MODELING ELLIPSOMETRY MEASUREMENTS OF MOLECULAR THIN-FILM CONTAMINATION ON GENESIS FLOWN ARRAY SAMPLES.

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Introduction: The discovery of a molecular thin-film contamination on Genesis flown array samples changed the course of preliminary assessment strategies. Analytical techniques developed to measure solar wind elemental abundances must now compensate for a thin-film contamination. Currently, this is done either by experimental cleaning before analyses or by depth-profiling techniques that bypass the surface contamination. Inside Johnson Space Center's Genesis dedicated ISO Class 4 (Class 10) cleanroom laboratory, the selection of collector array fragments allocated for solar wind analyses are based on the documentation of overall surface quality, visible surface particle contamination greater than 1 µm, and the amount of thin film contamination measured by spectroscopic ellipsometry. Documenting the exact thickness, surface topography, and chemical composition of these contaminates is also critical for developing accurate cleaning methods. However, the first step in characterization of the molecular film is to develop accurate ellipsometry models that will determine an accurate thickness measurement of the contamination film

Brown stain: Initial assessment of 112 collector fragments indicates greater than 95% have some degree of a thin film contamination. This is commonly referred to as "brown stain" [1] and has an average thickness of 47.38 Å (a median range from ~ 20 to 60 Å thick where the maximum thickness found was 148 Å and the minimum was 0 Å). These film thicknesses, assessed via ellipsometry, closely match the FIB/TEM images of a directly measured ~50 Å brown stain on flown Au foil [2]. The brown stain contamination is thought to be caused by UV polymerization of a hydrocarbon or siloxane contaminant [1] and would have been present on a nominal reentry. XPS results have shown that the brown stain is an organic contaminate with ~ 69 – 70 wt% C, ~ 1.8 – 3.5 wt% N, ~ 17 – 20 wt% O, ~3.6 – 4.3 wt% F, and ~3.8 – 4.5 wt% Si [1]. One candidate for contamination source is RTV566 which is a General Electric manufactured silicone rubber compound that is often used in space applications where low outgassing is required. RTV566 contains: Ethyl-Silicate 40, Diatomaceous Earth, Methylphenylsiloxane Copolymer, Red Iron Oxide, and Alkyl-Tin Carboxylate (curing agent).

Contamination Layers: The brown stain thin film is situated on the top layer of the manufactured wafer material and/or the native oxide, depending on the material. It is also situated below any particle contamination that was deposited due to the non-nominal spacecraft reentry. Figure 1 shows a typical thin film contamination model with a manufactured Si layer on the bottom, ~ 18 Å layer of native oxide (SiO_2), brown stain contamination, and statically charged surface particles (UTTR sediment and spacecraft debris) [3, 4]. Figure 2 shows a more complex model where the brown stain may not have allowed a native oxide layer to form. While preliminary results have not supported an oxide layer on top of the brown stain, figure 2 also shows that this complex scenario may exist.

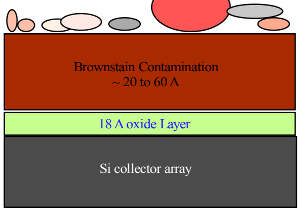

Figure 1: Thin Film Contamination Model

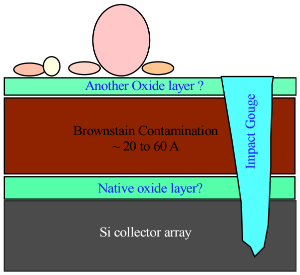

Figure 2: Alternative Contamination Model

OSEE (Optically Stimulated Electron Emission), FT-IR (Fourier Transform Infrared Spectroscopy), XPS (X-ray Photoelectron Spectroscopy), and Spectroscopic Ellipsometry are all proven analytical techniques for modeling thin film that were considered in planning for Genesis sample characterization. Ellipsometry was chosen as a rapid method requiring no sample preparation and capable of mapping large areas of collector surfaces. Ellipsometry is still effective, even on the smaller sizes of the broken collectors and it is relatively insensitive to particulate contamination. Further studies on ellipsometry beam size limitations confirms earlier estimates that an array fragment must have a surface area greater than 3 X 4 X 5 mm triangle and the surface area must be relativity free of surface abrasions and particle debris to achieve accurate results [3].

Ellipsometry Modeling: Due to the complex and unknown nature of the contaminant's exact chemical composition and optical properties, the thickness accuracy generated by ellipsometry WVASE32 [5] models is generally unknown. However, based on current modeling techniques, the WVASE32 Cauchy model produces the best solutions and the lowest mean squared error (MSE). This Cauchy model is derived from Augustin-Louis Cauchy discovery that the index of refraction n decreases with increasing wavelength in transparent material in the visible light range. The WVASE32 Cauchy model is as follows:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4},$$

$$k(\lambda) = \alpha e^{\beta(12400(\frac{1}{\lambda} - \frac{1}{\gamma}))},$$

where n is the index of refraction, k is the extinction coefficient, and λ is wavelength, along with an exponential absorption tail. The equation has six parameters for the modeling of the dispersion: A, B, and C, extinction coefficient α, the exponent factor β, and the band edge γ. Figure 3 shows flown Si array fragment modeled with Genesis-Si layer on bottom, SiO_2 native oxide layer at 18 Å, and the Cauchy fit on top to estimate the contamination layer thickness. (Red lines are model fits, green lines are data.) In this case, the Cauchy model gave an estimated thickness of 24.924 Å with an MSE of 61.66. However, on this delta plot, the model fit does not match the experimental results at the 75° angle of measurement. Figure 4 shows how the plot should look if the material in known.

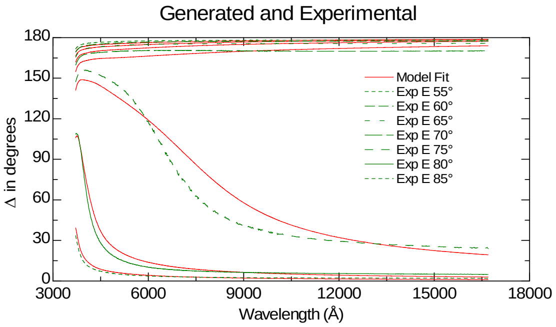

Figure 3: Δ Plot of Si sample 60170

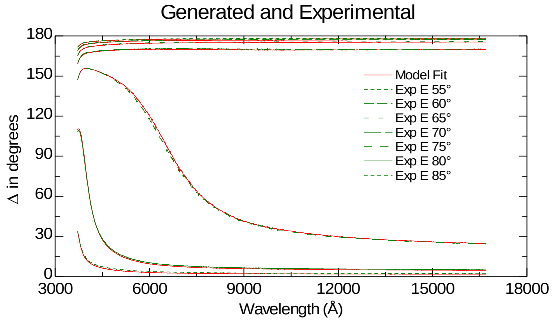

Figure 4: Δ Plot of Si sample 60170 with fitting n and k.

Since the brown stain is organically derived, it may not have traditional transparent optical properties as defined by the Cauchy models. The Cauchy models also do not work well for metals and semiconductor materials. Therefore, we have experimented with the Lorentz oscillator model. This model will closely relate the area under the absorption peak helping to identify each bandwidth. We have also attempted the parametric semiconductor layer model. This is used if there exists a direct bandwidth where the absorption can abruptly go to zero. However, in both cases with Lorentz or Parametric Oscillator models, the estimated thicknesses are well over 1200 Å with very high MSE. There is also the possibility that the material is not isotropic and could have optical properties of uniaxial or biaxial alignment. Figure 5 shows the same Si fragment with a biaxial component that resulted in 19.079 Å film thickness with 61.47 MSE (the *A* variable was not static with 1.5, 1.8, and 2.0 for each Cauchy layer). While the MSE is slightly lower and the result dramatically changes the estimated thickness, this may not necessarily suggest that a non-isotropic material is present.

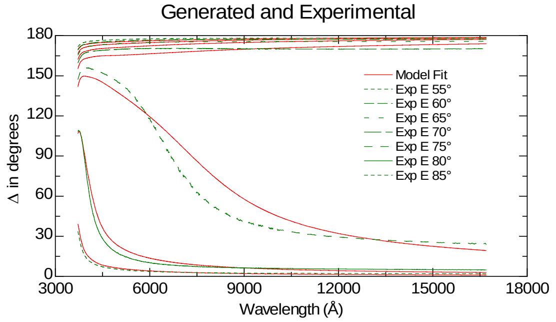

Figure 5: Si sample 60170 with biaxial/3 layers Cauchy

Figures 6 shows that Sapphire (SAP) fragments also generate noise when analyzed due to the transparent quality of the material. However, this has not impeded good thickness estimates. Gold on Sapphire (AuOS) fragment that were the most damaged during impact have shown some problems finding surface areas free of scratches or gouges (figure 7). However, the large beam size has accommodated a built-in statistical solution and has not impacted obtaining good analytical estimates of the thin-film thickness.

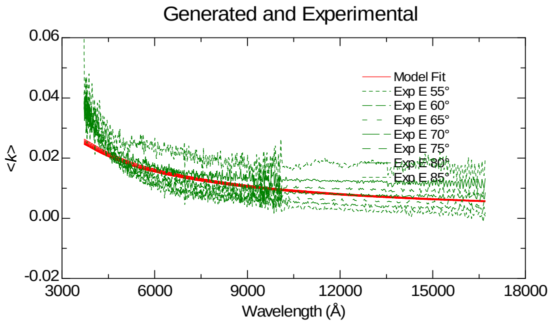

Figure 6: SAP sample 50719

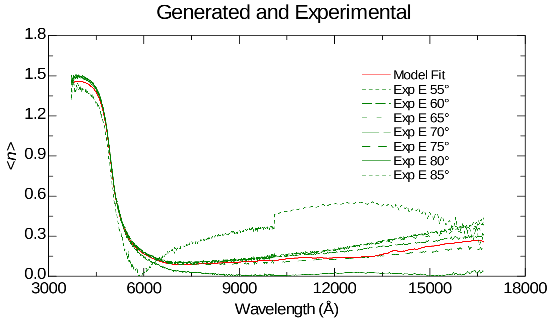

Figure 7: AuOS sample 60131

Conclusion: The non-nominal landing for Genesis has not dramatically impacted the analysis of the brown stain thin-film thickness. However, a correlation is needed between ellipsometry data and actual thin film thickness. Future work at JSC will use TEM analysis that will provide a detailed method for measuring the actual thickness of the brown stain on flown wafer fragments that can be compared with ellipsometry results. Once a correlation is made, a mathematical fit can be applied to past and future ellipsometry results providing a highly accurate and confident brown stain thickness on all array wafer surfaces.

References: [1] Burnett, D.B. (2005) LPS XXXVI, Abstract #2405; [2] Graham & Bradley (2005) LLNL; [3] Stansbery, E.K. (2005) LPS XXXVI, Abstract #2145; [4] McNamara, K.M. (2005) LPS XXXVI, Abstract# 2402; [5] J.A. Woollam Ellipsometry Modeling Software (2004).