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Optical Darkening During Space Environmental Effects Testing—Contaminant Film Analyses

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14. ABSTRACT

As a part of a space environmental effects test, two samples used as contamination monitors exhibited slight darkening. Analysis by ellipsometry indicates that 120Å of highly absorptive material had been deposited on them. Static SIMS confirms that a contaminant material was deposited during the test. It further suggests that the contaminant film is composed of polymerized silicones and hydrocarbons. An attempt to use grazing-angle FTIR spectroscopy to identify the film led to inconclusive results.

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The Aerospace protocol for performing space environmental effects testing requires that reference samples be included in the sample test matrix to monitor contamination. In previous tests, these samples showed some loss of reflectance and/or transmittance, so after a recent testing campaign, Lab Ops personnel were tasked to determine the source of the darkening. This test involved exposure to proton, electron, and UV radiation that was calculated to simulate the radiation environment of a particular orbit. Unfortunately, an explanation of the process for obtaining the simulation parameters is complicated and beyond the scope of this report. Proton exposures were performed in the Aerospace Low Energy Accelerator Facility (LEAF) with the proton energies, nominal fluxes, and fluences given in Table 1. Electron and UV exposures were performed in the Deathstar chamber with the energies, nominal fluxes and fluences given in Table 2. Xenon and deuterium lamps provided the equivalent of 4644 solar hours over the course of the test. Two reference samples were included in this testing campaign. The first sample, VDA-31, is a thin aluminum film on a silica substrate. The second sample, FS-20, is an uncoated 7980 silica substrate. Another thin aluminum film on silica, VDA-37, served as a control sample. It was not introduced to any of the radiation chambers.

The transmission spectrum of FS-20 was measured before irradiation and at several time increments during the test. The spectra are presented in Figure 1. Examination of the spectra shows that the samples grow more lossy after each test increment, suggesting the growth of an absorbing layer over the course of the test. One might hypothesize that the darkening occurred because of radiation damage of the substrate material; however, damage to these materials at the prescribed radiation doses has

Table 1. Proton Exposure. Fluence is in protons/cm^2/equivalent year. The total fluence is the sum of exposures in protons/cm^2.

Energy (keV)	Flux, nA/cm^2	Fluence	Total Fluence
400	3	1.0E+12	1.0E+13
300	4	1.4E+12	1.4E+13
200	5	7.0E+12	7.0E+13
100	10	9.0E+13	9.0E+14
40	15	8.0E+14	8.0E+15
20	20	5.0E+15	5.0E+16

Table 2. Electron Exposure. Fluence is in electrons/cm^2/equivalent year. The total fluence is the sum of exposures in electrons/cm^2.

Energy (keV)	Flux, nA/cm^2	Fluence	Total Fluence
100	0.5	2.8E+14	2.0E+15
50	1	7.0E+14	4.9E+15
35	2	1.6E+15	1.1E+16
20	4	5.0E+15	3.5E+16
10	8	5.3E+15	3.7E+16
3	10	4.4E+15	3.1E+16
1	10	4.0E+15	2.8E+16

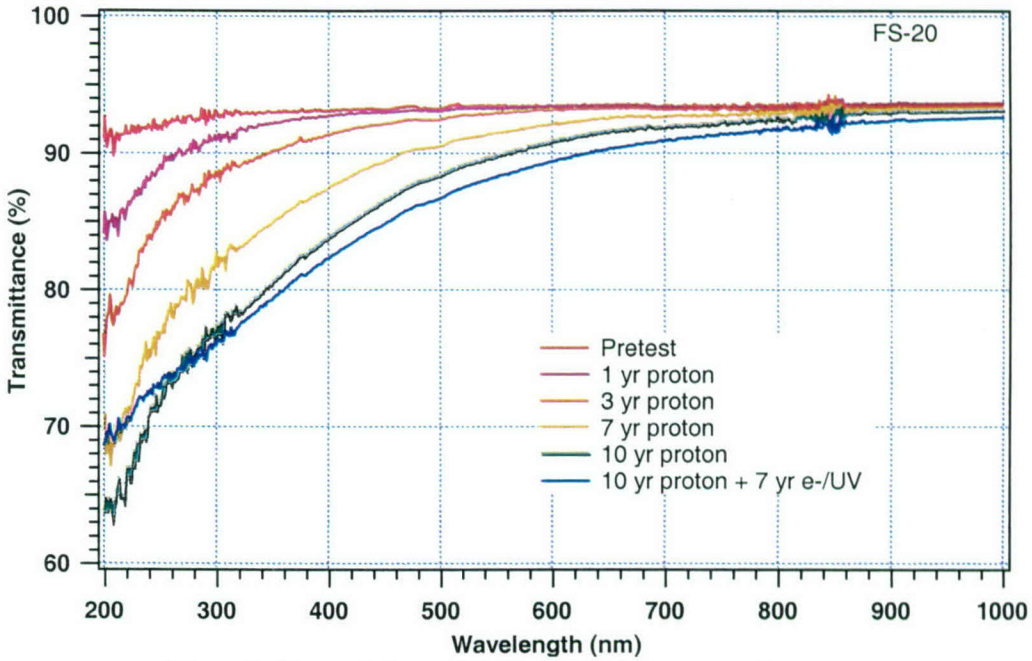

Figure 1. Transmission of FS-20 after each incremental exposure.

not been previously observed. Furthermore, the damage mechanisms in aluminum and silica (amorphous silicon dioxide) are very different, and unlikely to produce similar darkening given a similar radiation dose. Regardless, the darkened layer is likely to be very thin, which suggests that one employ surface-sensitive techniques like ellipsometry, static SIMS (Secondary Ion Mass Spectroscopy), and glancing-angle FTIR (Fourier Transform Infrared spectroscopy).

Ellipsometry is a very sensitive technique for characterizing optical surfaces. It involves measuring the ratio of polarized reflectances and measurement of the optical phase change upon reflection. Those values (Psi and Delta) are then fit to an optical model to determine layer thicknesses and refractive indices (n and k). For the first test, an unexposed aluminum mirror (sample VDA-37) was measured, and its optical properties were derived. The best fit was obtained with 47.5Å of aluminum oxide on optically thick aluminum. The measured and fit spectra are presented in Figures 2 and 3.

After that, Psi and Delta were measured for VDA-31, the exposed sample. Measurements were made at 3 angles to allow the analysis software (WVASE-32) to solve for an unknown single thin film on top of the previously characterized aluminum oxide and aluminum films. The unknown film was shown to be an absorbing material that can be modeled with two Lorentz oscillators. The measured and fit ellipsometry data is presented in Figures 4 and 5. The film thickness was determined to be 120Å; its n and k data are given in Figure 6. From n and k, the absorption coefficient can be derived as $\alpha=4\pi k/\lambda$. It is presented in Figure 7.

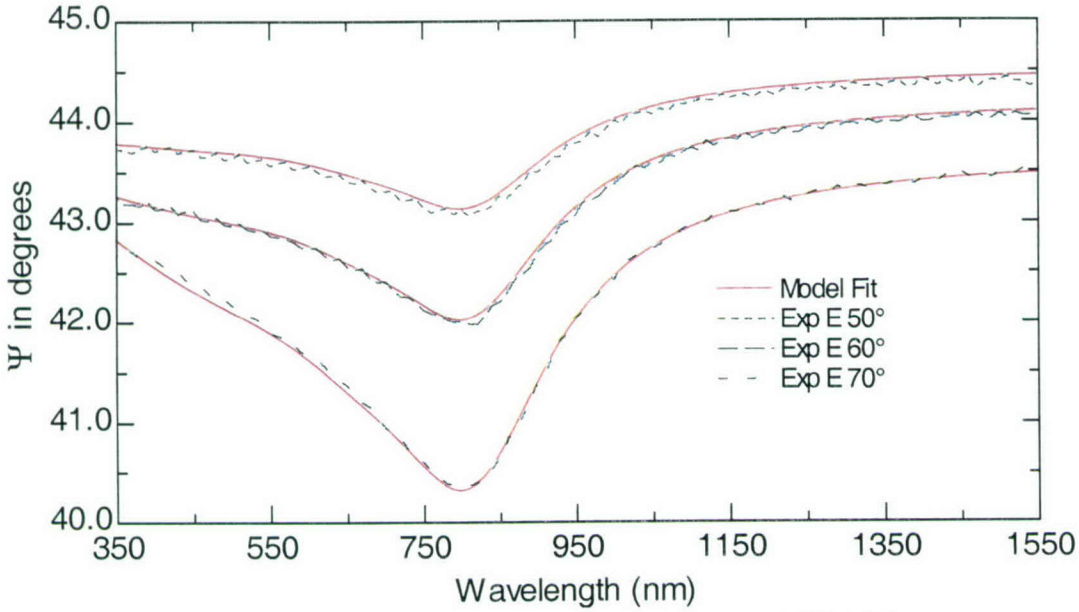

Figure 2. Measured and fit Psi spectrum on unexposed VDA-37.

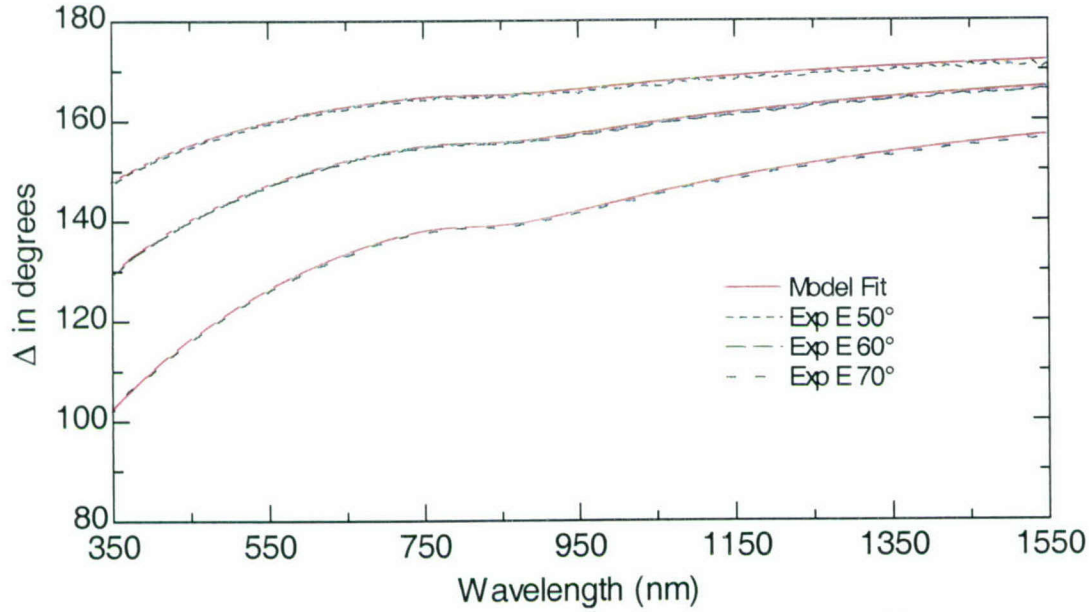

Figure 3. Measured and Fit Delta spectrum of unexposed VDA-37.

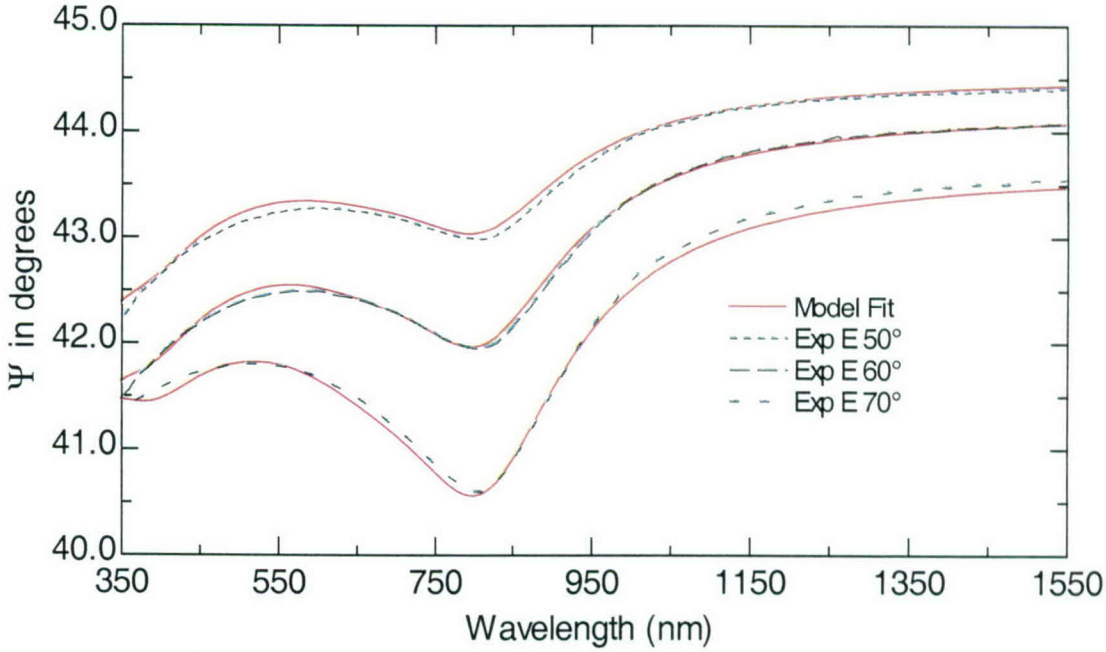

Figure 4. Measured and Fit Psi spectrum for VDA-31 post exposure.

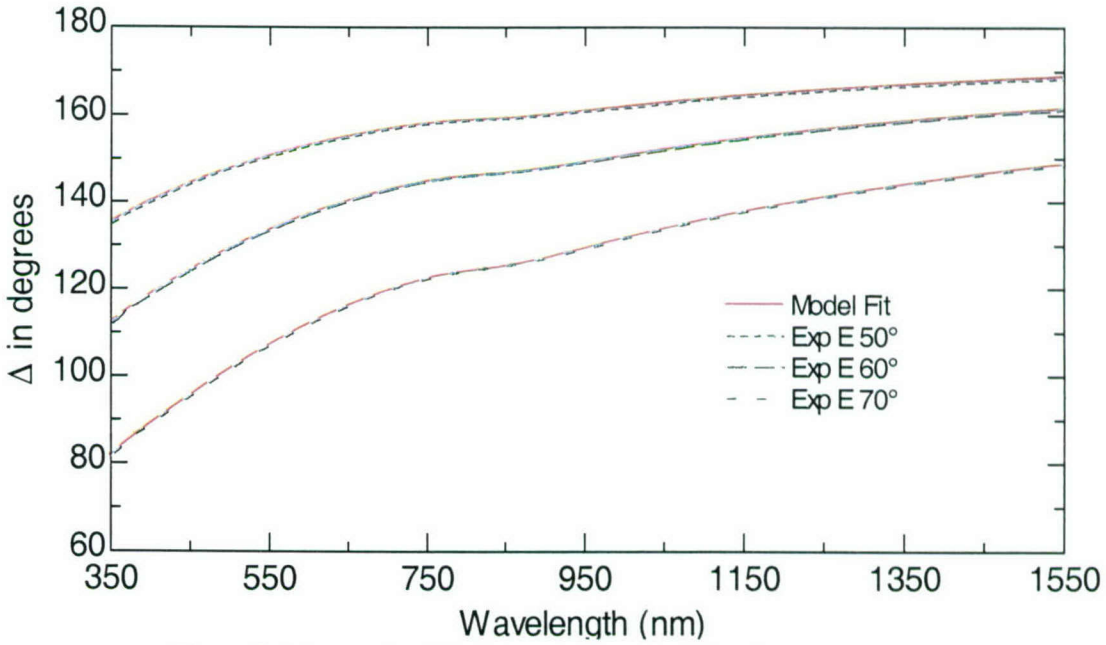

Figure 5. Measured and Fit Delta spectrum for VDA-31 post exposure.

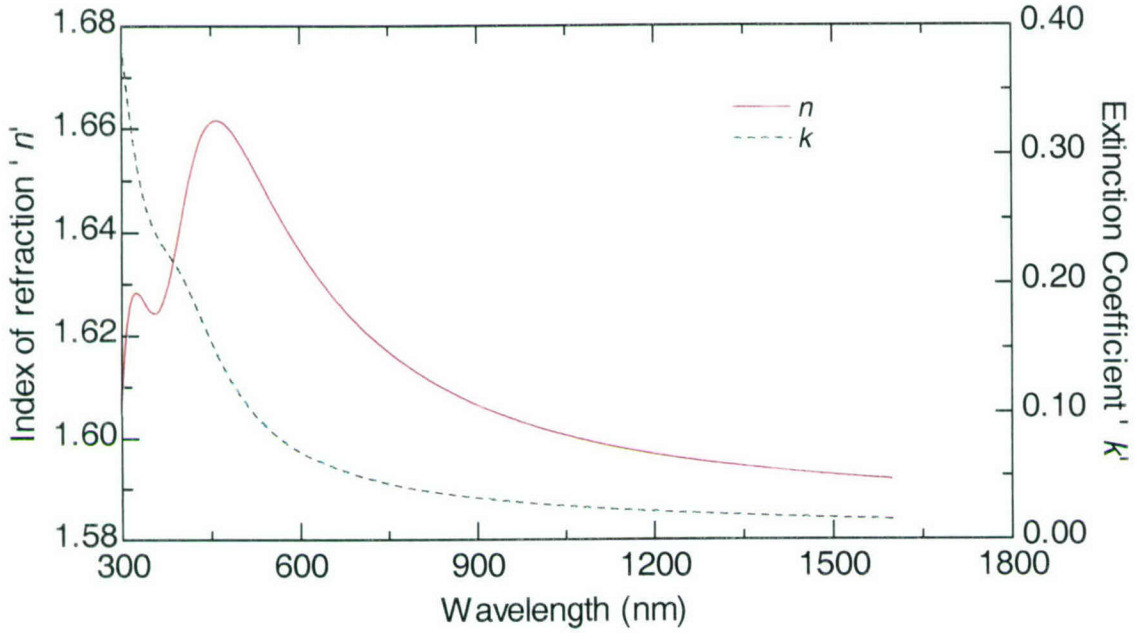

Figure 6. Refractive index and extinction coefficient of contaminant film deposited on VDA-31.

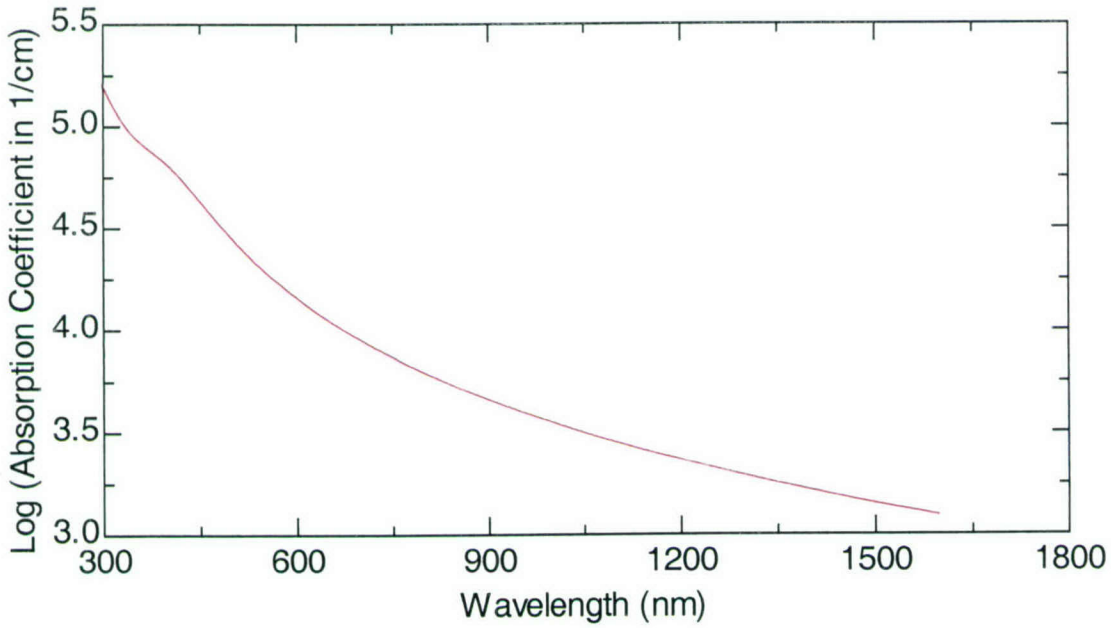

Figure 7. Absorption coefficient of contaminant film deposited on VDA-31

To test the conclusion that 120Å of an unknown contaminant was deposited on both the aluminum and silica references, the theoretical reflectance of the film on aluminum was generated and is compared with measurements onVDA-31 in Figure 8. Similarly, the theoretical transmittance of the contaminant film on silica was generated; it is compared with post-test transmission measurements in Figure 9. The measured and predicted curves are consistent within the accuracy of our measurements and the limits of the chosen optical models.

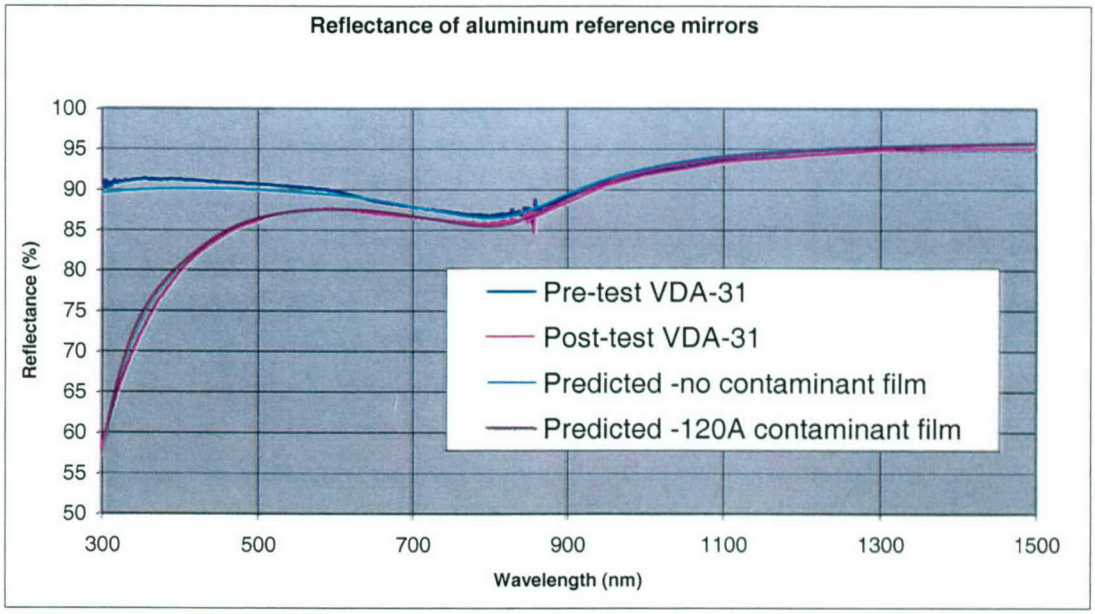

Figure 8. Measured and predicted reflection from VDA-31.

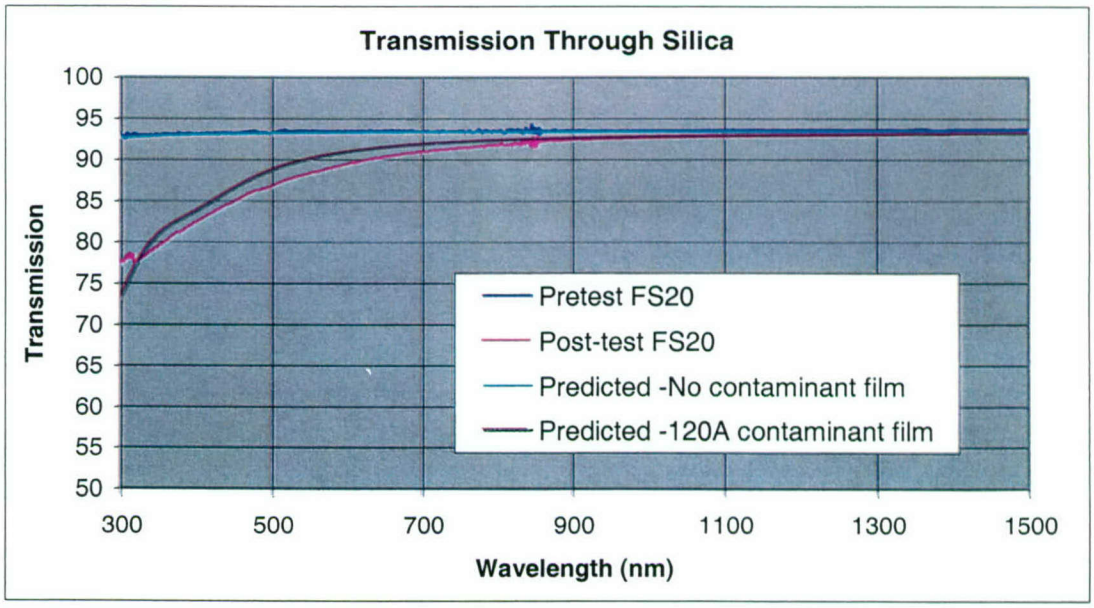

Figure 9. Measured and predicted transmission from FS20.

An attempt to identify the unknown film was made using glancing angle FTIR. In this technique, the IR beam impinges upon the sample at 80° from normal. The shallow incident angle can enhance the signal from very thin films. However, as shown in Figure 10, the reflectance spectra are featureless and the small differences between VDA-37 and VDA-31 were not significant enough to lead to conclusive identification. Furthermore, Standard reflectance and micro-reflectance FTIR spectra were also inconclusive.

Static secondary-ion mass spectrometry was performed using a time-of-flight instrument (together, TOF SIMS) to analyze the film's composition. TOF-SIMS is a very sensitive technique for characterizing surfaces with milli-amu mass resolution. In this technique, the sample is sputtered with a pulsed and rastered ion beam; material that is sputtered off the surface is sampled with a mass spectrometer. In some cases, the cracking pattern of unknown materials can be compared with a database and then identified. Figures 11 and 12 show the low-mass positive-ion spectra of VDA-37 and VDA-31. VDA-37 was unexposed, and the salient features are the peaks at 26.98 amu and 27.99 amu, which are aluminum and aluminum hydride, respectively. VDA-31 was exposed, and the aluminum peak nearly disappeared, indicating that the aluminum/aluminum oxide surface has been overcoated by another material. The peak at 27.976 amu is silicon, and the most abundant laboratory source of silicon is silicone, which is used in everything from adhesives to pump oils to mold release agents. Silicones normally have a prominent peak progression of 43, 73, 147, 207, 221..., but these peaks are absent, suggesting another silicon source, or more likely that the bombardment from energetic electrons, protons, and photons has cross-linked, "pre-cracked," or otherwise significantly altered the silicone film's bonding. Such a film would certainly have a TOF-SIMS cracking pattern that would be different from that expected. Lastly, Figures 13 through 16 show the positive- and negative-ion spectra at higher masses. The abundance of high-mass peaks is consistent with the presence of a polymer film, perhaps the radiation cross-linked form of the original contaminant molecules.

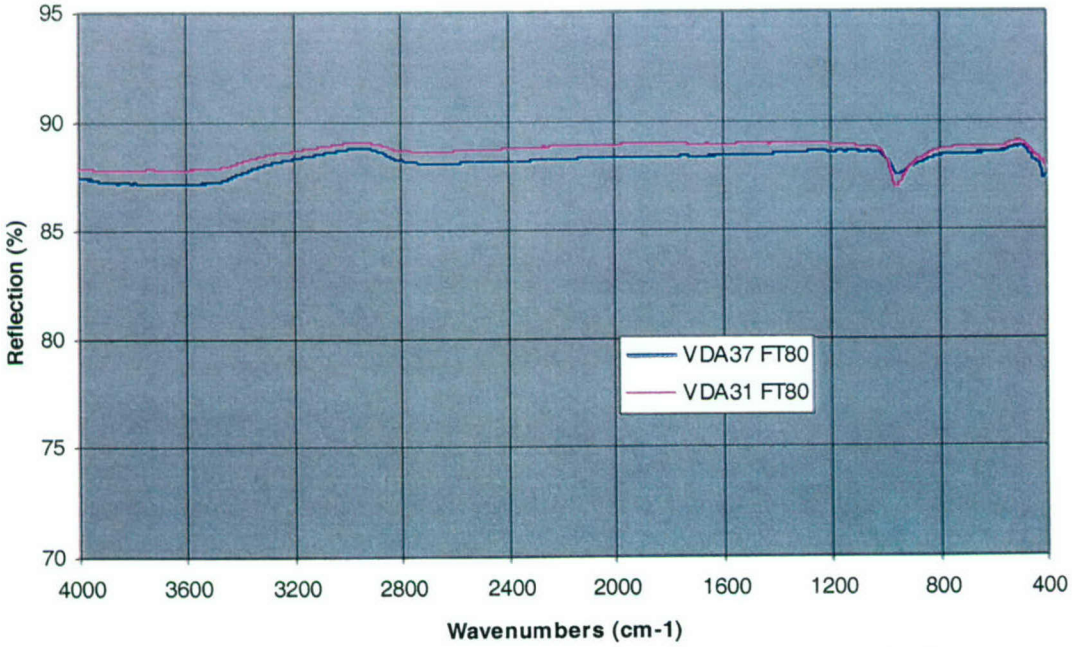

Figure 10. Glancing angle FTIR of unexposed VDA37 and exposed VDA31.

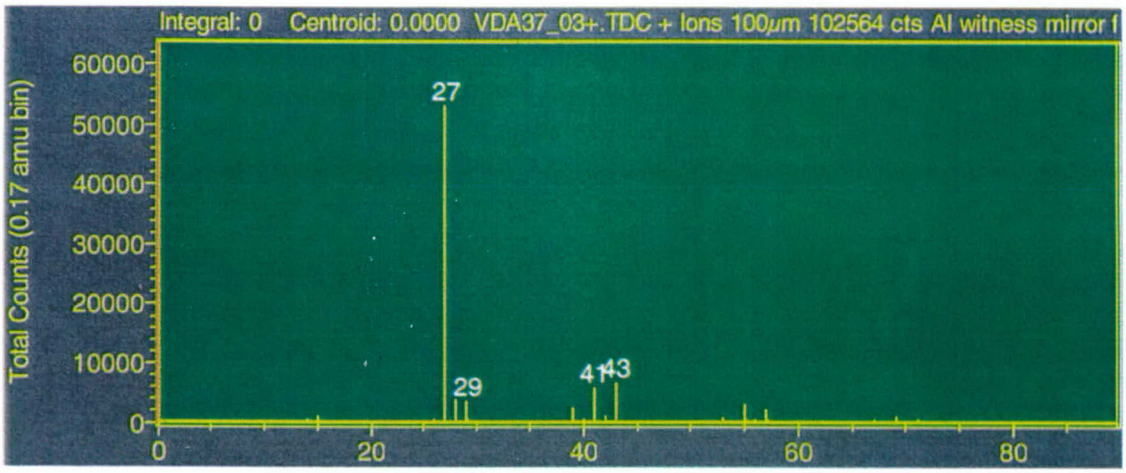

Figure 11. Positive ion spectra for VDA-37.

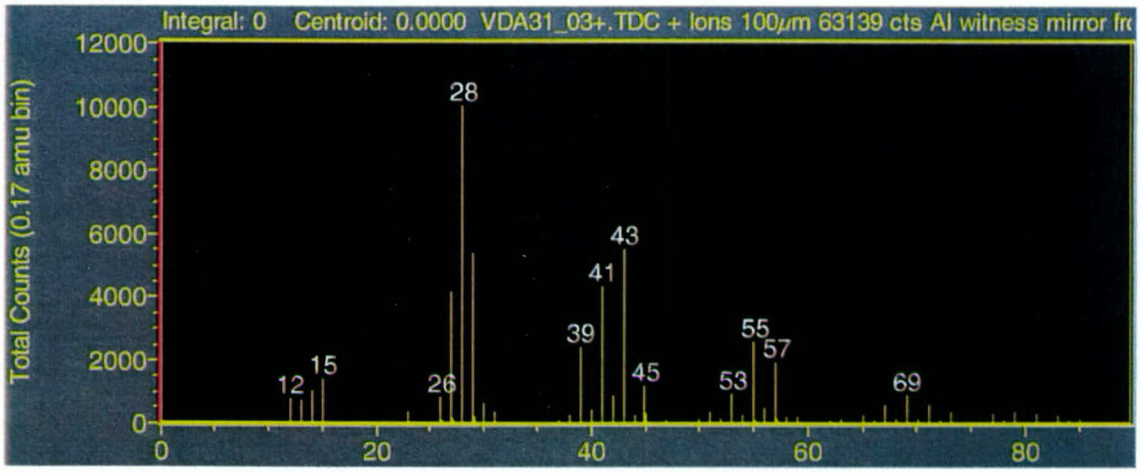

Figure 12. Positive ion spectra of VDA-31 after exposure.

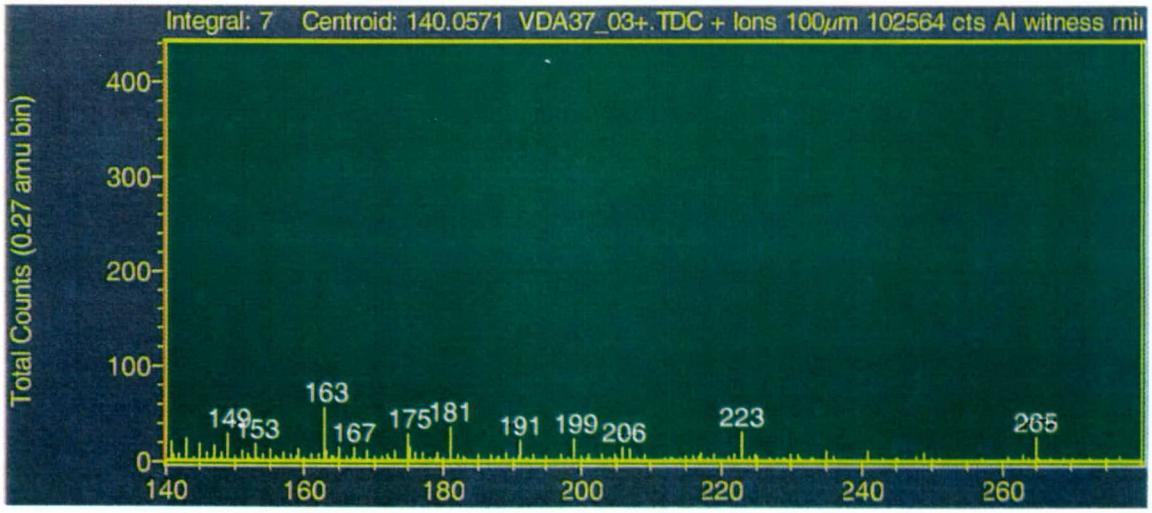

Figure 13. Positive ion spectra for VDA-37.

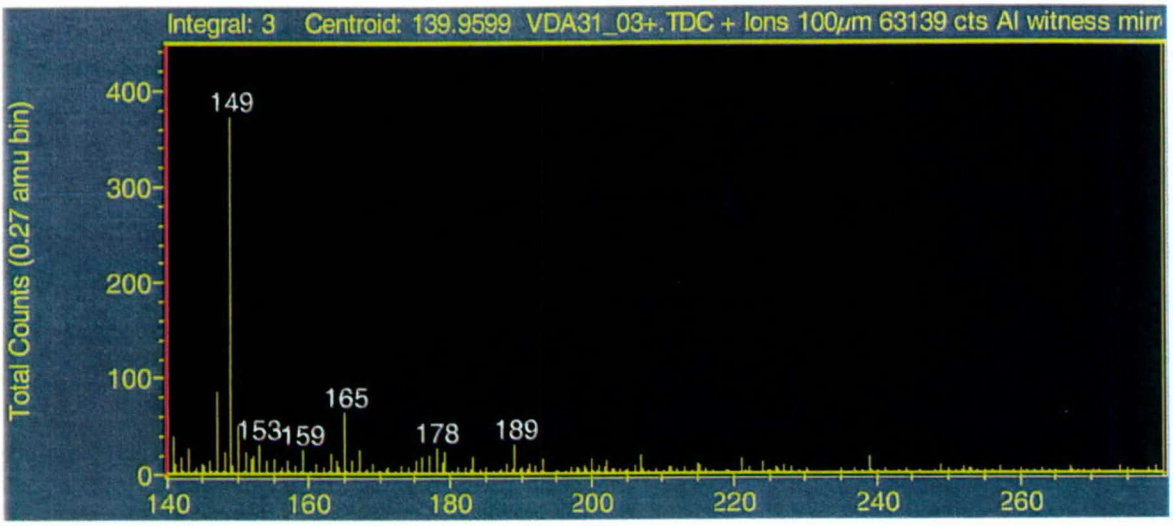

Figure 14. Positive ion spectra for VDA-31. Peak 149 is consistent with phthalate, which can be found in many plastic storage containers.

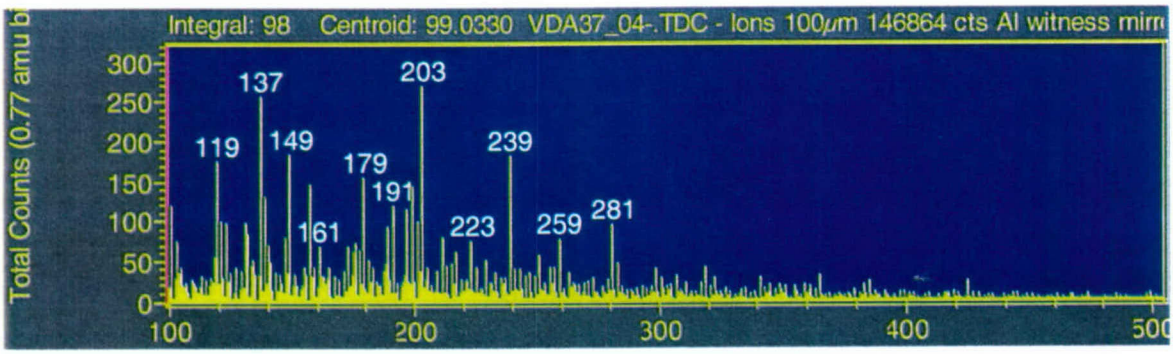

Figure 15. Negative ion spectra for VDA-37.

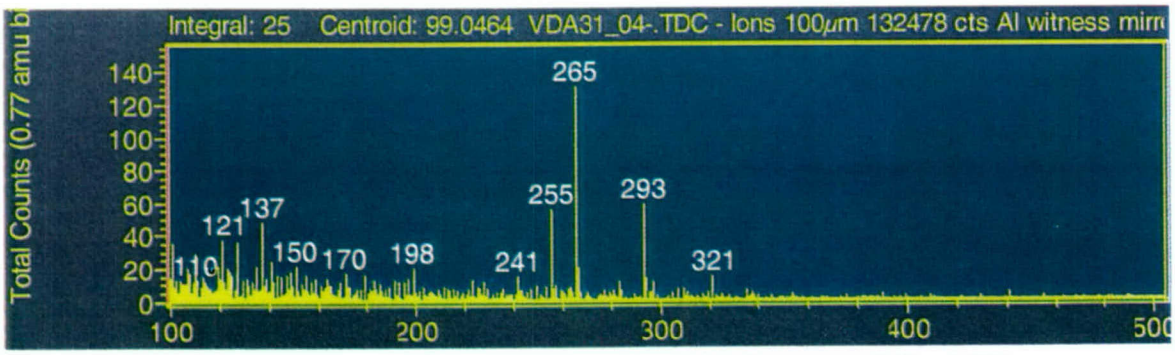

Figure 16 Negative ion spectra for VDA-31. Note that masses 265 and 293 are consistent with the cracking pattern of lauryl, a long chain hydrocarbon.

The data presented leads one to wonder about the source of contamination. Since the measured optical spectra show that the samples grew more lossy after each proton irradiation, one could hypothesize that the contamination occurs in the Low-Energy Accelerator Facility (LEAF) during proton irradiation. If that were the case, one would expect that the loss would be proportional to the time spent in the proton beam. To test this, the transmission spectra of FS-20 was converted to optical density units (OD = –log(T%/100), and the OD is plotted for several wavelengths versus equivalent proton years. The data are presented in Figure 17. If the samples were exposed to a constant flux of contaminant, the OD vs. time plot should be linear for all wavelengths (neglecting interference effects.) Clearly, this is not the case. For all wavelengths above 265 nm, the optical density curve has a positive curvature meaning that the *rate* of darkening is increasing with irradiation at those wavelengths. The curves below 265 nm all have negative curvature, which, of course, means that the *rate* of darkening is decreasing. One possible explanation is that darkening is a two-part process. One part involves volatile contaminants slowly condensing upon the sample. The second part involves irradiating the condensed species that inefficiently causes the condensate to react to form a new material with lower energy absorption. Thus, the radiation converts the condensate that strongly absorbs at the shorter wavelengths into a new species that absorbs over a broader range of wavelengths (that is, it turns brown.) Furthermore, while condensation only occurs at the surface, the proton radiation is sufficiently energetic that it penetrates the entire contaminant film, promoting further reaction throughout the film. The static SIMS results suggest that these compounds could be silicones and possibly hydrocarbons depositing on the samples, which then polymerize with irradiation.

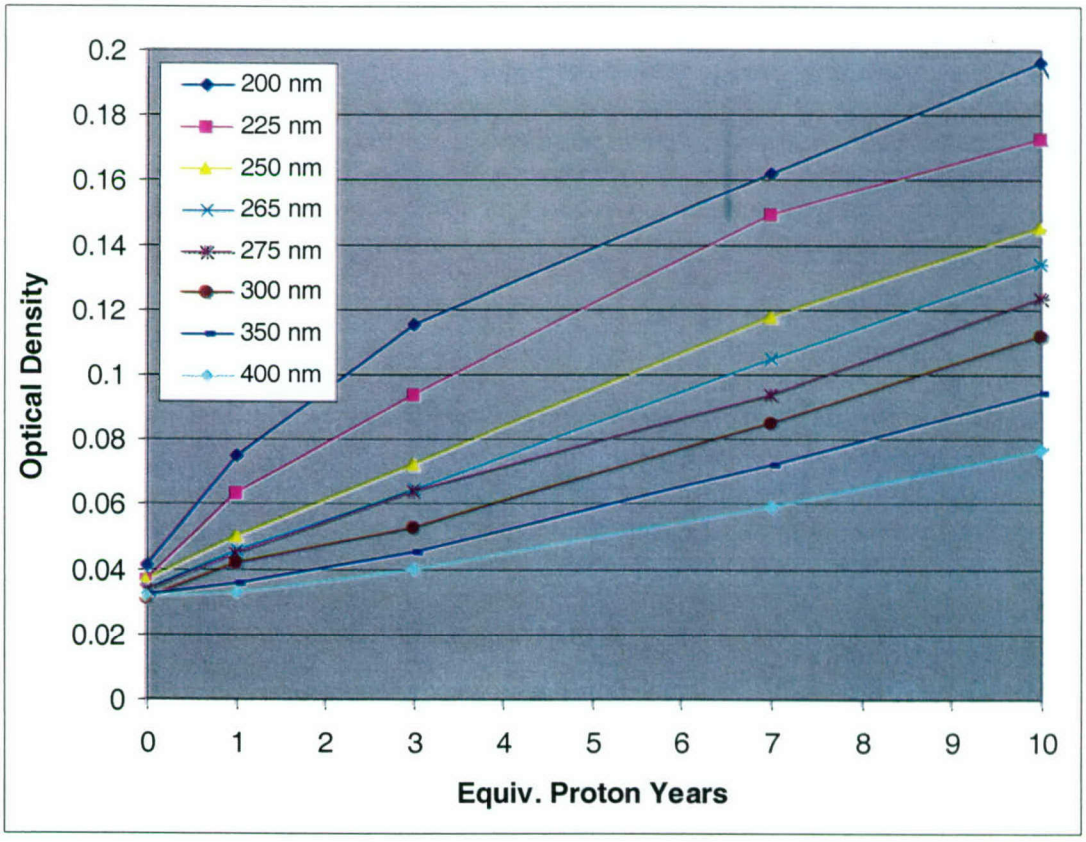

Figure 17. Optical density of FS-20 vs. proton irradiation for several wavelengths.

This hypothesis might also explain the post-test curve in Figure 1. The chamber used to perform electron and UV irradiation operates in the low 10 nanoTorr range, and aluminum and silica samples don't typically darken as during electron and UV exposure in that chamber. This suggests that the electron irradiation chamber (Deathstar) is an unlikely source of further contamination. However, comparing the 10-year proton spectra with the spectra that, after an additional 7 years of electrons and UV, one finds that the absorption below 265 nm decreases and the absorption above 265nm increases, suggesting that 265 nm is an isobestic point. It appears that in the absence of an additional source of contamination the electron and/or UV radiation also promotes the same chemical reaction that occurred in the LEAF; i.e., the irradiation continues to convert the short wavelength absorber (condensate) and convert it to a brown polymer. The film may not be growing, but it continues to darken.

Conclusions

A contaminant film was observed to deposit and darken upon exposure in a radiation environment. Some fraction of the contaminant film was probably silicone. Normally, silicones are surface mobile and transparent in the visible range. In this case, they appear to have cracked and cross-linked, forming 120Å of an optically dark film.