



Genesis DoS Wafers: What Every SIMS Analyst Needs to Know Before Measuring Solar Wind.

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Introduction

A. Overview

The Genesis Mission flew diamond-like carbon (DLC) films on silicon (DoS) wafers as a subset of the solar wind (SW) collectors [1]. Because DLC is conductive, it was assumed that “carbon is carbon” and that the films would be easy to analyze by secondary ion mass spectroscopy (SIMS). Instead, precise and accurate SIMS analysis of SW from the DLC films of Genesis DoS wafers has been problematic for a decade [2,3,4]. Issues with SIMS analysis were not recognized pre-flight because (1) data from each individual analysis often looks superb and (2) pre-flight analyses were cursory, designed to look for signs of retention or diffusion of elements. Only when accurate quantification of ion yields was required – and it was found that relative sensitivity factors (RSF) varied spatially – did the idiosyncrasies of DLC become an issue [4]. Later, attempts to measure Mg isotopes encountered instrumental mass fractionation (IMF) and molecular ion-yields which were spatially variable [3]. Without previous experience with DLC films, expert SIMS analysts evaluating these data assumed something amiss with the instrumental set-up or analytical technique. To shorten this learning curve for others, we present issues encountered during SIMS analysis of SW in DLC and how we’ve dealt with them.

B. Experimental

This study uses multiple SIMS data sets (2006-present) from various DoS wafers implanted commercially with Mg isotopes at various energies, as well as Genesis-flown DoS collectors. Data were taken at either Caltech (Cameca IMS 7f) or ASU (Cameca IMS 6f) using an O₂⁺ primary beam with a ~6keV impact energy. Other parameters (e.g., raster size, primary beam current, mass resolving power, use of O₂ bleed, etc.) varied with the analysis session.

This work was implemented in two steps. First, we examined a single data set having extremely well constrained parameters, including a slow sputter rate, high Mg signal for all three isotopes, and two matrix ions (¹²C and ¹³C). Any anomalous results within that data set were assumed to be due to properties the DLC film, not the SIMS set-up or operator. A year of intense study was required and included some sample characterization by electron microscopy and optical interferometry, as well as a few additional SIMS analyses [3, 4]. Numerical modeling of the properties of the DLC film was also done (cf., [4] and discussion below in C. **Uses and Limitations of SRIM**). Eventually we created a set of internally-consistent hypotheses for how properties of the DLC film were manifested by the observed analytical anomalies [4].

Our second step was to compare the first data set with other data sets to see if those hypothesis explained anomalies in SIMS data from Genesis DLC on a wider scale. Here we preview those results.

C. Uses and Limitations of SRIM

A large portion of our understanding of the structure of the diamond-like carbon film through this study comes from the use of the free-ware program SRIM (*The Stopping and Range of Ions in Matter*) available at www.srim.org [5]. Designed to teach undergraduates the basics of ion implantation, this program has been accurate enough that it is an excellent resource for many general uses, especially when a homogeneous, conductive material is impacted by high-energy ions. However, it has limitations. For example, SRIM’s “billiard ball” approximation of implantation does not adequately include non-ionizing energy-loss to electrons at low energies. Moreover, the program is over-constrained. For example, the same implant profile can be a result of varying composition or the compound correction. A full discussion is given in the supporting materials available at [5]. Still, if the limitations are considered, SRIM can be incredibly useful for understanding SIMS analysis in DLC (e.g., Figure 1).

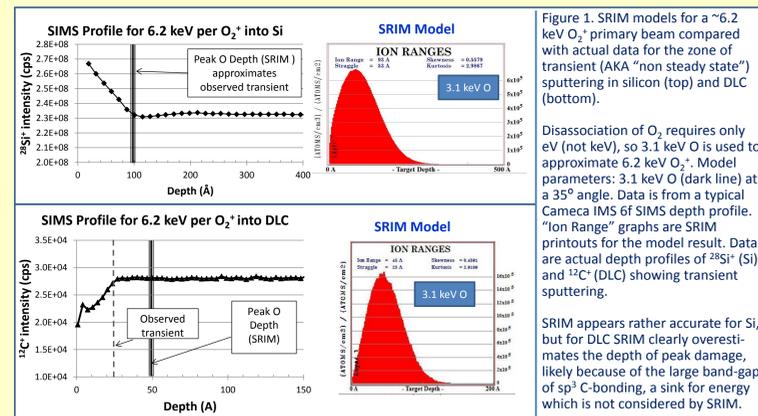


Figure 1. SRIM models for a ~6.2 keV O₂⁺ primary beam compared with actual data for the zone of transient (AKA “non steady state”) sputtering in silicon (top) and DLC (bottom).

Disassociation of O₂ requires only eV (not keV), so 3.1 keV O is used to approximate 6.2 keV O₂⁺. Model parameters: 3.1 keV O (dark line) at a 35° angle. Data is from a typical Cameca IMS 6f SIMS depth profile. “Ion Range” graphs are SRIM printouts for the model result. Data are actual depth profiles of ²⁸Si (Si) and ¹²C (DLC) showing transient sputtering.

SRIM appears rather accurate for Si, but for DLC SRIM clearly overestimates the depth of peak damage, likely because of the large band-gap of sp³ C-bonding, a sink for energy which is not considered by SRIM.

References

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Acknowledgements

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Idiosyncrasies of DLC films affect SIMS analysis of Genesis DoS solar wind collectors.

Here we suggest methods for obtaining accurate and precise solar wind data despite these issues.

Essentials of DoS wafers

DoS were chosen for the Genesis mission for reasons including: a low molecular weight providing low back-scatter during solar wind (SW) collection and relatively few potential mass interferences during analysis as well as retentiveness of SW (especially volatiles), as well as physical and chemical durability [1]. The DLC portion of the DoS (which collected the SW) is amorphous, anhydrous, and has a high sp³/sp² bonding ratio cf., [6], [7]). However, high internal stresses, layered structure, and chemical inhomogeneity are features of the film and makes analysis by SIMS complicated [4]. The following points are important for SIMS analysts to recognize ([4] and references therein):

- Internal stresses can be high: diamond crystals have formed in films during sputtering.
- DLC is intrinsically chemically reducing: trace silicon carbide has been found.
- “Chemical Sputtering” (AKA “etching”) of DLC may occur when exposed to an O⁺ or O₂⁺ primary beam, or an O₂-bleed. This process would limit build-up of O in the matrix, explaining observed relatively low ion yields.
- Minor Si can limit etching by forming a non-gaseous byproduct, allowing build-up of O in the matrix, explaining relatively increased ion yields observed. Si is non-uniformly distributed in the DLC.
- Ion yield depends on the O concentration of the matrix, but the changes in the element of interest relative to changes in matrix ions may differ, so RSF may differ with O concentration.
- Genesis DoS is not a perfected commercial product: defects such as particulates and local inhomogeneity in structure and chemistry are present.
- Electrical conductivity varies with location on the sample. Thus, sample voltage can vary from spot to spot, indirectly changing the ion yields (and RSF).

Figures 2 - 6 give an idea of some of the physical inhomogeneity in the DLC film. Figure 2 is a flight era (Jan 2000) DoS test wafer with an anomalously thick DLC film (3.4μ). Note the Newton’s rings, which are likely a function of both thickness and stress state. All Genesis DLC films are fabricated stepwise, deposited as layers ~1000Å thick [6]. The wafer is annealed after each step to relieve a proportion of the enormous internal stress of the newly-deposited layer. These layers can be seen easily in photos of the DoS Concentrator target (flight sample #6000; Figure 3). Some of these features can be recognized in SIMS depth profiles (Figures 4 - 6) and so their contributions to the SIMS signal can be subtracted (or those profiles can be discarded) when quantifying the solar wind. However, major issues the analyst will encounter are caused by the subtle variations in electrical and bonding properties of the DLC film. While these variations may change SIMS-derived values by factors of two, their effects are often not easily recognized.

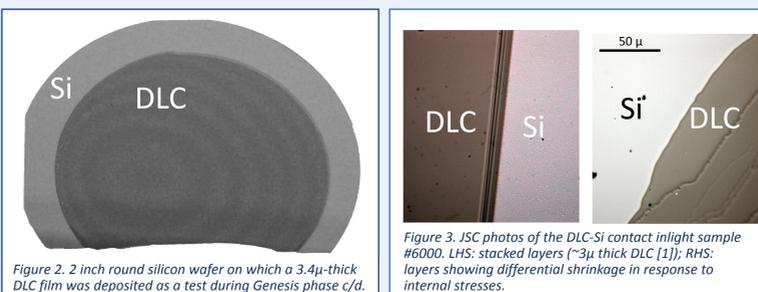


Figure 2. 2 inch round silicon wafer on which a 3.4μ-thick DLC film was deposited as a test during Genesis phase c/d.

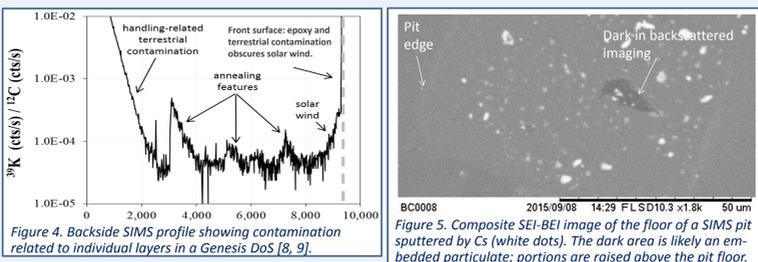


Figure 3. JSC photos of the DLC-Si contact in-flight sample #6000. LHS: stacked layers (~3μ thick DLC [1]); RHS: layers showing differential shrinkage in response to internal stresses.

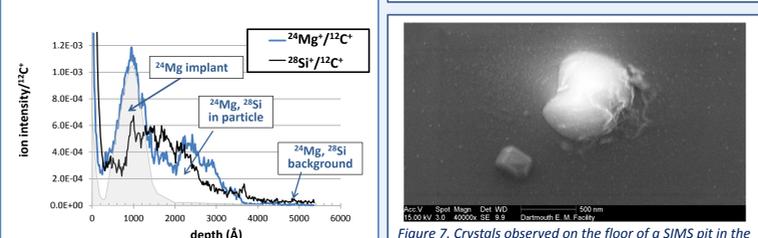


Figure 4. Backside SIMS profile showing contamination related to individual layers in a Genesis DoS [8, 9].



Figure 5. Composite SEI-BE image of the floor of a SIMS pit sputtered by Cs (white dots). The dark area is likely an embedded particulate; portions are raised above the pit floor.

Hacks for Interpreting Data

A. SRIM Models for Density and Composition

Figure 8 compares the shape of measured depth profiles (circles) of mono-energetic Mg implants into DLC with SRIM models (lines). If data falls on a line, the model is consistent with local properties of the film, and the position gives an effective density [4]. SRIM models using #906 graphite (black lines) are consistent with data from 75 keV and 43 keV implants but the 25 keV data are offset from the line. If this offset is real, as the internal consistency suggests, SRIM suggests a relatively high Si content for some profiles [4]. Alternatively, the implant may be in a region of DLC with an extreme sp³/sp² ratio: i.e, a ratio beyond the scope of SRIM modeling at these low energies. Or, perhaps, there is a near-surface property of DLC not yet considered. To date, we have not yet relocated individual SIMS pits for the re-measurements needed to confirm the data.

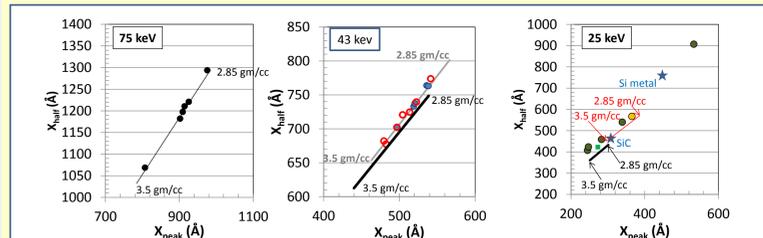


Figure 8. SIMS data vs. SRIM models. X_{peak} is the depth below the surface at which the maximum Mg concentration occurs; X_{half} is that depth beyond X_{peak} where the concentration has dropped to half the peak value. Each line is a best fit to a set of SRIM models for that implant in which matrix composition and structure are constant but density varies. Black lines have SRIM’s 906 graphite catalog material as a matrix; grey line is for that material with a compound correction (CC) of 0.6 but is very similar to the result for 906 graphite+8% Si; red line is for that same material but with 25% additional Si and a 0.6 CC. The CC is empirical, and models non-ionizing energy loss to electrons or other non-ideal properties. Markers: circles= depth profile data (different colors = different analysis sessions). 25 keV plot, only stars = individual SRIM models assuming SiC and Si metal matrices; green square = 906 graphite at 3.5 gm/cc and a CC of 0.2

B. Understanding Variations in RSF

The RSF for elements in DLC vary spatially. To account for this variation, analysts can implant a reference isotope (e.g., ²⁵Mg for measuring ²⁴Mg) directly into the sample [2]. This “internal reference” procedure was useful for quantifying Fe and Mg [2]. But, a variation of this technique (removing the Si-wafer and implanting reference Na into the DLC film from the back) gave results which look ~2-3x low [8, 9]. Analysts may try to account for the variation of RSF by parametrization. Figure 9 plots RSF (for Mg) vs. ¹²C₂/¹³C₂, a parameter which appears to reflect both chemical and electronic properties [4]. Using this empirical method the RSFs form linear trends, but SW values are generally lower than standard values. No change in RSF was observed in a test in which a measurable dose of H was implanted alongside Mg, but the H was not at full SW H concentrations. The significant radiation damage from SW H- and SW He- may have locally changed the DLC structure.

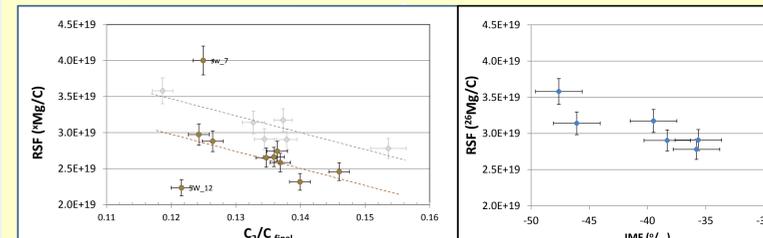


Figure 9. Variations in RSF (Mg/C) with variations in ¹²C₂/¹³C₂ after [4]. ¹²C₂/¹³C₂ likely reflects DLC structure and electrical conductivity, which co-vary. Grey=standards; brown= SW collectors (calculated using a SW fluence [11]); lines show parallel but offset trends. SW12 includes a particle. SW 7 is as yet unexplained.

Figure 10. Variation of RSF vs instrumental mass fractionation (IMF) calculated using a standard implant with a known isotopic ratio. Data from the same analysis session as in Figure 9. By inference, electrical properties vary with the C₂/C₂ parameter.

C. Isotopes: Variable Interferences and IMF

Figure 11 plots SW Mg isotope data from the data set used in Figures 9 and 10 [3, 12]. The mass resolving power (MRP) used in the analysis (~1700) was chosen because no molecular interferences (e.g., MgH) were observed in high-resolution mass scans (~3600 MRP) and all peaks from observed molecular ions were well separated. However, Figure 11 clearly indicates interferences in most of the analyses. DLC is slightly variable in composition: perhaps molecular interferences did not exist where we tuned. Alternatively, we used a primary ion flux of ~1 to 4E14/cm² which gave average sputtering rates of only 0.25±0.03 Å/s, near the lower limit of what is useful for dynamic SIMS. Perhaps temporal spikes in the sample voltage due to the sporadic presence of non-conductive crystals reduced the impact energy of the primary ions enough that, occasionally, additional molecular fragments were ionized. Combining Figure 9 and 10 dictates that IMF can be parametrized using C₂/C₂.

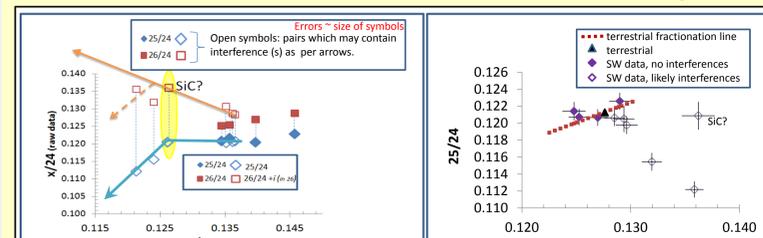


Figure 11. Two plots of the SW Mg isotope data of [3, 12]. Left: ²⁵Mg/²⁴Mg, ²⁶Mg/²⁴Mg pairs vs. ¹²C₂/¹³C₂: the regularity suggests molecular interferences are a function of local matrix properties (cf., Figures 9, 10). The data without molecular interferences have high initial and final ¹²C₂/¹³C₂ values. Right: three isotope plot – interferences cause deviation from the terrestrial fractionation line. Markers labeled in legend; solid lines apparent trend of increasing interferences [3].