APPLICATION OF SEMICONDUCTOR INDUSTRY CLEANING TECHNOLOGIES FOR GENESIS SAMPLE COLLECTORS. S. Sestak[1], I. A. Franchi[1], A. B. Verchovsky[1], J. Al-Kuzee[2], N. St J. Braithwaite[2] and D. S. Burnett[3]; [1]Planetary and Space Sciences Research Institute, Open University, Milton Keynes, MK7 6AA, UK, (s.sestak@open.ac.uk); [2]Oxford Research Unit, The Open University, Foxcombe Hall, Boars Hill, Oxford, OX1 5HR, UK; [3]California Institute of Technology, Pasadena, CA 91125.

Introduction: Genesis was the fifth NASA Discovery mission launched in 2001 with its primary goal to return samples of Solar Wind (SW) for analysis of isotopic and elemental compositions in terrestrial laboratories [1]. This was accomplished by exposing ultrapure materials to the solar wind at the L1 Lagranian point for a period of 884 days of SW collection [2], and resulted in approximately 10^{20} ions or ~0.4 mg of SW being implanted. The SW ions implanted into the collector materials will have accumulated with a maximum concentration at a depth of up to a 100 nm.

The crash of the Genesis Sample Return Capsule (SRC) in 2004, caused severe damage to the capsule and a breach of the science canister in the field [3]. The crash had two major consequences: 1) significant fracturing and loss of a major proportion of the fragile collector materials and 2) exposure of the ultra-clean SRC and semiconductor sourced collector materials to desert dust and debris from the Genesis SRC [4].

The work reported here is focused on analyzing the isotopes of carbon (C) collected in Float Zone (FZ) silicon collector materials, although it does have application to a wide range of analyses. The preferred analysis strategy for carbon at PSSRI has been stepped combustion followed by static vacuum Mass Spectrometry (MS) [5].

The Genesis collectors contain <100 pg of bulk SW implanted carbon per cm^2. At these ultra-low analyte concentrations, several factors became very significant. Apart from bulk purity, surface contamination for light elements such as carbon and oxygen was always going to be unavoidable. To this end, the proposed extraction techniques were always going to have to offer 'depth sensitivity' as a means of separating surface contamination from the extracted SW. In the case of carbon analysis, this discrimination would be achieved by utilizing stepped combustion. Terrestrial surface carbon is oxidized at ≤600˚C typically and removed as carbon dioxide (CO_2). The SW implanted carbon is not released from the silicon until >1000˚C. Hence, in this case temperature control allows 'depth sensitivity' to separate surface contamination from SW implanted species.

The majority of the contaminants introduced were in the form of particulates, from a large array of sources, and of particular consequence to the carbon analysis included materials such as desert dust, carbon-fibre heat shield material and and carbon filter material from the capsule re-pressurisation filter [6]. Stepped combustion of all these C-rich materials has demonstrated that the contaminating carbon can be readily removed by 800˚C, i.e. before the SW C is released from the Si wafer. Added to this particulate load was the proliferation of scratches and gouges into the polished collector wafers with ground-in contaminants. Perhaps the most challenging contamination is the presence of a thin molecular (highly cross-linked) film characterized as a 'brown stain' in solar exposed surfaces in the order of tens of Angstroms thick. Deposited on virtually all surfaces of the spacecraft during the mission this material was uv-photo hardened to a chemically resistive film on the sun-facing solar wind collector surfaces [7].

Removal of both the C-rich particles and the molecular film are essential for a successful measurement of the implanted solar wind. The removal of particulates is critical to almost all proposed solar wind analyses and is being addressed by a number of laboratories utilizing an array of physical and chemical approaches, although each solar wind analysis and collector material requires careful refinement of the cleaning protocols. However, removing the C-rich molecular film, with a carbon coverage approximately 10^4 times that of the implanted solar wind is critical to a successful solar wind carbon analysis. Fortunately, we could draw upon the extensive experience of the cleaning technologies that have been developed by the semiconductor industry over the past 30 years in dealing with problems which at first order are similar to those presented by the 'Genesis samples'.

In order to successfully remove all the particulate, surface damage-related contamination and molecular film a combination of different cleaning steps will be required. Physical (e.g. ultrasonication) and chemical processing have been shown to be well suited for removal of particulate and surface damage-related contamination but so far have shown no effect on the molecular film. Reported here are the results from an investigation of the suitability and efficiency of plasma etching and UV-ozone radiation induced cleaning techniques for the removal of the molecular film.

Methods: Oxygen (O_2) and hydrogen (H_2) plasmas generated by Rf excitation in Reactive Ion Etchers (RIE) were investigated at the Oxford Research Unit

as a dry etching procedure to remove organic contaminnats [8]. The RIE was a capacitively coupled Rf system with 150 mm stainless steel (SS) electrodes set 30 mm apart. Typical discharges were obtained at a pressure of 100 mTorr for O_2 and H_2, frequency of 13.56 MHz, power of 100 W, O_2 flow rate of 60 sccm and a hydrogen flow rate of 80 sccm. The O_2 plasma was operated in negative mode with a DC bias of -352 V while the H_2 plasma operated in positive mode with a DC bias of +320 V. The plasma was operated in a pulse mode to mitigate overheating of the substrate. Hydrogen plasma cleaning was investigated as it more closely mimics the space environment Genesis experienced while collecting SW and may have applications where the presence of a large amounts of O_2 is unwanted.

Radiation Induced cleaning is a combination of ultraviolet (UV) radiation and O_2 [8]. A UV/ozone chamber was built using SS material and a low-pressure mercury lamp in a quartz housing. UV radiation at 185 nm generates ozone (O_3) from oxygen while a second emission band at 254 nm breaks down the O_3 to form highly reactive atomic oxygen (O) and photo-activates organic molecules adsorbed at the surface. The reaction of O with the excited state organic molecules results in the formation of CO_2 gas and water vapor (H_2O), leaving no residue behind.

Results: Oxygen and hydrogen plasma generation in RIE's was investigated as a means of removing residual organic ('brown stain') contamination with minimal processing. It was found that both the O_2 and H_2 plasmas were able to reduce the surface carbon contamination, although it did take 25 % longer process time for the H_2 to achieve the same level of cleaning. Due to the nature of the experimental RIE used, the SS electrodes caused a small amount of sputtering back onto the Si wafers. This was confirmed by XPS surface analysis which reported decreased levels of carbon and fluorine contamination but the appearance of iron, nickel and chromium from the SS electrodes. One established approach which can mitigate against this effect is to use different materials for the electrodes (e.g. aluminium). Equally, control of the pulse programming can be used to reduce sputtering. As used above to control the heat input into the sample by lowering the ON duty cycle, it can be further lowered such that the ON time is only 1-5 µs, but OFF for ~35 µs. Energetic ions are generated which decay rapidly but the atomic and radical species decay at a much slower rate. In this mode of operation virtually all of the cleaning effect is achieved via the atomic/radical species with minimal risk of metal sputtering.

The UV/O_3 method was also targeted at the intractable 'brown stain'. By ensuring the sample wafers were less than 10 mm from the lamp surface, submicron thick organic contamination loads on test samples of Al foil were successfully cleaned (at least to visual inspection). Further work is in progress to establish the efficacy of this technique with flight material from Genesis with the uv-hardened molecular film and measurement of residue with XPS. A positive result is anticipated as the UV/O_3 cleaning process is an established 'finishing' step in the semiconductor industry where it is used to remove the last layers of carbon contamination (~100 Å or more), comparable to that of the molecular film on the Genesis samples, once other methods have removed the gross layers [6]. The technique is ideal for the Genesis samples as it does not heat the substrate to more than 50˚C and leaves no organic residue as the product of oxidation are gases that are pumped away. Due to the low reaction temperatures encountered, oxidation of the underlying Si wafer will be limited to near-normal room temperature controlled diffusion of O through the SiO_2 oxide layer, hence minimal risk of destroying the implanted SW. Equally, there is no limit to sample size or clamping as the process occurs under a very low flow of oxygen gas at ambient pressure.

While a number of steps remain to be finalized in conclusion it is proposed that the final cleaning process will include three main steps: 1) ultrasonication in solvents to remove gross particulates by physical means; 2) chemical oxidants/acid etches to remove gross organics and sub-micron sized particles and 3) Rf plasma or UV/O_3 to remove the last atomic layers of adsorbed organic contamination. While it is not expected that any cleaning process can quantitatively remove all of the huge contamination load on the Genesis collectors, the stepped combustion method to be employed for the actual carbon analysis is capable of offering excellent resolution of the SW carbon from the carbon contamination if the load can be reduced by 2 to 3 orders of magnitude.

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