RAMAN AS A TOOL FOR QUANTIFYING SIMS ANALYSES OF GENESIS DOS COLLECTORS

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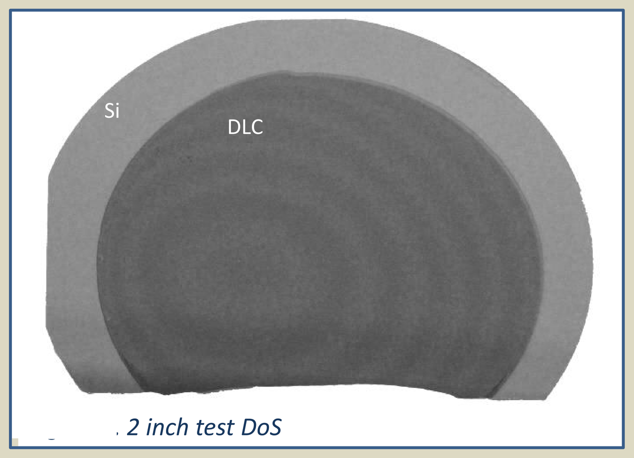
------------The Problem Illustrated ------------

We Wanted:

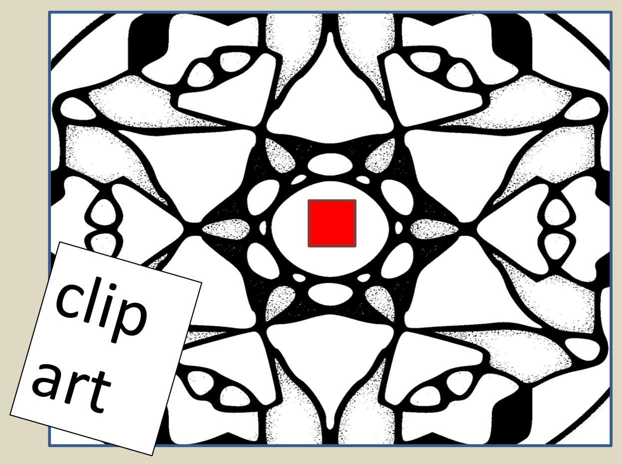
Uniform carbon

It Looked Like;



Uniform carbon

SIMS Response:

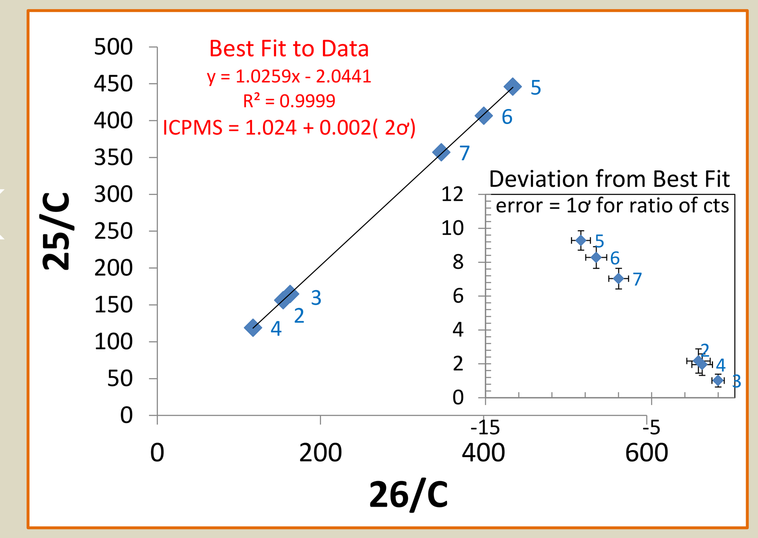


Extreme heterogeneity

Diamond-like Carbon (DLC) has extremely non-uniform physical, chemical and electrical properties *[1]*

What is Needed to Quantify the data?

Example: SIMS Standard Data (Mg^+ by O_2^+ primary)



- calibrated implant standard
- $^{26}Mg/^{25}Mg$ = 1.024 (+ 0.002)
- no measurable variation of Mg in co-implanted silicon
- Same analysis session
- Same analysis conditions

Current Range ~17 – 24 nA;
5 of 6 analyses 23 nA ± 1 nA

Introduction to Genesis and DLC

The Genesis mission sampled and returned solar wind for analysis in terrestrial laboratories *[2]*. Once precisely and accurately determined, the SW composition will be used to define the composition of the outer portion of the Sun and, by extension, the composition of the solar nebula from which our solar system formed *[3]*. Diamond-like carbon (DLC) on silicon (DoS) comprised only 18 of the 275 full hexagons flown in the Genesis collector arrays. But proportionately more DoS than silicon survived the UTTR crash and DoS is relatively easy to clean.

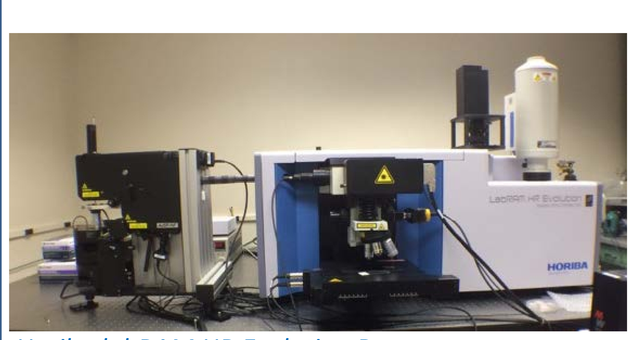
Made at Sandia National Laboratory by pulsed-laser deposition from a hot-pressed graphite target *[2]*, Genesis DLC is ~1µ thick, amorphous, anhydrous, carbon. It is electrically conductive, has excellent SW retention, and the carbon matrix creates few interferences during SIMs analysis. The depths profiles for SW obtained by SIMS from DLC often have much higher signal to background than from silicon. But, even SIMS data having great counting statistics are difficult to quantify because of natural spatial variations in the material properties *[1]*.

The banner illustrates heterogeneity of DLC under SIMS. DLC is carbon and looks uniform, but behaves as a mixture of matrices.

Why DLC isn't a "typical" C-coating

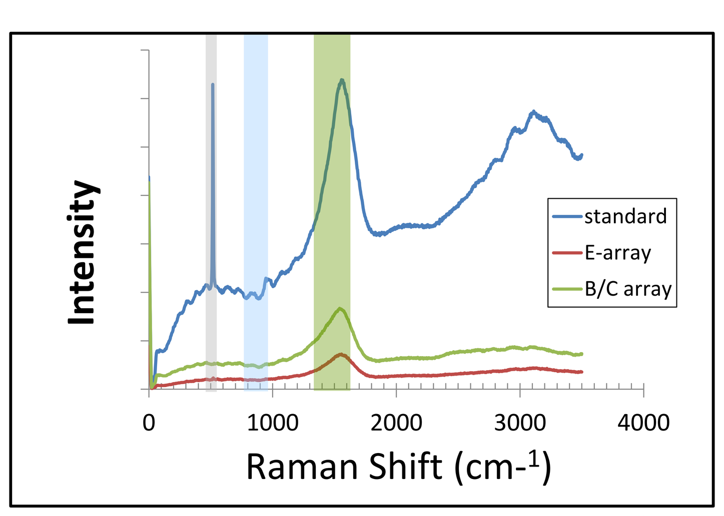
By definition, DLC is amorphous carbon with a high ratio of sp^3 to sp^2 bonds (>50%). Genesis DLC was made by laser vapor-deposition of multiple ~100 nm thick, highly-stressed layers of carbon. This carbon is initially in the diamond stability field *[4]*, so perturbations may cause nanodiamond and/or small diamond crystallites to form spontaneously to relieve residual stress (*[1], cf.[5]*). After each deposition, the wafer is annealed to lessen internal stress. Annealing coarsens the texture and decreases the sp^3/sp^2 ratio *[6]*. The repeated annealing with deposition can create a gradient in properties, with the initial layers of the film coarser or more graphitic than later (less annealed) layers. Impurity silicon (ubiquitous in all carbon) may segregate, in the extreme case forming SiC *[7]*. Also, occasional embedded particulates of dust or silicon metal have been found *[1],[7]*.

Method



Horiba labRAM HR Evolution Raman spectrometer in Dartmouth EM facility: (532nm laser used)

Spectra have large-scale similarities of shape but differences can be likened to fingerprints. Spectral features correlate to specific bonds (e.g., bars graph to right) and / or textures (width of D peak *[9]*). Interpretations relied mostly on *[8]* for Si and SiC, *[9]* for DLC, and *[10]*. The green laser gives weak SiC and sp^3 signals but does less damage than UV.



Raman lines vs. Raman shift for surfaces of two flown Genesis collectors and a flight spare containing a standard implant. Bond types are represented in different areas of the spectrum ; e.g, bars (L→R): c-Si and a-Si, a-SiC and c-SiC, and sp^2 and sp^3 carbon (a=amorphous; c=crystalline). Far right intensity can be related to H- and unannealed (random) bonds.

Raman Observations

and correlation with SIMS data

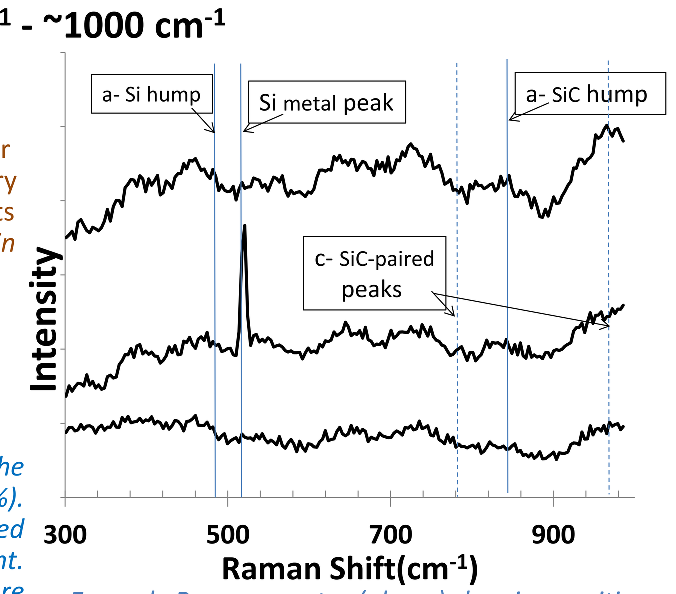
Raman spectroscopy is useful for understanding heterogeneity in the diamond-like carbon and, therefore, understanding variations in SIMS data. Some Raman observations have decisive chemical interpretations; e.g., the presence of silicon metal bonds, which emit strongly under the 532 nm laser. Accordingly, these can be used to definitively interpret the variations in SIMS data (cf., Example 1). Other observations are used more like fingerprints; e.g., relative heights and positions of peaks related to carbon (cf., Example 2). These portions of the spectrum may have multiple reasonable interpretations. In addition, although Genesis collector-array films are about 1 µm thick, the activation volume of the green laser appears to be close to 1 µm: Raman spectra for some films contain the signature of the silicon substrate and/or vary directly with thickness (cf., Example 3). Accordingly, either the thickness of the films or the transparency to 532 nm varies spatially, or perhaps both vary *[cf. [11], optical properties]*.

Example 1: Presence/absence of silicon or SiC bonds: Raman Zone of interest: ~400 cm^{-1} - ~1000 cm^{-1}

SIMS Observations:

- ***Change in sputter rate (slower with Si present)***
  Hypothesis: chemical vs. physical sputtering. O (either residual in vacuum (Cs sputtering) or from the primary beam (O^-, O_2^+ sputtering)) creates gaseous byproducts for C, solid byproducts for Si *[1] and references therein*
- ***Increase in ion yield in the presence of Si (O added)***
  Hypothesis: solid residue allows incorporation of ions from (O^-, O_2^+) primary beam and thereby increases absolute ion yield by adding O to matrix *[1]*

SIMS data (below) from a single session shows scatter in the sputtering rate with small changes in Cs^+ beam current (~15%). Sputtering rate in a homogeneous material would be expected to be essentially linear with small changes in beam current. Raman data imply that silicon species in the DLC are responsible for the scatter.



Example Raman spectra (above) showing positions of crystalline and amorphous Si-species

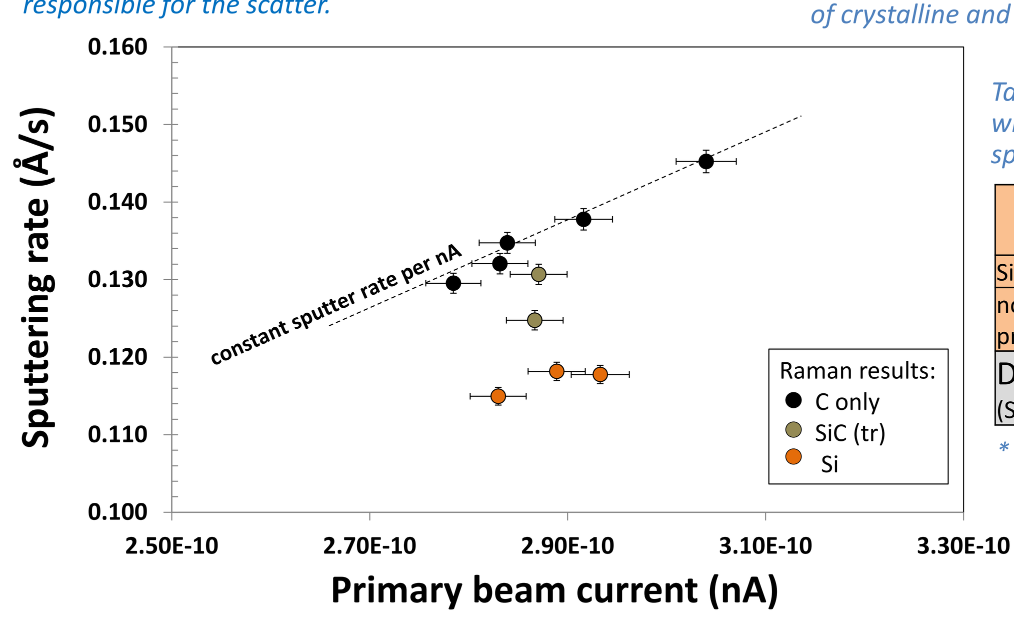


Table: RSFs for data at left correlate with presence or absence of silicon species in the Raman spectrum.*

RSF	Average /10^{23}	Variation ($1\sigma/10^{23}$)
Si or SiC present	3.059	0.039
no Si species present	2.694	0.040
Difference (Si species –no Si)	0.336	

** RSF (Relative Sensitivity Factor) gives the efficiency of ionization for an element of interest relative to that of a matrix species (here, $^1H^-/^{12}C^-$).*

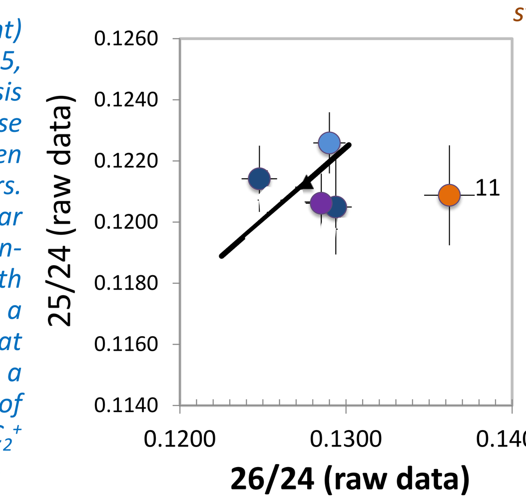
Example 2: Carbon bonds (sp^2, sp^3) bonds: Raman zone of interest ~1000 cm^{-1} - ~2000 cm^{-1}

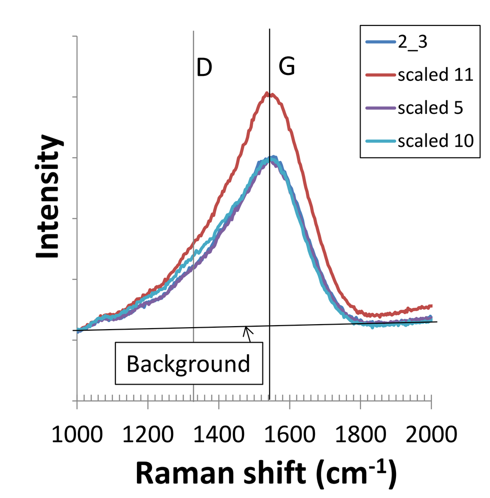
Signals from Raman D ("D"isorder) and G ("G"raphite) peaks are nominally defined as 1360 cm^{-1} and 1580 cm^{-1} respectively [8]. Weak sp^3 signals occur at 1150 cm^{-1}, 1270 cm^{-1}, 1332 cm^{-1},and 1500 cm^{-1}[8],[4]. All signals may shift their peak position in DLC.

SIMS Observation:

- ***Heterogeneity of DLC*** *(Hypothesis: MRP required to separate peaks may vary spatially)*

Mg isotope data (right) from analysis pits 2, 3, 5, 10 and 11 in Genesis sample 20732-2 whose spectra (below) are given in corresponding colors. Data from 2-10 fall near the terrestrial fractionation line (black with triangle) but 11 shows a significant interference at mass 26, possibly a contribution by the tail of an anomalously big $^{13}C_2^+$ peak (cf., Raman below).



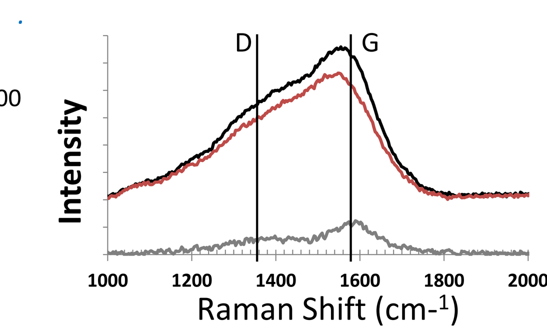


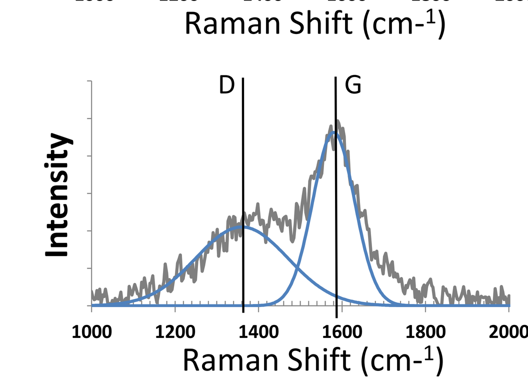
(left): Comparison of peak shape and intensity of Raman spectra taken adjacent to analysis pits for data above (coded by color). Labels correspond to the analysis number (ie., #2, 3, 5, 10 and 11). Spectra are scaled (multiplied by a constant) so that all spectra match the intensity of #2 at 1000 cm^{-1}. Note: 2-10 have similar G-peaks, but 11 is significantly higher.

SIMS Observation:

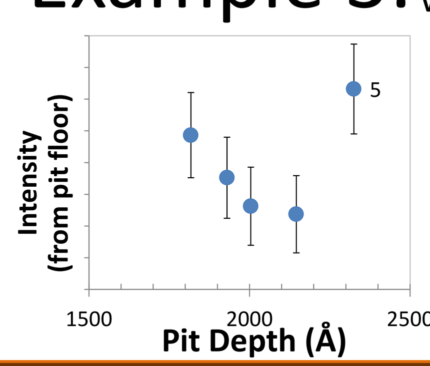
- ***For Mg, the RSFs calculated for shallow SW implants and deep standard implants were different [1].***
  Hypothesis: repeated sequential annealing of DLC during the fabrication process coarsens and graphitizes the deeper layers of DLC during the process of relieving internal stresses [4], [6] and RSF may change with sp^3/sp^2 at depth.
  Hypothesis: the solar wind H implant weakens near-surface DLC sufficiently to allow relaxation of internal stress, perhaps forming additional sp^3 bonds.

*Structural change with depth is corroborated by Raman ([4] and figure below). **(top)** Spectra from: (1) an analysis pit about 4000 Å deep (black line), and (2) the collector surface, scaled so intensity at 1000 cm^{-1} matches (1). **(top & bottom)** The difference of these spectra [(1)-(2)] (grey line) can be modeled by Gaussian fits to the D and G peaks [8] (blue curves).*





Example 3: Recognizing spectra of Genesis DLC films when the substrate is sampled



Note the decreasing trend in intensity of the G-peak sampled on pit floor plotted vs. pit depth. Deeper pits mean less DLC thickness between the pit floor and substrate. Peak position is shifted in these spectra, and both Si and trace SiC from the substrate will be visible but will not be relevant to the SIMS data.*

**"5" is an exception: perhaps there is an embedded graphitic particle in the DLC column.*

Summary and Conclusions

Raman spectra taken using the 532 nm laser can be extremely useful in understanding "scatter" in the heterogeneous DLC collectors. In the 400-1000 cm^{-1} range, the presence or absence of silicon species strongly effects SIMS analysis (both (+) and (–) secondary ions). In the 1000-2000 cm^{-1} range, the positions, widths, and intensity of sp^2 peaks (as variations are likely caused by small sp^3 peaks) may also correlate with SIMS data. This study has not correlated changes in Raman spectra 2000 cm^{-1} and above with SIMS data. However, this is the spectral range for C-H peaks *[9]*, as well as the range for viewing relaxation of bonds during annealing *(cf. [10])* and may prove to be useful. Finally, there is the issue with the activation volume occasionally penetrating through the DLC layer into the substrate as there is some variation in DLC thickness and probably transparency *[11]*. Accordingly, Raman on these films must be used in conjunction with SIMS, SEM, EPMA or other data for accurate interpretation.

References

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