

RAMAN AS A TOOL FOR QUANTIFYING SIMS ANALYSES OF GENESIS DOS COLLECTORS. A. J. G. Jurewicz^{1,3}, E. Koeman-Shields², G. Huss² and C. Daghlian³, ¹Center for Meteorite Studies, ASU m/c 6004, Tempe AZ 85287 (Amy.Jurewicz@asu.edu), ²Hawaii Institute of Geophysics and Planetology, Uni. Hawai'i at Mānoa (Post 602), Honolulu, HI 96822, ³Dartmouth College, Hanover NH 03755.

Introduction: The purpose of the Genesis Mission was to return a sample of solar wind (SW) in order to measure the composition of the minor SW ions accurately and precisely. The SW composition defines the composition of the outer portion of the Sun and, by extension, the composition of the solar nebula from which our solar system formed [1].

Diamond-like carbon (DLC) on silicon (DoS) was one type of SW collector flown on Genesis [2]. The DLC film, made at Sandia National Laboratory by pulsed-laser deposition from a hot-pressed graphite target [3], was $\sim 1\mu$ thick, amorphous, anhydrous, and had a high ratio of sp^3 to sp^2 bonds ($>50\%$). Mostly carbon, DLC has low backscatter during SW collection and is extremely retentive of volatiles. The high percentage of sp^3 bonding makes it both hard and tough; it is also relatively inert and thus fairly easy to clean. However, equilibrium clusters of sp^3 bonds are diamond-like and so electrical insulators (in fact, some portions of the film are stressed such that the carbon is within the diamond stability field [cf. 4]). In contrast, clusters of sp^2 bonds are graphitic and good electrical conductors. Local spatial variation in both sp^3/sp^2 bonding and interconnectivity of these clusters affect electrical conductivity [3] and ion yield [4], making quantification of SIMS analyses difficult. In additions, local variations in the amount of impurity silicon also influences the standardization and quantification of SIMS data by modifying the matrix structure [4]. Variations of ion yield under the same conditions during the same analytical session can be so striking that SIMS data has been used to characterize the local structure of the DLC [4]. For accurate quantification of SIMS data, independent methods used to understand the local structure of the DLC allow individual SW analyses to be matched with matrix-appropriate standard data.

Here we use Raman Spectroscopy to map these variations in DLC from Genesis DoS wafers and apply the results to standardization of solar wind SIMS analysis.

Methods: Raman spectroscopy was done at Dartmouth, in the electron microscopy lab, using the Horiba LabRAMHR Evolution Raman spectrometer with the 532 nm laser in spot mode. Four collection periods, each of five seconds (i.e., 20 sec total), collected Raman signal from -5 to 3500 cm^{-1} . An exception: the E array pits, which only counted for 2 seconds (8 sec. total). Two spectra were taken on each analysis pit: (1) on the floor of the pit; (2) on the fragment's surface

adjacent the pit. *Only samples analyzed using a Cs^+ primary beam were used, so artifacts due to oxidation of silicon or silicon-carbide during analysis were not an issue.* Features of spectra were identified assuming the DLC was primarily carbon, with hydrogen (SW or commercial implant) and variable silicon impurities.

Silicon and SiC peaks were identified using the specifications of [5], which focused on features of amorphous silicon carbide films. For interpretation of the carbon species, we relied primarily on [6], a detailed overview of the characterization of diamond-like carbon films. Unfortunately, using Raman with the 532 nm wavelength laser, the peaks between 1000 cm^{-1} – 2000 cm^{-1} appear to be non-unique leading to an ambiguous interpretation of sp^3 vs. sp^2 bonding. For example, the 1350 cm^{-1} and 1580 cm^{-1} peak, called D (“diamond”) and G (“graphite”) in the literature, are generally attributed to sp^2 bonds, but true diamond has a peak near the D at 1332 cm^{-1} . Chu and Li [6] indicate that peaks at 1150 cm^{-1} and 1500 cm^{-1} have been inferred to be nanocrystalline diamond and sp^3 bonds. However, those sp^3 peaks are either absent or swamped by the D and G peaks in the spectra presented here. So, here, the Raman peaks between 1000 cm^{-1} and 2000 cm^{-1} are mostly used as “fingerprints”, noting that differences in carbon structure seen by Raman does not necessarily translate into variations in SIMS sensitivity.

Results: Fig (1) gives example Raman shift profiles in the region silicon species can be observed (300 cm^{-1} – 1000 cm^{-1}). two contain measureable Si metal (Si) or amorphous silicon carbide (a-SiC). Si gave a strong signal if present. SiC and a-SiC peaks were weak when present; but, [5] indicated that these peaks gave little signal at 532 nm even for pure SiC films. Two of the flight samples studied did not show definite Si or SiC – related peaks. Raman spectra also suggested local variations in the sp^3/sp^2 ratio (Figs. 2-4). Data in Fig. 3 suggests that the ratio varies with the C_2/C SIMS parameter (cf., [4]). [4], using (+) secondaries, inferred the presence of significant silicon from dramatic changes in sputtering and ion yield; here, Raman clearly shows that silicon species are a separate factor in SIMS. We note that sputtering rates of the DLC containing Si or SiC were higher than silicon-free fragments. Fig. 4 suggest that the sp^3/sp^2 ratio decreases with depth, consistent with [3,4].

Conclusion: Raman can give insight into local variations of the DLC which may have affected ion yield

during SIMS analysis. It holds the potential of pre-mapping individual fragments to insure the standard will have a matrix similar to the collector. Raman spectra also confirm changes of DLC structure with both SW implantation and depth, the latter likely due to multiple annealing steps (cf. [3]).

References:

[1] Burnett D. S. et al. (2003) *Spa. Sci. Rev.* 105, 509-534. [2] Jurewicz A. J. G et al. (2003) *Spa. Sci. Rev.* 105, 535-560. [3] Sullivan J. P. et al. (1998) *Mater. Res. Soc. Symp. Proc.* 498 97. [4] Jurewicz A. J. G et al. (2017) *Jour. Mater. Sci.* DOI 10.1007/s10853-017-1267-3. [5] Janz S. (2006) Univ. Konstanz, (www.ub.uni-konstanz.de/kops/volltexte/2007/3201/) [6] Chu P. K. and Li L. (2006) *Mater. Chem. & Phys* 96, 253-277.

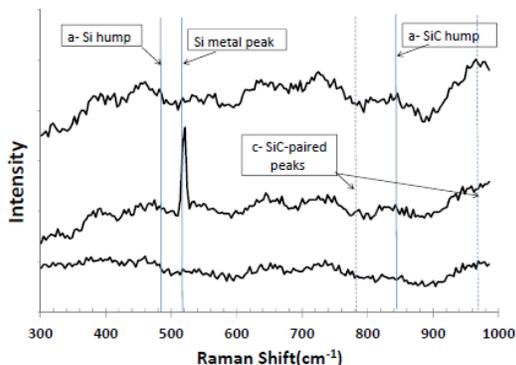


Fig. 1. Three example Raman spectra: vertical lines mark peak positions. Profiles contain:(top) amorphous SiC; (middle) Si; (bottom) no definite Si species. Intensity is as measured. Note: relative intensity between samples was not correlated with SIMS results; DLC film thicknesses are all ~1µm.

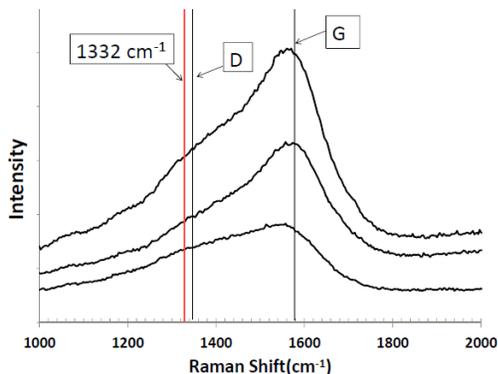


Fig. 2. Raman spectra of Fig. 1 in the 1000-1600 cm-1 range. Vertical lines are positions of: a weak sp³ peak as well as the D and G sp² peaks.

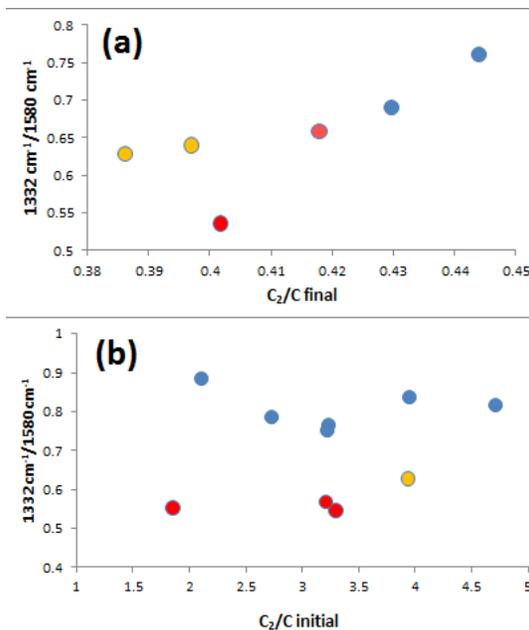


Fig. 3. Correlation of SIMS data with Raman signal (a) standard data, (b) SW data. Symbols indicate Raman results: Red (Si present); Orange (SiC or amorphous SiC present); Blue (no silicon species observed). The ratio of the peaks at 1330cm⁻¹ and 1580cm⁻¹ is a rough estimate of the relative sp³/sp² ratio. Summation of Gaussians for each peak is required for a true estimate. All data are from runs using same SIMS conditions. As per [4], C₂/C can be related to the sp³/sp² ratio, but silicon species have a strong effect.

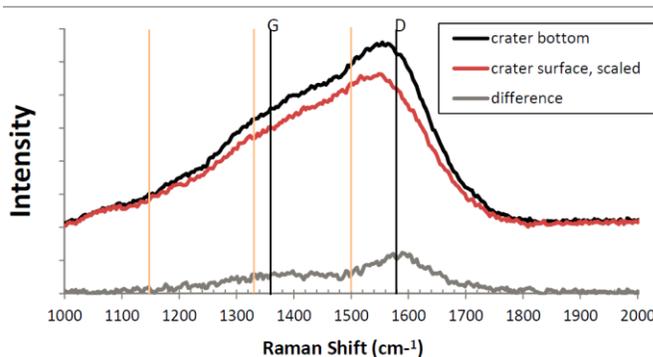


Fig. 4. Estimate of change in relative the sp³/sp² ratio with depth. Raman for a pit in DLC without definitive silicon species present. Raman shift for crater surface has been scaled so that the background matches with that for the crater floor. D and G peaks are sp²; peach vertical lines mark position of weak sp³ lines [6].

This work supported by NASA grant #NNX14AF26G.