

**CLEANING AND PRESERVING THE SURFACES OF GENESIS SOLAR WIND COLLECTORS FOR BULK AND REGIME CARBON, NITROGEN, AND OXYGEN ANALYSIS.** K. D. Rieck<sup>1</sup>, A. J. G. Jurawicz<sup>2,3</sup>, D. S. Burnett<sup>4</sup>, Y. Guan<sup>4</sup>, J. Nogan<sup>5</sup>, W. Ross<sup>5</sup>, A. R. James<sup>5</sup>, and R. C. Wiens<sup>1</sup>, <sup>1</sup>Los Alamos National Laboratory, ISR-2, MS-D434, SM-30, Bikini Atoll Rd., Los Alamos, NM 87545, USA; kdrieck@lanl.gov, <sup>2</sup>CMS, SESE, Arizona State University, Tempe, AZ, USA, <sup>3</sup>Earth Sci., Dartmouth College, Hanover, NH, USA, <sup>4</sup>Geo. & Pl. Sci., Caltech, Pasadena, CA, USA, <sup>5</sup>Center for Integrated Nanotechnologies Core Facility, Albuquerque, NM, USA.

**Introduction:** The Genesis spacecraft spent 852.83 days in space passively collecting bulk samples of solar wind (SW) in wafers of silicon, and other materials. Prior to measuring SW, each collector wafer must be cleaned to remove native oxide, particulates, and a space borne organic film. This cleaning must be performed carefully to minimize damage to the irradiated surface. As we push our detection limits to measure elements at ever lower concentrations (e.g., in collectors that were only deployed for certain SW regimes), it becomes increasingly important to obtain accurate measurements as close to the collector surface as possible. Solar wind is distributed across the upper 100 nm of the collector. Refining our cleaning techniques would indirectly increase our accuracy and precision for the measurement of SW-implanted carbon, nitrogen, and oxygen abundances by accessing solar material only nanometers from the surfaces of the irradiated flight wafers [cf. 1-4].

We tested new cleaning techniques on non-flight, ion-implanted silicon wafers, as well as on one Genesis bulk B/C SW collector (#61164). We compared the relative effectiveness of solvents commonly used to clean silicon wafers. We also tested whether applying a patterned coating of silicon film to freshly-cleaned Si collector surfaces protects the surfaces from new contamination or oxidation.

Successful sample preparation reduces interferences from terrestrial sources, allowing us to not only replicate the results of earlier studies of bulk SW C, N, and O, but also to accurately measure these elements at lower concentrations in fast, slow and CME SW samples. This data will help us better understand the elemental differences between the Sun and SW, and allow us to test hypotheses concerning SW-forming processes, and nebular composition [5].

**Methodology: Test Wafers.** Five test wafers were made from non-flight, float-zone (FZ) silicon (4 to 6 mm in diameter). Hydrogen was implanted by Southwest Research Institute (SWRI) at  $\leq 7.7$  keV H;  $1.8 \times 10^{16}$  H/cm<sup>2</sup>. Like Genesis flight wafers, the surfaces of these wafers became contaminated with terrestrial particulates and oxides. Exposure to particle radiation and some terrestrial contamination makes these wafers our best analog to Genesis SW collector wafers.

**Cleaning Solvents.** Each test wafer was cleaned using one of the following series of solvents:

- 1) Ultra-pure water (UPW; exclusively)
- 2) Xylenes (X), acetone (A), methanol (M), UPW

- 3) X, A, M, UPW, 40% ammonium fluoride (AF)
- 4) X, A, M, UPW, dilute hydrofluoric acid (1:100 49% HF:UPW)
- 5) X, A, M, UPW, 1:100 Buffered Oxide Etch (49% HF:40% AF; BOE)

Genesis sample 61164 was cleaned according to solvent series #4. All the solvents in series #4 have been commonly used for cleaning Genesis Si in preparation for measuring inorganic elements. Xylenes has been used to clean SiC for O analysis [1].

**Si film.** To try to protect freshly cleaned surfaces from environmental C, N and O, a patch of Si film was selectively applied to the front surface of each wafer using e-beam deposition at the Center for Integrated Nanotechnologies (CINT) Core Facility in Albuquerque, NM. That is, wafer edges were masked during Si deposition so only the center (analysis) area of the wafer was coated with a protective layer of Si film. Leaving the outside edge bare of Si film allowed the wafer to better adhere to mounting epoxy used in subsequent sample preparation steps.

**Shadow Masks.** Wafer edges were shielded from Si deposition using shadow masks. Fabrication of the shadow masks was performed by staff at the CINT Core Facility. Each mask had a 2 to 3 mm diameter window. The window would be centered over the front surface of a wafer and clipped into place for e-beam Si deposition.

**E-beam Si deposition.** We used a dedicated Si source in a tungsten crucible for our e-beam work. Wafers, shadow masks, and Si source material were loaded into the e-beam chamber, and the vacuum system pumped down until the vacuum reached a steady state ( $9.6 \times 10^{-7}$  Torr for test wafers,  $8 \times 10^{-8}$  Torr for Genesis 61164). 100 nm of Si were deposited at a rate of  $\sim 1$  Å/s.

**Back-side polishing.** All samples were mounted (front side down) and polished (from the back side) by EAG Laboratories. This is now common practice for preparing Genesis wafers, as it allows for SIMS back side depth profile analysis, which reduces interference from surface contaminants [e.g., 4; Fig. 1]. Four of the six wafers were polished to a thickness of  $\sim 2.5$   $\mu$ m, as per request, but two others, including Genesis #61164, were accidentally polished too thin. #61164 succumbed to the applied stresses and/or physical defects and partly delaminated during the polishing process. Portions of Genesis #61164 that were not coated with Si film generally resisted delamination, and may have protect-

ed the intact Si-coated portion of the sample. None of the test wafers suffered delamination.

**Reference ion implantation.** After polishing, all samples were implanted by Leonard Kroko, Inc. with a nominal dose of  $1 \times 10^{13}$  atoms/cm<sup>2</sup> (each) <sup>13</sup>C, <sup>15</sup>N, and <sup>18</sup>O (75 keV). External standards were used to calibrate the implant fluences, and in turn the implanted ions were used to calibrate our <sup>12</sup>C, <sup>14</sup>N, and <sup>16</sup>O measurements. Implanting minor species allows us to easily distinguish reference ions from most terrestrial contaminants, and SW profiles, which are primarily composed of major species.

**C, N, O measurement with SIMS.** Depth profiling was performed using the Cameca ims 7f-Geo Secondary Ion Mass Spectrometer (SIMS) at Caltech. A rastered 3 keV Cs<sup>+</sup> primary beam (10 to 13 nA) was used to sputter into the Si wafers [Fig. 2]. Negative secondary ions of 2 keV were measured. <sup>14</sup>N<sup>28</sup>Si<sup>-</sup> and <sup>15</sup>N<sup>28</sup>Si<sup>-</sup>, served as proxies for N abundances, as these molecules are more abundant as negative ions than <sup>14</sup>N or <sup>15</sup>N.

**SIMS background signal reduction.** Prior to measurement, the SIMS was baked for 48+ hrs. to reduce background levels of C, N and O. The sample chamber pressure was kept low ( $4.0 \times 10^{-10}$  to  $3.9 \times 10^{-11}$  Torr) through the intermittent use of blank Si sputtering, a sublimation pump, and a liquid nitrogen trap.

Most measurements were conducted using 3,000 mass resolving power (MRP), which eliminated many mass interferences, but we were unable to separate signal from <sup>28</sup>Si<sup>13</sup>C<sup>1</sup>H<sup>-</sup> (5,179 MRP), <sup>30</sup>Si<sup>12</sup>C<sup>-</sup> (6,738 MRP), <sup>29</sup>Si<sup>12</sup>C<sup>1</sup>H<sup>-</sup> (9,720 MRP), and <sup>28</sup>Si<sup>12</sup>C<sup>1</sup>H<sub>2</sub><sup>-</sup> (3,338 MRP) from our <sup>14</sup>N<sup>28</sup>Si<sup>-</sup> measurements. Similarly, we were unable to separate signal from <sup>30</sup>Si<sup>12</sup>C<sup>1</sup>H<sup>-</sup> (9,426 MRP), and <sup>28</sup>Si<sup>14</sup>N<sup>1</sup>H<sup>-</sup> (3,983 MRP) from our <sup>15</sup>N<sup>28</sup>Si<sup>-</sup> measurements. However, the contributions from most of these interferences are insignificant (at least at the current precision levels) to the <sup>14</sup>N<sup>28</sup>Si (Genesis 61164) and <sup>15</sup>N<sup>28</sup>Si (<sup>15</sup>N implants) profiles, because they are either species of minor isotopes (<sup>29</sup>Si, <sup>30</sup>Si, <sup>13</sup>C), or much lower in abundance than <sup>15</sup>N<sup>28</sup>Si in implants. When N was not analyzed, the instrumental background levels of C and O were measured at an MRP of ~500. We were able to compare these levels with earlier C and O measurements made by [4].

**Results: Solvents.** During cleaning, some small droplets of BOE adhered to its wafer, causing localized over-etching and pitting. Solvent series 3 may have slightly outperformed series 1 and 2. Wafer cleaning with solvent series 4 and 5 showed an unexpected near-surface O signal in our test samples that extends ~1,500 Å deep. The effects on C and N are still being evaluated.

**Si film.** At the time of writing, our SIMS depth profile data are still being processed, so the benefits of the Si film are still undergoing evaluation.

**Discussion and Conclusions:** Adhesion of BOE solvent to Si wafers was also observed by M. Sharma and G. J. Paramasivan (Dartmouth; verbal communica-

tion). It is possible that the relative proportions of HF and AF need to be adjusted before solvent series 5 can be safely used. Solvent series 4 and 5 may have revealed a previously unknown accidental implant of O in our non-flight test samples by removing native oxide from the surface. Accidental implantation of O may have occurred during H-implantation. It is possible other elements, e.g., C, and N, were also implanted. Trace gasses in the e-beam sample chamber offer another source of C, N, and O, but these species would only be observed at the wafer-film interface, or incorporated into the Si film during deposition. We must take into consideration both accidental implantation and contributions from the e-beam vacuum system when evaluating the benefits of our solvents and Si film.

Care must be used when polishing Genesis samples coated with Si film, as they may be more likely to delaminate than non-flight wafers. However, as #61164 was polished too thin, it is difficult to make a direct comparison.

**References:** [1] McKeegan K. D. et al. (2011) *Science*, 332, 1528-1532. [2] Marty et al. (2011) *Science*, 332, 1533-1536. [3] Huss G. R. et al. (2012) *Meteoritics & Planet. Sci.*, 47, 1436-1448. [4] Heber V. S. et al. (2013) *LPS 44*, Abstract #2540. [5] Heber V. S. et al. (2014) *Chem. Geo.*, 390, 61-73.

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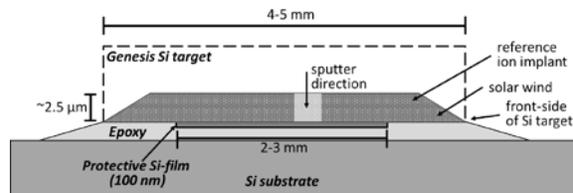


Fig. 1. Schematic side view of back side depth profiling. Adapted from [5].

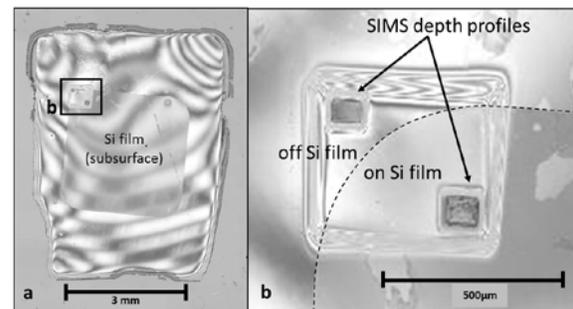


Fig. 2. SIMS craters in a test sample (a) that was cleaned with solvent series #2, coated with a 3×3 mm patch of Si film, mounted face-down, and back-side polished to a thickness of ~2.5 μm. Depth profile measurements were made by one corner of the Si film to compare surface contamination levels in Si-film-free and Si-film-coated areas (b).