SYNCHROTRON TOTAL-REFLECTION X-RAY FLUORESCENCE (SR-TXRF) OF GENESIS RETURN SAMPLES.

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Introduction: For the past decade we have been using Total-reflection X-Ray Fluorescence (TXRF) to study surface contamination of silicon wafers in collaboration with the semiconductor manufacturing community. We have developed equipment and methods which enable us to measure levels of contamination of transition metals which is below what was previously achievable, due to the brightness of the synchrotron beam. TXRF is possible because the index of refraction for most materials is slightly less than one in the x-ray regime. Thus, Snell's Law indicates that below a small grazing angle of incidence the x-rays are totally reflected from the surface. The typical angle of incidence used in TXRF for sapphire substrates is 0.2 degree.

Due to the non-nominal arrival of the return capsule, techniques that can distinguish between surface and implanted trace elements have increased in importance. Another area which has increased in importance is evaluating methods of non-destructively cleaning the samples in a way which removes the surface contamination (both Utahogenic and brown-stain).

Experimental Methods: A special-purpose chamber was fabricated for these experiments. This chamber sits in an enclosed, ultra-clean environment within the beam line hutch on end-station 6-2 at the Stanford Synchrotron Radiation Laboratory. The mini-hood surrounding the chamber has an ULPA-filtration laminar flow hood to ensure that the samples are handled in a low-particle-count environment. Standard semiconductor clean room techniques are used for personnel and equipment. The chamber is mounted on a high-precision goniometer which allows the x-ray angle of incidence onto the sample to be positioned very accurately. A scan of the scattered intensity off of the substrate vs. angle of incidence is used to calibrate the true angle of incidence. Figure 1 shows the results of two of these angle scans. These scans are fitted to a very simple Fresnel-like calculation using the known index of refraction for the specific substrate and photon energy. This measurement, in addition to being extremely sensitive to the angle of incidence, is also very sensitive to surface roughness. These scans will be discussed in more detail below.

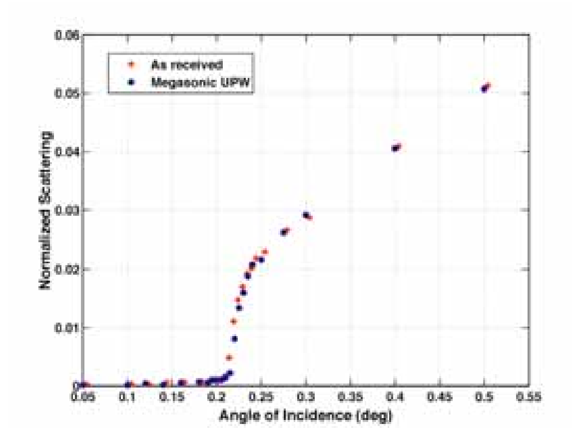

Fig. 1: Scattered intensity vs. angle for two flight-spare sapphire wafers at an incident energy of 11 keV.

Experimental Results: Several samples were measured during the most recent experimental run. They included flown sapphire sample pieces and two control sapphire wafers. One of the issues being addressed by the curatorial staff at JSC is what techniques can be safely used to clean the flown wafer samples. A cleaning technique used in the semiconductor industry, Megasonic UPW (ultra-pure water), is being considered as a technique for removing both particulate and surface contamination. A concern raised about the use of this technique is that it has the potential of increasing the sample surface roughness during the cleaning process. They therefore sent us two 4” sapphire control wafers, one of which had been cleaned using the Megasonic UPW process, the other as-received. As discussed above, a significant increase in surface roughness would be observable as a softening of the abrupt increase in scattered intensity at the critical angle (in this case, roughly 0.22 degrees). It would also be seen as an increase in scattered light at angles below the critical angle (i.e. between 0.15 and 0.2 degrees). As can be seen in Fig. 1, there is essentially no difference between the two samples, indicating very little, if any, increased roughness as a result of the cleaning process.

The other issues of concern for the cleaning process is whether it reduces the number of particles on the surface and whether it removes monatomically dispersed contamination present on the surface. The two control sapphire wafers we measured were sufficiently free of adventitious particles that we were not able to distinguish any difference in particle levels between the before and after cleaning samples. Figure 2 shows the fluorescence spectra from the two samples, as the log of the intensity, with the red curve from the cleaned wafer and the blue curve from the as-received wafer. There is essentially no difference between the two curves.

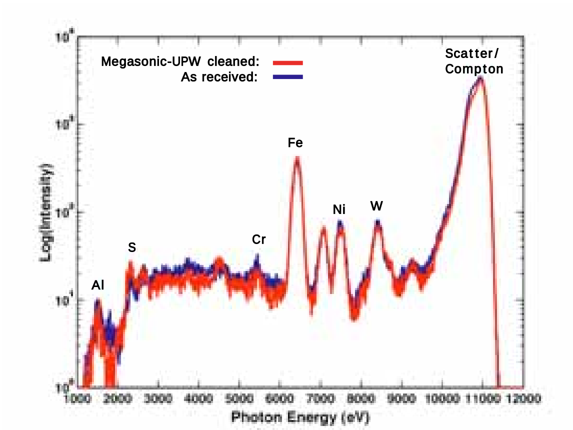

Fig. 2: SR-TXRF spectra from two sapphire control wafers, one cleaned by Megasonic UPW, the other as-received. Angle of incidence is 0.2 degrees.

Flown sapphire samples were measured at a number incidence angles both below and above the critical angle. One of the questions to be answered in this preliminary assessment was whether the brown stain observable using ellipsometry was also visible using x-rays. One of the challenges of looking at low levels of contamination on a sample surface is the high fluorescence yield from the substrate despite the very grazing angle of incidence. In order to reduce the signal from the substrate (the aluminum fluorescence peak), a 25 micron Teflon filter was placed in front of the detector window. This has the effect of reducing the signal at the Al fluorescence energy (1486 eV) by a factor of 10^4 and reducing the signal at Si by a factor of 500, while only reducing the signal at Fe (~6400 eV) by ~10%. The experiment is detector count-rate limited, so the reduction in substrate signal has a dramatic effect on the sensitivity of the experiment at low angles of incidence where surface sensitivity is most important. At higher angles of incidence where one is measuring the implanted signal as well as the bulk substrate signal the difference is less of an issue.

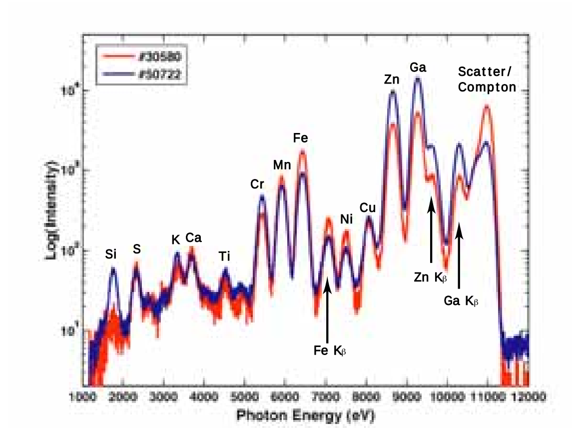

Fig. 3: SR-TXRF spectra from two flown Genesis sapphire samples. Angle of incidence is 0.2 degrees.

Figure 3 shows the spectra from two flown samples, (as the log of the intensity) one which has a measurable brown stain (#50722), the other (#30580) which does not. This is confirmed by the TXRF measurements: the Si fluorescence signal at 1740 eV is a factor of 5 stronger on the #50722 surface. The Al fluorescence, reduced a factor of 20 relative to the Si due to the Teflon filter, is hidden in the shoulder of the Si signal. The reduced scatter peak for sample #50722 may be related to surface roughness related to the presence of the brown stain. A broad range of additional surface contaminants are observable. We note that Ge fluorescence would be observed in the deep trough between the Zn Kβ and the Ga Kβ, indicating little Ge contamination on these two surfaces. We are currently analyzing the spectra at higher angles of incidence and will be able to determine which of these are strictly surface contaminants once those analyses are finished.

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