Ground and Space Based Optical Analysis of Materials Degradation in Low-Earth-Orbit*

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There is strong interest in being able to accurately and sensitively monitor materials degradation in both ground-based and space-based environments. In this paper we review two optical techniques for sensitive degradation monitoring, namely spectroscopic ellipsometry and photothermal spectroscopy. These techniques complement each other in that ellipsometry is sensitive to atomically thin surface and sub-surface changes, and photothermal spectroscopy is sensitive to local defects, pin-holes, subsurface defects, and delaminations. Our progress in applying these spectroscopies (both ex situ and in situ) to atomic oxygen degradation of space materials is reviewed.

Introduction:

Quantitative evaluation of material degradation rates and mechanisms is important for design of future long term space missions. Certain techniques for evaluation of materials on earth after space exposure are effective but can't be adopted for use in space. Examples are electron microscopy and weight loss. The purpose of this paper is to briefly review two optical techniques that are effective diagnostic instruments on earth but can also be potentially adapted for in situ space monitoring.

We have successfully applied spectroscopic ellipsometry to several space materials systems, including reflector materials, after exposure to a series of pure oxygen plasma ashings. These experiments yield information on changes in thicknesses of thin films of both metals and dielectrics as well as information on microstructural damage due to oxygen exposure. More recently we've developed in situ spectroscopic ellipsometry on vacuum chambers. This involves getting polarized light beams through stress free windows.

The hardware for ellipsometry is now light weight, compact and reliable. Adaptation entirely to a vacuum environment is promising, and will be highly desirable for potential real time materials degradation measurements on space missions.

Photothermal spectroscopy has been developed for general material defect analysis, but until now has not been used for atomic oxygen degraded materials. Much of the hardware for this technique is similar to that used for ellipsometry and can thus be thought of as a related technology. An important difference from ellipsometry is that photothermal measurements involve thermal waves, and are highly effective in locating pinholes, delaminations, and sub-surface defects.

Several examples of applications of both spectroscopies to space materials degradation studies will be given.

Simplified Theory of Ellipsometry

The complete details of the theory are algebraically messy and won't be repeated here. In short, linearly polarized light having in-plane (p-polarized) and out-of-plane (s-polarized) light vector components is incident on a material under study. The reflected ray is elliptically polarized, and the ellipticity and orientations of the ellipse are determined using a second (rotating) polarizer. The simplest geometry is shown in Figure 1 for a material with no surface roughness and no films. The incoming light beam makes an angle of incidence of ϕ to the sample normal, and incident and reflected beams define the plane of incidence. Real materials are more complicated, and ellipsometry can be used to determine layer thicknesses, surface and interfacial roughnesses, and alloy fractions in complicated materials systems.

In our system the initial polarizer is at a fixed azimuth and a second polarizer (analyzer) is rotated. The relative (not absolute) intensity of light as a function of analyzer azimuth is measured. Figure 2 shows a system we call VASE (for Variable

Angle Spectroscopic Ellipsometry). Under computer control are the wavelength of light, polarizer and analyzer azimuths, a shutter and filter, and the angle of incidence. The system is fast, and data at a large number of angles of incidence and wavelengths can be taken.

For in situ applications (including potential space flights) ellipsometers are remarkably compact. Figure 3 shows a schematic of an ellipsometer recently adapted for vacuum systems.

Measured is the complex reflectance ratio $\rho = \tan \psi \exp (j\Delta) = Rp/Rs$ where Rp and Rs are the complex Fresnel Reflection coefficients for p- and s- polarization vector components. These coefficients contain information of interest about the material, such as layer thicknesses, alloy fractions, void fractions, and general optical constants.

The analysis procedure is to calculate ρ based on an assumed structure for the material and to compare the experimental and calculated ρ. A regression analysis is done to minimize the differences between experimental and calculated ρ, where the variables are the unknown materials parameters such as layer thicknesses.

There are two important caveats in ellipsometric analysis. The first is that the sensitivity to measurement of a system variable depends strongly on angle of incidence and wavelength as a result of the spectral dependence of the optical constants of solids. This means that the user must have both angle of incidence and wavelength under control in order to gain proper sensitivity.

Secondly, parameters are often correlated, meaning the value found for one layer thickness depends on the value found for another. To avoid or minimize correlation the user can select a proper number of measurements at the best angle and wavelength conditions. Often even this is not enough and the user needs to know when variables are correlated. Commercial systems with one wavelength and limited angle of incidence selection generally meet neither the sensitivity, nor the correlation criteria.

Thus we are strong proponents of a full VASE analysis, with ability to calculate sensitivities and correlations.

Thus when done properly ellipsometry can be an extremely sensitive tool. It can be performed in a wide variety of ambient conditions, including a wide range of pressures and temperatures, and can even be performed in an aqueous environment. It is also completely non-destructive. (Even electron beams in SEMs damage surfaces). The experiments can be performed remotely, and real time operation in space is a realistic possibility.

Simplified Theory of Photothermal Spectroscopy

Photothermal spectroscopy can be performed in several modes. In this paper we discuss the version known as photothermal beam deflection spectroscopy, which is a sensitive non-contacting and non-destructive evaluation technique. It has a number of applications including thermal imaging of defects, optical absorption coefficient, film thickness, and thermal diffusivity measurements. The spectroscopy is especially useful for imaging subsurface defects, not normally visible, such as delaminations and subsurface damage.

Figure 4 shows the experimental apparatus layout. The sample is mounted on a computer controlled x-y translation stage, and one light beam "skims" just above the surface of the sample. A second beam is directed perpendicular to the sample and is chopped at a controlled (variable) frequency. Absorption of this radiation causes periodic heating of the sample at the chopped frequency. Heating causes a periodic index of refraction gradient resulting in a small but measurable deflection of the sensing ("skimming") beam. The deflection is detected with a position sensitive solid state detector using a lock-in-amplifier.

Example Ellipsometry Applications to Space Materials

Atomic oxygen is known to enlarge pinholes and erode materials even beneath a coating. In addition it can cause uniform oxidation over larger areas, and uniform erosion of materials including metals and carbonaceous materials. A major purpose of ellipsometric analysis of space materials is to detect and follow (with monolayer sensitivity) changes in surfaces, interfaces, and films after exposure to atomic oxygen for even very short times. Thus it is sensitive to degradation very early in a mission.

Figure 5 shows the thickening of an oxide, and simultaneously the thinning of a silver metal film monitored by ellipsometry. Note the very fine scale of error bars for measurement. Figure 6 similarly shows the formation of aluminum oxide from an aluminum reflector exposed to atomic oxygen.

Examples of Photothermal Imaging

Figure 7 shows a photothermal image over the surface of a silicon semiconductor wafer showing the edge of a film having 1000 Angstroms thick tin oxide covering 400 Angstroms thick silver which was deposited on the wafer.

Figure 8 shows the photothermal image of a pulsed laser evaporated "strip" of copper removed from a substrate. The removal was not "clean", and residual metal was left in central regions, but the spectra are dominated by excess metal piled up at the edges of the "strip".

Figure 9 shows a photothermal image of a defect hole in a film of 300 Angstroms of silver on 25 Angstroms of aluminum on a silicon wafer. The hole is approximately 1000 microns wide. Figure 10 shows that the hole has widened and eroded after 3 hours of ashing to 1300 microns width.

We are in the early stages of applying photothermal imaging to space coatings, and the resolution and scale of data presented above will likely improve dramatically in the near future. It will be especially useful for quantitatively detecting film undercutting and delamination due to atomic oxygen.

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Ellipsometry

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Photothermal Imaging

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(3) G.C. Wetsel Jr., F.A. McDonald, "Resolution and definition in photothermal imaging", J. Appl. Phys. 56(11), 3081-3085, (1984).
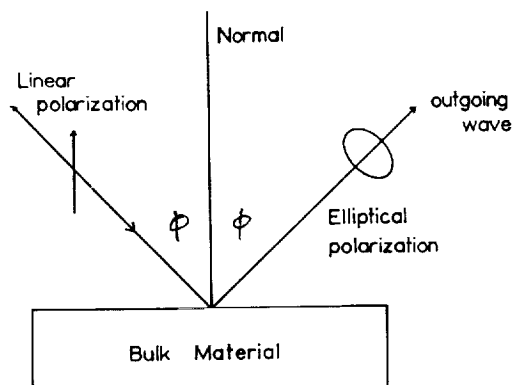
Figure 1
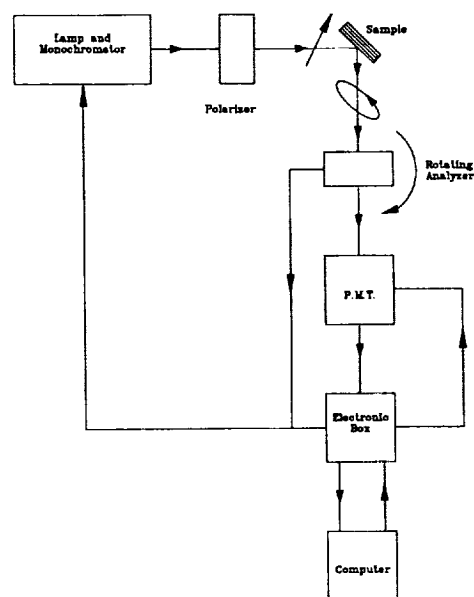Ambient-bulk model for ellipsometric
analysis

Figure 2
Schematic diagram of a variable angle
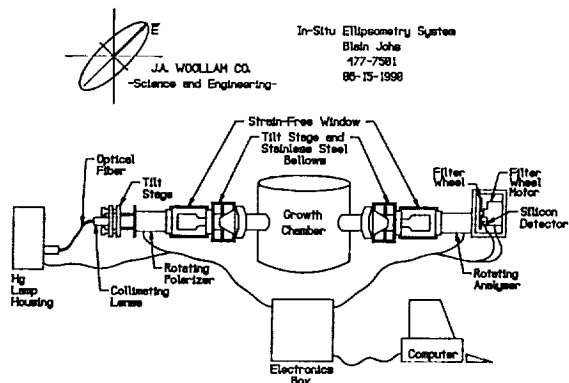spectroscopic ellipsometer (VASE)

Figure 3
Schematic of in situ ellipsometer
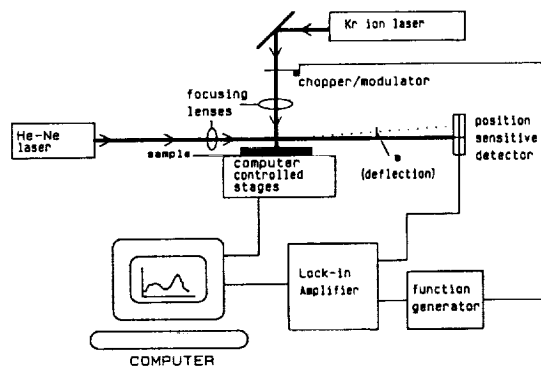
PHOTOTHERMAL BEAM DEFLECTION SPECTROSCOPY

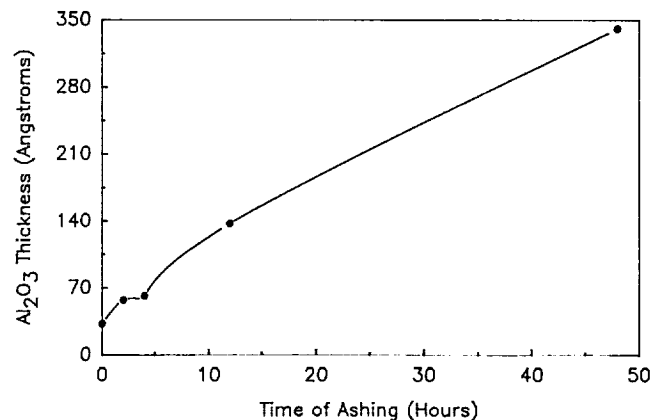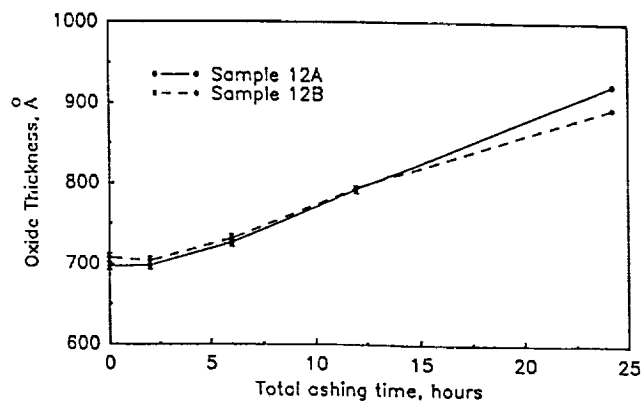Figure 4
Schematic of photothermal beam deflection
spectrometer

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Figure 6
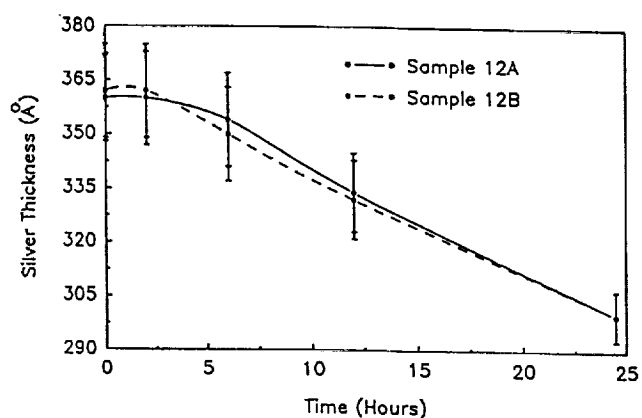Thickening of Al2O3 on aluminum due to
ashing, monitored ellipsometrically

Figure 5
Thicknesses of SiO2 and silver films as a
function of ashing time determined
simultaneouly in one sample using
ellipsometry
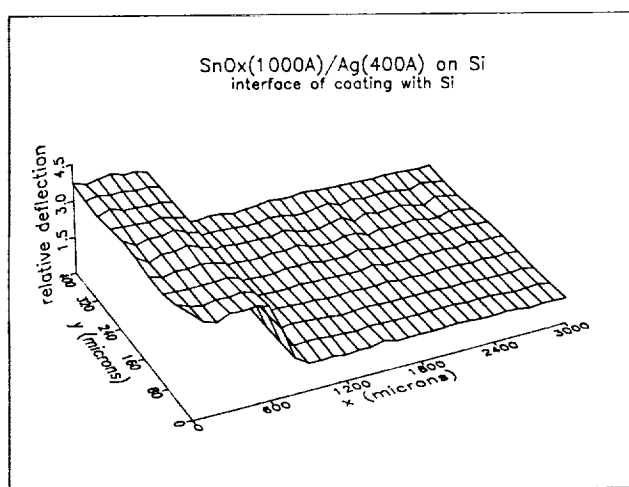
Figure 7
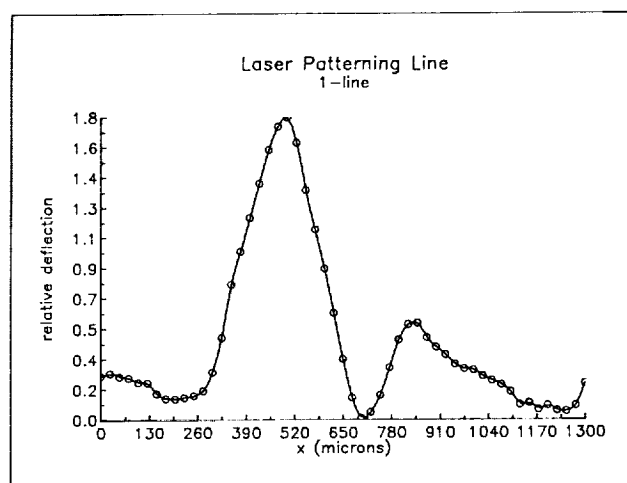Photothermal image of edge of a film of
tin oxide on silver on silicon

Figure 8
Photothermal image of removal of copper
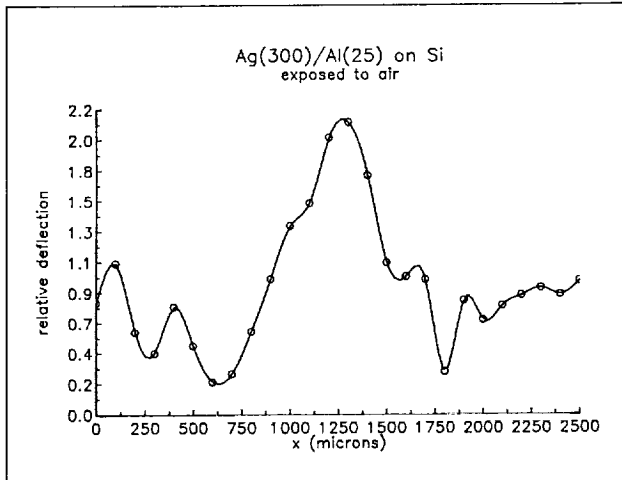in a strip geometry (using laser ablation)

Figure 9
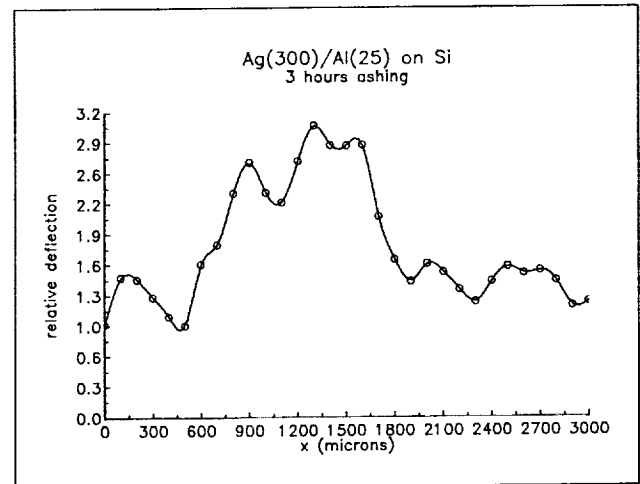Photothermal image of a defect hole in a film on a silicon wafer substrate

Figure 10
Photothermal image of hole from Figure 9 sample after 3 hour exposure to oxygen ashing