

PROTON DENSITY WITHIN SILICON ALLOWS RELIABLE GENERATION OF SILICON OXIDE THIN FILMS IN GENESIS COLLECTORS. M. Sharma¹, G. Janakiraman Paramasivan¹, A. Jurewicz¹, and D. Burnett². ¹Department of Earth Sciences, 6105 Fairchild Hall, Dartmouth College, Hanover, NH 03755, ²Division of Geological & Planetary Sciences, MS 170-25, Caltech, Pasadena CA 91125.

Introduction: Genesis-returned solar wind (SW) provides a unique opportunity for determining Os isotope composition of the solar photosphere and the time integrated Re/Os ratio of the solar system. The latter would provide a benchmark against which early alteration processes on meteorite parent bodies and planetary evolution scenarios could be evaluated [1]. Direct measurement Genesis SW Os concentration and isotope composition would also give insight into the Re abundance of the photosphere. Osmium is among the rarest elements in the solar spectrum and its analysis in Genesis collectors presents several technical challenges. The 2-year Genesis array Os fluence is estimated to be 1.3×10^6 Os atoms/cm² (2.2cm²/fg) [2]. Our analysis of different Genesis collector material indicates that Os blank of silicon collectors is low and therefore suitable for Os isotope measurements. However, due to the crash-landing of the Genesis spacecraft, several small fragments of the collectors will need to be combined to make an allocation of only ~ 2.2 cm² of surface area; that is, a maximum of ~ 1 fg of SW Os (= 3 million atoms of Os) will be available to measure. This has necessitated the development of a high chemical yield and low blank protocol that is geared specifically to extract Os from silicon. This procedure is then combined with a technique that gives high ion yield, low interference and optimal duty-cycle permitting precise and accurate determination of Os isotopes using negative thermal ionization mass spectrometry. However, the first and foremost challenge to surmount has been the problem of cleaning of Genesis collector surface, which is contaminated with dust from Utah desert, organic residue, metal, and possibly Si welded onto itself. Extensive experimentation has shown that organic residue is highly refractory and it cannot be removed by chemical means. Removal of surface contamination must then be done by sequentially etching away top 15nm of Si-wafer (Fig. 1) in such a way that it does not compromise SW Os, which has been modeled to be buried throughout the zone of 15 nm to 250 nm below the collector surface (Fig. 2).

After extensive experimentation, we developed an ultra-clean procedure that involves creating a silicon oxide layer by immersing it in warm HNO₃ and then a separate step that uses dilute HF to etch the silicon oxide layer. The oxidation and etching steps are repeated again to remove any re-deposited contaminant. Oxidation by nitric acid adapted from Asuha et al. [3] creates a atomically smooth interface between Si-oxides and Si

[4]. Dissolution of silicon oxides using HF leaves the silicon surface stable with hydrogen termination.

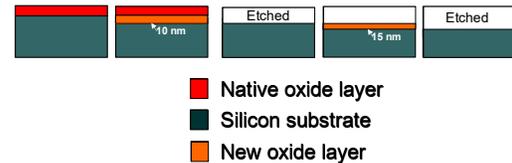


Fig. 1. Procedure to clean surface contaminants in four separate steps: Grow silicon oxide layer below the existing native oxide layer to a depth of 10 nm and then etch it. Grow a new 5 nm thick silicon oxide layer and then etch it. Note that silicon oxide growth below the existing native oxide layer takes place via transport of oxidizing agent to the SiO₂/Si interface.

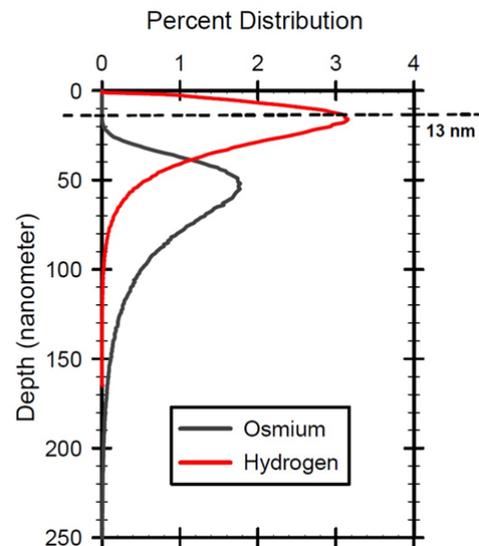


Fig. 2. Distribution of solar wind Hydrogen and Osmium in Si wafer (modeled using SRIM, Chad Olinger, Los Alamos & West Point).

We used Nd implanted silicon wafers (flight spares and flown) to evaluate the depth of oxidation and to calculate oxidation rate. Surprisingly, we have discovered that for the flown wafers there is a parabolic relationship between the oxidation rate and number of protons in the etched layer and a linear relation between rate constant and SW protons (Figs. 3 and 4).

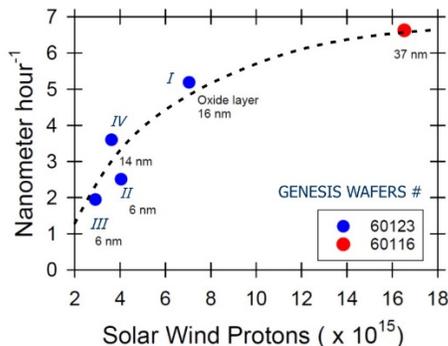


Fig. 3. Parabolic relationship between oxidation rate and SW protons accumulated in different depth intervals as calculated from SRIM. Roman numerals give the order of oxide layer creation and its corresponding thickness.

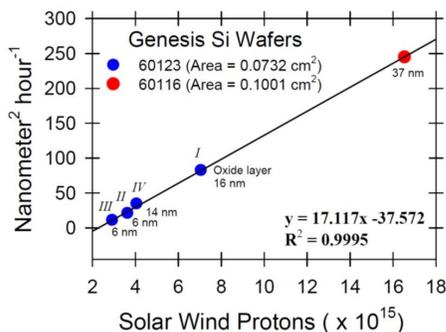
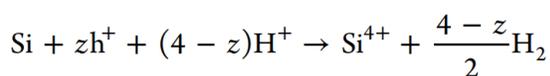


Fig. 4. Linear relationship between rate constant and SW protons. This relationship is used to evaluate the time for immersion for generation of oxide layers of a certain thickness.

The reaction involving reduction of nitric acid and oxidation of Si that results in production of hydrogen [5-6] may be written as:



Where z is the number of electrons removed during oxidation of Si that combine with H^+ to produce H_2 gas and h^+ represent the holes created by electrons. This suggests that in flown Si wafers the SW protons are an extra source of H^+ that can readily combine with Si^{4+} to generate H_2 .

We therefore find that by decoupling the oxidation and etching steps we can create silicon oxide thin films with precision. This will allow us to remove surface contamination. Since the entire procedure is done in a

closed system, the extent to which an element (e.g., contaminant) is released can also be estimated by isotope dilution. For example, the Utah desert soil osmium concentration was estimated to be 26 pg g^{-1} and $^{187}\text{Os}/^{188}\text{Os}$ ratio is $1.76 \pm 0.04 (2\sigma)$. In comparison, measured Os concentration and isotope composition of HNO_3 used for oxidation are 73 fg g^{-1} and 0.2, respectively. Measurement of Os isotopes released during sequential etching can therefore give the extent to which Os Utah soil is present and removed.

Following sequential etching Os is extracted from the wafers using with acidic bromine solution (ABS, 10M HF + 0.5M HBr + 10mM Br_2) [8], purified using microdistillation and its isotope composition measured. Fig. 5 below shows the isotope composition of Os implanted with Genesis wafers 60116, 60123 and a pot sample. Our initial data suggest high chemical yields for the ABS procedure. These data will be discussed.

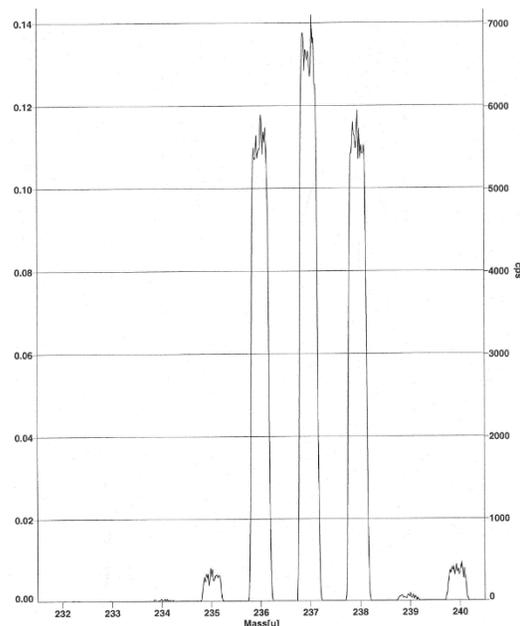


Fig. 5. Spectrum of OsO_3^- ions implanted in a flight spare. The isotope composition of the implant is profoundly different from natural Os allowing us to evaluate the chemical yield of sequential etching experiments.

References: [1] Sharma et al. (2015) *LPS XLVI* Abstract #2361. [2] Riesenfeld et al. (2013) *Space Sci. Rev.* 175 125-164 (SOM); [3] Ashua et al. (2002) *Applied Physics Letters*, 81, 3410-3412; [4] Imai et al. (2008) *Applied Surface Science*, 254, 8054-8058; [5] Acker et al. (2012) *The Journal of Physical Chemistry C*, 116, 20380-20388; [6] Kooij et al. (1999) *Electrochemical and Solid-State Letters*, 2, 178-180; [7] Bressers et al. (1996) *J. Electroanal. Chem.*, 406(1), 131-137.