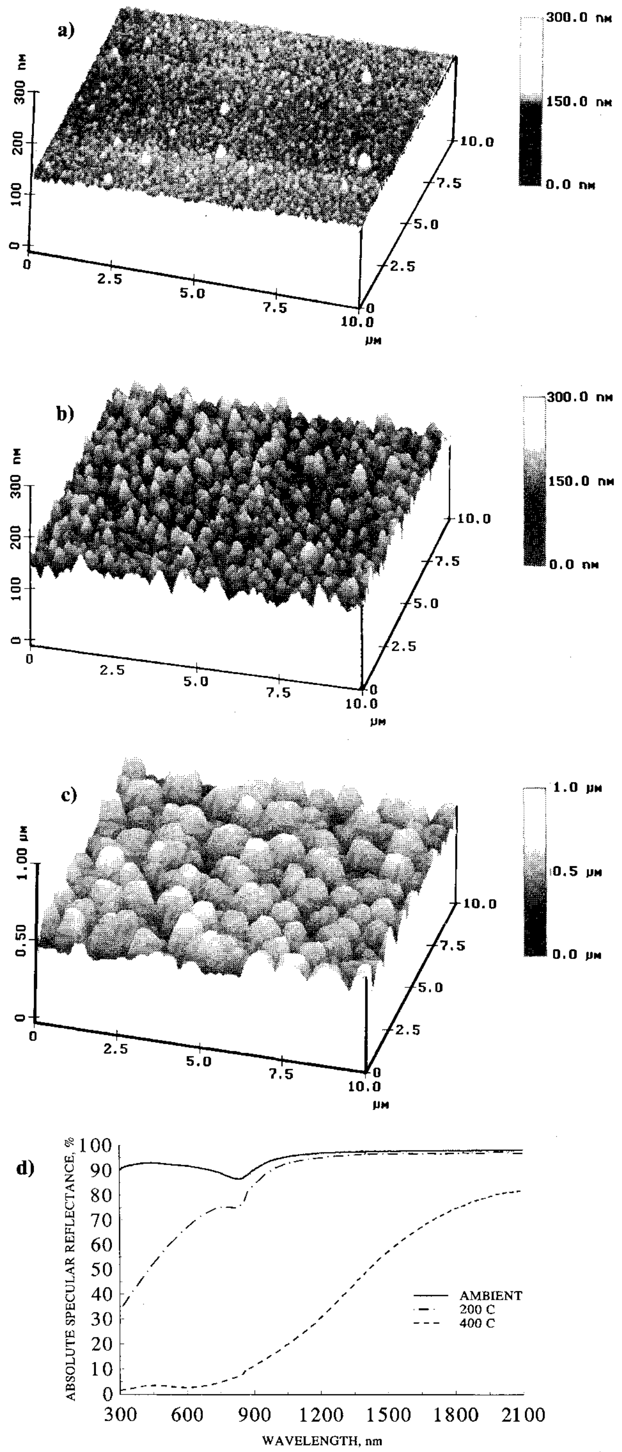

Fig. 2 Surface plots of sputtered Al/Si samples deposited at different substrate temperatures. Specular reflectance is also shown. a) Surface plot of sample deposited at 19°C, b) surface of sample deposited at 200°C, c) surface of sample deposited at 400°C, and d) specular reflectance of these three samples showing the effects of surface roughness on specular reflectance.

Optical spectrophotometry allows for the accurate determination of transmittance and reflectance of surfaces. A Perkin-Elmer Lambda 9 spectrophotometer is used to quantify changes in the transmission and/or specular reflectance of surfaces in the wavelength range of 170 to 3200 nm as a function of simulated LEO exposure. The authors have employed spectrophotometric techniques along with surface roughness studies using atomic force

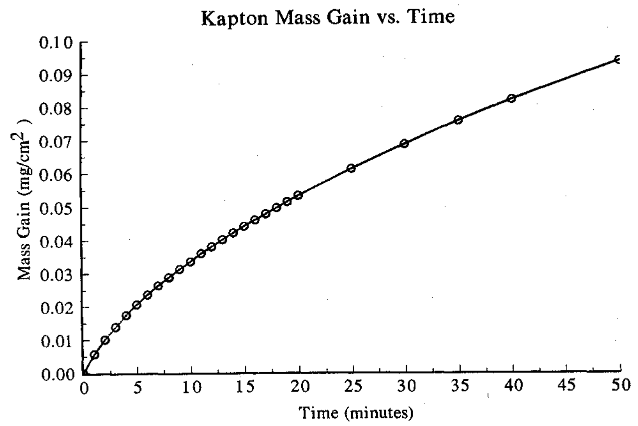

Fig. 3 Mass gain of Kapton HN due to absorption of moisture in air. The sample had been previously stored in vacuum.

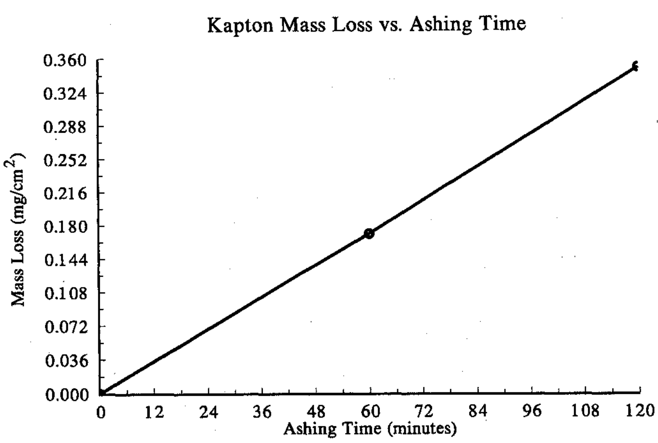

Fig. 4 Mass gain of Kapton HN due to absorption of moisture in air. The sample had been previously stored in vacuum.

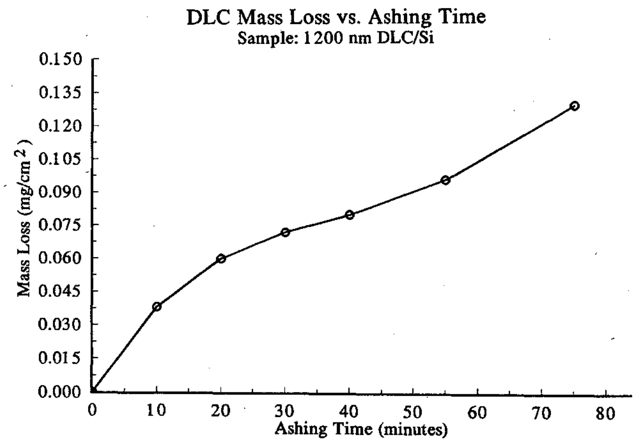

Fig. 5 Mass loss of diamondlike carbon as a function of oxygen plasma exposure. DLC loses mass at a rate of approximately 0.1 mg/cm^2/h. The nonlinearity in the curve is most likely due to slight variation in plasma flux inside the ashing chamber.

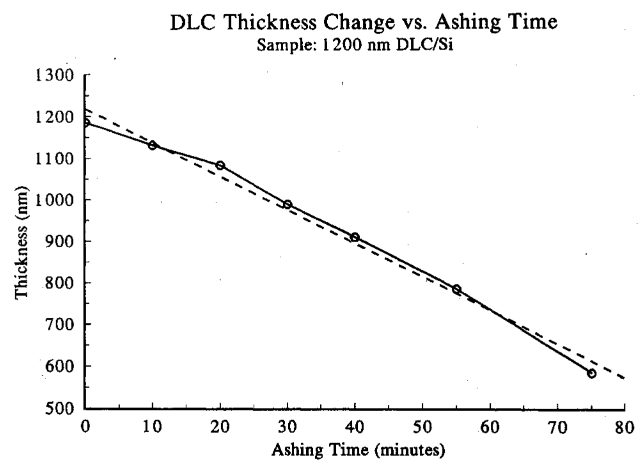

Fig. 6 Change in DLC thickness as a function of ashing time as determined by stylus profilometry. The plotted line of best fit indicates that DLC thins at approximately 7.7 nm/min.

microscopy to relate surface microstructure to the macroscopic specular reflectance, as shown in Fig. 2.[6–8] Figures 2a, b, and c are surface plots of AFM data showing the measured roughness of aluminum films sputtered at 19, 200, and 400°C, whereas Fig. 2d shows the associated loss in specular reflectance with increasing grain size due partly to diffuse scattering from the rough sample surfaces. The thickness of these aluminum films was 150 nm.

Experimental Results

Diamondlike carbon (DLC) thin films show promise for use as a secondary standard for accurately measuring atomic oxygen fluence on short space flights, as well as in ground-based LEO simulations.[9] The current method used to determine fluence is mass loss of Kapton polyimide. However, the accuracy of Kapton mass loss measurements suffers due to absorption of atmospheric moisture by the polyimide. To minimize moisture absorption problems, the Kapton needs to be dried out in vacuum for several days before use to remove water. Figure 3 shows the mass gain of Kapton HN after being removed from vacuum as a function of time.

DLC films, however, do not absorb moisture, and our films lose mass at a rate comparable to that of Kapton. Figure 4 illustrates the mass loss of Kapton HN samples as a function of ashing time in a plasma asher, showing Kapton losing mass at a rate of approximately 0.18 mg/cm^2/h. Figure 5 shows mass loss for a diamondlike carbon film as a function of ashing time deposited on a Si substrate. The mass loss rate of these DLC films was approximately 0.1 mg/cm^2/h. Figure 6 shows thickness erosion of a DLC film as a function of time in a Plasma Prep II asher as measured by stylus profilometry. The thickness loss is approximately 7.7 nm/min. Preliminary results using pure oxygen gas in the ECR source show DLC thickness erosion of approximately 6.0 nm/min. The flow rate used was 9.5 sccm of oxygen, the pressure 0.3 mTorr, and the power 175 W. This erosion rate is very similar to that of the asher. It has also been found that a lower flow rate at the same pressure gives a lower etching rate. Thus, another advantage of ECR simulation is that the beam parameters can be optimized to most accurately simulate the LEO environment.

Since diamondlike carbon films can contain up to 40% hydrogen, the thickness erosion and mass erosion rates for DLC films may vary as a function of hydrogen content since the hydrogen content is directly related to the "hardness" of the films. Thus, DLC films used for determining atomic oxygen fluence must currently be calibrated against a standard (Kapton). The University of Nebraska intends to measure thinning and mass loss of four different DLC films deposited under different conditions aboard Space Shuttle mission STS-46 (see Table 1). This direct determination of DLC erosion in LEO will allow DLC films to be calibrated as a standard for subsequent ground- and space-based fluence measurements.

Summary

The low Earth orbit environment is commonly simulated in laboratory situations using commercially available semiconductor plasma ashers, but electron-cyclotron resonance sources show great promise as an effective LEO simulation technique due to the directional nature of the ion beam, the larger ion energies in the beam, and greater control of the plasma parameters than can be achieved in ashers. Thin-film coatings can be effectively characterized by optical techniques such as variable-angle spectroscopic ellipsometry, optical spectrophotometry, and laser scatterometry. These optical techniques can be combined with microstructural characterization techniques such as atomic force microscopy and electron microscopy to provide complete materials characterization.

Acknowledgment

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References

[1]Asmussen, J., "Electron Cyclotron Resonance Microwave Discharges for Etching and Thin Film Deposition," *Handbook of Plasma Processing Technology*, Noyes Publications, Park Ridge, NJ, 1990, pp. 285–307.

[2]Matsuo, S., "Microwave Electron Cyclotron Resonance Plasma Chemical Vapor Deposition," *Thin Film Deposition Processes and Techniques*, Noyes Publications, Park Ridge, NJ, 1988, pp. 147–169.

[3]Woollam, J. A., and Snyder, P. G., "Fundamentals and Applications of Variable Angle Spectroscopic Ellipsometry," *Materials Science and Engineering*, Vol. B5, No. 2, 1990, pp. 279–283.

[4]Alterovitz, S. A., Woollam, J. A., and Snyder, P. G., "Variable Angle Spectroscopic Ellipsometry," *Solid State Technology*, Vol. 31, No. 3, 1988, pp. 99–102.

[5]Azzam, R. M. A., and Bashara, N. M., *Ellipsometry and Polarized Light*, North-Holland, New York, 1977.

[6]Rugar, D., and Hansma P., "Atomic Force Microscopy," *Physics Today*, Vol. 43, No. 10, 1990, pp. 23–30.

[7]Altshuler, T. A., "Atomic-Scale Materials Characterization," *Advanced Materials and Processes*, Vol. 140, No. 3, 1991, pp. 18–23.

[8]Synowicki R., Kubik, R. D., Hale, J. S., Peterkin, J., Nafis, S., Woollam, J. A., and Zaat, S., "Oxygen Plasma Ashing Effects on Aluminum and Titanium Space Protective Coatings," *Thin Solid Films*, Vol. 206, Nos. 1–2, 1991, pp. 254–258.

[9]Hale, J. S., Synowicki, R. A., Nafis, S., and Woollam, J. A., "Atomic Oxygen Plasma Effects on CVD Deposited Diamond-Like Carbon Films," in *Proceedings of the Fall MRS 1991*, Boston, MA (to be published).

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