USING COMBINATION OF NEAR SURFACE SIMS AND TOF-SIMS DEPTH PROFILES AS A SUCCESS CRITERIA FOR GENESIS SOLAR WIND COLLECTOR CLEANING. Y.S. Goreva[1], D.S. Burnett[2], A.J. Jurewicz[3], Y. Guan[2]. [1]NASA Jet Propulsion Laboratory, Pasadena, CA, [2]California Institute of Technology, Pasadena, CA; [3]Arizona State University, Tempe, AZ.

Introduction: This work is an on-going effort to characterize and remove crash-derived contamination from the surface of Genesis Solar Wind collectors in order to maximize the scientific return from the Genesis Solar Wind sample return mission. A subset of Genesis Mission collector fragments are being subjected to extensive study via various techniques [1-9]. Here we present an update on the sample 60336, a Czochralski silicon (Si-CZ) based wafer from the bulk array (B/C).

Sample 60336 has a complex history. It has undergone multiple cleaning steps (see the Table below): UPW spin wash, aggressive chemical cleanings (including aqua regia, hot xylene and RCA1), as well as optical and chemical (EDS, ToF-SIMS) imaging. The effectiveness of cleaning was verified by JSC optical imaging, ToF-SIMS (Smithsonian), NovaSEM (Smithsonian) and dynamic SIMS (Caltech).

Last year we presented reassuring results of the RCA1 treatment [7]. The choice for RCA (a standard semi-conductor procedure for removing contaminates from silicon wafers) was made based on the organic contaminants such as “Flounder” appearing on the 60336 surface [1, 2]. Post-RCA ToF-SIMS imaging showed that the surface of 60336 appears to be clear of contaminants, with remaining particles within the Flounder and other areas investigated are likely embedded (welded?) Si and/or pits [7].

SIMS Solar Wind depth profiles: The ultimate test of the cleanliness of Genesis collector is the SIMS front side depth profiling. The solar wind profiles in Si are often observed only at depths beyond about 600Å, while at shallower depths the solar wind profiles are overprinted by the surface contamination. The shape of the surface contamination profile is determined in part by the size distribution of surface particulate contaminants which varies from spot to spot on the surface. But most of the surface contamination signal present at depths more shallow than roughly 200Å reflects “mixing” (forward scattering) from collisions of the primary ion beam with contaminant atoms, driving them to deeper depths relative to where they were originally located. We refer to this process as “gardening”. *The success criteria for 60336 cleaning is to see the near-surface peak in the solar wind front side depth profile*.

SIMS depth profiles were obtained at Caltech for Mg, Na, K, Ca and Al. The results vary from element to element, with Mg exhibiting the best (cleanest) solar wind profile, and Al – the worst (dirtiest). Here we report the best and the worst case scenarios. Fig. 1 shows results for ^{24}Mg profile in 60336 compared to a control 20733-1 Si. It is evident that the near-surface Mg solar wind peak is clearly resolved. The 60336 profile is closer to the surface by about 60Å, but this is within the error of the depth measurement. There is no measurable effect of NH_3-H_2O_2 treatment (RCA) of 60336 on measured SW Mg depth profile: The fluence from 60336 agrees within error with that from 20733-1 (1.56 ± 0.07 x 1012 atoms/cm^2 vs. 1.66 ± 0.12 x 1012 atoms/cm^2 respectively), indicating no RCA-induced erosion.

2/21/07	Imaged; no flounder is visible
2/26/07	UPW cleaned 5min @40C at JSC. *The Flounder can be seen in this image.*
2/26/07	Sent to PI Grabowsky
2/16/12	PI returned unopened sample
5/14/13	Imaged using DM6000M at JSC
sum2013	SEM analysis at PSI. Kim finds Flounder
8/1/2013	Imaged using DM6000M at JSC
8/6/13	UPW cleaned and imaged at JSC
8/13/13	Aqua regia and hot xylene at Caltech
9/12/13	Imaged using DM6000M at JSC
9/16/13	UPW cleaned and imaged at JSC
10/14/13	ToF SIMS analysis at Smithsonian
10/21/13	Optical imaging at Smithsonian
11/12/13	Low-vacuum nanoSEM at Smithsonian
11/12/14	Imaged using DM6000M at JSC
11/24/14	10 min RCA1 cleaning at Dartmouth
12/2/14	25 min RCA1 cleaning at Dartmouth
12/4/14	Imaged using DM6000M at JSC
12/4/14	UPW clean 5min, 40C at JSC
12/4/14	Imaged using DM6000M at JSC
12/18/14	ToF SIMS analysis and SEM at Smithsonian
2/24/15	Imaged, UPW clean, re-imaged AT JSC
3/3/15	ToF SIMS analysis at Smithsonian
3/15	SEM imaging at Smithsonian
3/15	SIMS analysis at Caltech
4/15	SIMS pit measurments at Dartmouth
5/7/15	Imaged, UPW cleaned at JSC
5/15	ToF SIMS ion images at Smithsonain
6/15	ToF-SIMS depth profiles at Smithsoanian

From the Mg profile alone, we cannot rule out etching of some areas of 60336 by the NH_3-H_2O_2 treatment and that, by chance, our analysis was on an unaffected area. However, our experience with etched Si samples is that if etching is irregular and significant compared to solar wind depths, the surface of the sample is visibly mottled. The post-RCA images of 60336 are bright, smooth, and uniform with no evidence of significant differential etching of the Si surface.

Unlike the Mg profile, the Al profile fails to resolve a SW peak from contamination, but there is a clear transition between dirt and SW and a suggestion of a peak around 500Å (Fig. 2).

Below about 350Å, the spectrum is dominated by gardened Al surface contamination. The contamination overprint gradually tapers off becoming an Al solar wind profile beyond 400Å. Profile 3 included a hot spot in the Al ion beam image of the analyzed area. Deeper than about 600Å the two profiles agree. The 200-600Å region shows the addition of the hot spot Al. The ion beam image for profile 3 was initially uniformly bright but on a 10-100 sec time scale, the hot spot appeared, and could be tracked visually until it disappeared around 300-350 sec corresponding to the disappearance of the counting rate bump in the profile around 600Å.

ToF-SIMS near-surface depth profiles. To investigate the discrepancy between "ToF-clean" Al images and a clear Al surface contamination revealed in SIMS profiles, we performed high spatial resolution near-surface depth profile analysis using the Smithsonian ToF-SIMS. ToF-SIMS pulsed primary beam (Bi+) is much gentler than the one used in conventional dynamic SIMS analyses, minimizing the "gardening" effect. In addition, we utilized a clustered Bi3+ beam, distributing the primary beam target energy over a larger area thus minimizing the "gardening" effect even further. Figure 3 presents our preliminary results. The depth of Al peak (and an oxide layer) is not calibrated but, from the first principles (primary ion dose density and the area rastered), we estimate it at ~ 110Å. It is plausible that the SiO_2 layer formed (or increased in thickness) after the RCA1 treatment. Si could react with the H_2O_2 and form a SiO_2 layer on top of the Al surface contamination layer. The first principles estimation of the 100Å oxide thickness layer is reasonable in this case. The 100Å oxide layer is shallow enough for oxide layer removal without affecting SW profile. Standard semiconductor practices will be employed for an oxide layer removal.

Conclusions:

1. ToF-SIMS ion imaging verified that RCA treatment successfully removes residual organic contamination.
2. SIMS view of 60336 cleanliness:
   - Except for Al, sample 60336 is pretty clean with solar wind measurable below about 300Å.
   - Verified that RCA treatment does not etch solar wind (Mg, Ca, Na profiles)
3. ToF SIMS depth profiles suggest oxide formation on the collector surface during RCA treatment
   - Al is "buried" on the oxide/Si boundary, contributing to gardening effect during SIMS analyses.
4. Genesis collector fragments that appear clean to surface sensitive techniques (XPS and/or ToF-SIMS) may still carry contamination if oxidizing cleaning techniques were employed.

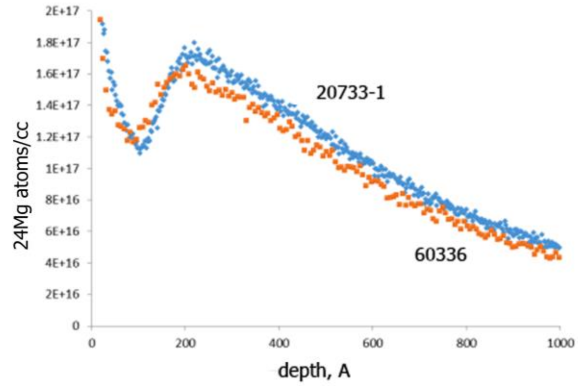

Figure 1. SIMS Mg profile on "RCA-clean" Genesis sample.

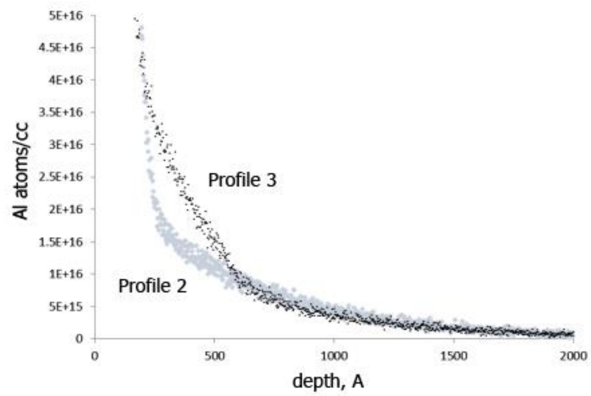

Figure 2. SIMS Al profile on "RCA-clean" Genesis sample.

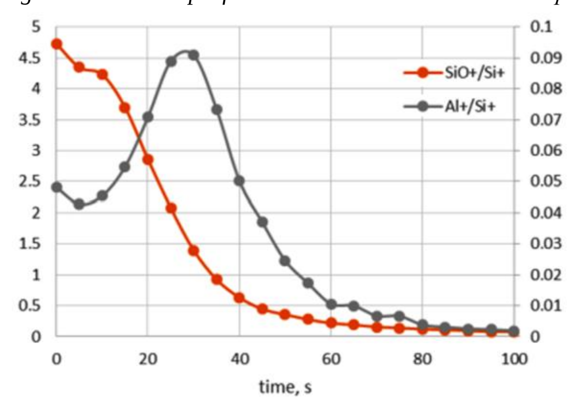

Figure 3. ToF-SIMS near-surface depth profiles for Al+ and SiO+ yield normalized to Si+.

References: [1] Kuhlman K. R. and Burnett D. S. (2007) LPS 38, 1920. [2] Goreva Y. S. and Burnett D. S. (2013) LPS 44, 2109. [3] Schmeling M. et al. (2013) LPS 44, 2465. [4] Calaway M. J. et al. (2007) LPS 38, 1627. [5] Calaway M. J. et al. (2009) LPS 40, 1183. [6] Goreva Y. et al., (2014) LPS 45, 2568. [7] Goreva Y. et al. (2015) LPS 2333. [8] Allton J. et al, (2015) LPS 46, 1896. [9] Allums et al (2015) LPS 46.

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