Preliminary report for HE-2202 18th-24th February 2007

X-Ray photoelectron emission microscopy applied to case studies originally cited in the Long Term Proposal (25/01/2006)

The present experiments with the NanoESCA XPEEM instrument installed on ID08 follow on from the second round of CEA purchased beamtime (see experimental report IN-564) and were carried out during shifts awarded following the submission of a Long Term Project. Three systems are presented.

1. $SrTiO_3$ ceramic

This research is part of the INCEMS project (EU FP6 project n° NMP3-CT-2005-013862) which aims at predicting the properties of multifunctional ceramics. We have imaged the polycrystalline surface at the Sr $3d_{5/2}$, Ti $2p_{3/2}$ and O $1s$ levels. Clear chemical contrast is observed between grains. The degree of grain surface polarity is expected to be a function of the cation present in the surface layer. These results will be correlated with the spatially resolved work function contrast in order to quantify the grain termination and orientation dependence of the basic electronic properties of the ceramics.

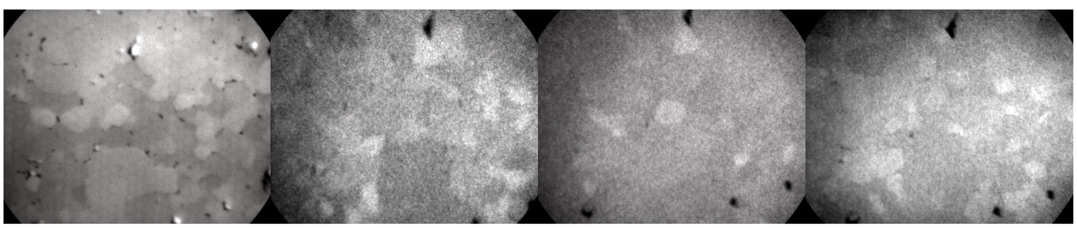

Figure 1 Energy filtered images with a 38 µm field of view from left to right: threshold (4.3 eV); Sr $3d_{5/2}$ (136 eV); Ti $2p_{3/2}$ (460.5 eV); O $1s$ (531 eV). The chemical contrast of the grains is to be correlated with the work function contrast at threshold.

2. Effect of heterogeneous n type doping of Si on molecular grafting

Simple electrografting on heterogeneous substrates is an important subject for future molecular electronics. We have produced micron sized n-type (10^{21} cm^{-3}) motifs using P implantation on an intrinsic silicon substrate. The substrate was cleaned using HF acid solution prior to grafting to thin the native oxide layer (doping dependant) and accentuate the role of doping on grafting. Thin diazonium nanometer layers were polymerised on the substrate, and characterized using AFM, showing the doped areas constitute wells several nanometers deep. The estimated thickness of the polymer is estimated at 2-3 nm over the implanted zones, less in the intrinsic zones.
Using 400 eV photons the *NanoESCA* is sensitive to the polymer (one nitrogen marker per molecule), the thinned SiO_2 layer and the silicon substrate.
We used the variable iris situated after the contrast aperture to isolate the doped patterns in the microscope field of view. Figure 2 shows the patterned substrate with three Si 2p spectra with an energy resolution of 0.26 eV: the ion implanted disk (black), an adjacent intrinsic zone (red) and finally, with a larger iris, an average signal covering both intrinsic and doped layers (blue). Fine differences in the ratio of the Si^0 to Si^{4+} peak intensity confirm that the polymer thicknesses correlate with the native oxide thickness. There are clearly subtle changes in the core level binding energies which are not due to the shift in the Fermi level with doping, since

the microscope references the sample Fermi level. These may be due to variations in the band-bending at the oxide/substrate interface. Further analysis is underway.

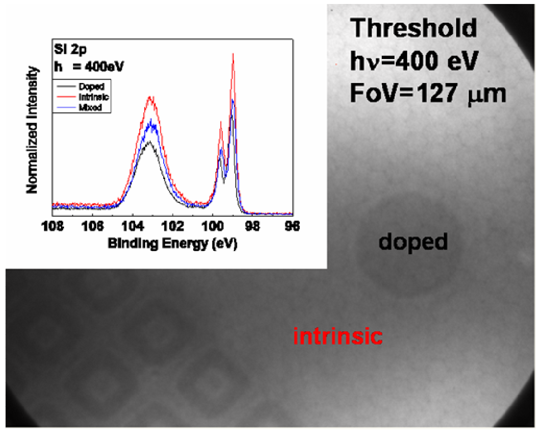

Figure 2 Threshold image of the grafted n-type patterned substrate. The inset shows the Si 2*p* spectra obtained by closing down the iris on specific areas of the field of view of the image, thus giving spectroscopic chemical information from each region.

3. Identification of single SiC grains from the Murchison meteorite

In collaboration with Prof. G. Schönhense's group from Mainz University (Germany) we have used the unique energy filtering capacity of the *NanoESCA* to study the chemistry of the meteorite grains. We have identified the position of the micronic SiC grains, known to be of pre-solar origin for future nano-SIMS isotopic analysis.

Figure 3a) shows a typical threshold image obtained from the grains. There is work function contrast, but no clear signature of the localization of the pre-solar grains. The chemical preparation of such samples can lead to oxidation of the outer part of the grain. Together with the important topological variations which defocus the electrons this makes it difficult to identify genuine pre-solar grains from a standard Si *2p* energy filtered image. However, by using higher photon energy (1 keV) we probe deeper into the grains, and obtain an energy filtered image of the Si *2p* emission associated with SiC (binding energy 101 eV). The result is shown in Figure 3.b) and is to our knowledge the first ever obtained using a specific core level characteristic of a pre-solar grain.

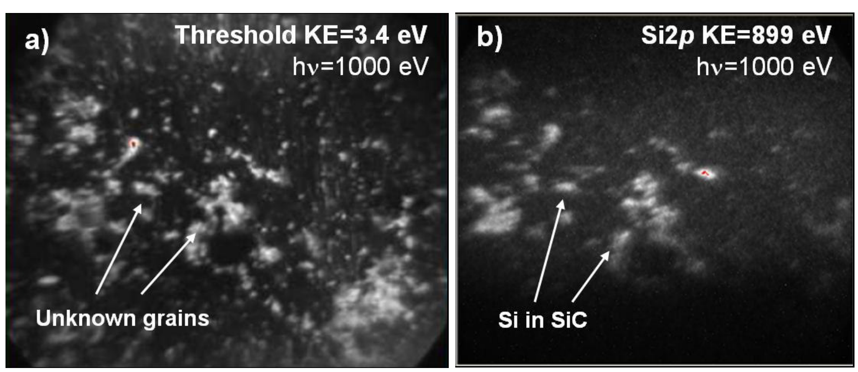

Figure 3 a) threshold image of unidentified grains on sample holder; b) energy filtered image of the Si 2p electrons from SiC pre-solar grains (binding energy 101 eV). Field of view 58 μm, acquisition time 5 minutes.

This is the only instrument capable of furnishing such non-destructive chemical information for cosmochemistry. We believe this will be an important step forward in improving the reliability of analysis of matter from space.