

Supporting information

Nucleation and growth of Fe nanoparticles in SiO₂: A TEM, XPS and Fe L-edge XANES investigation

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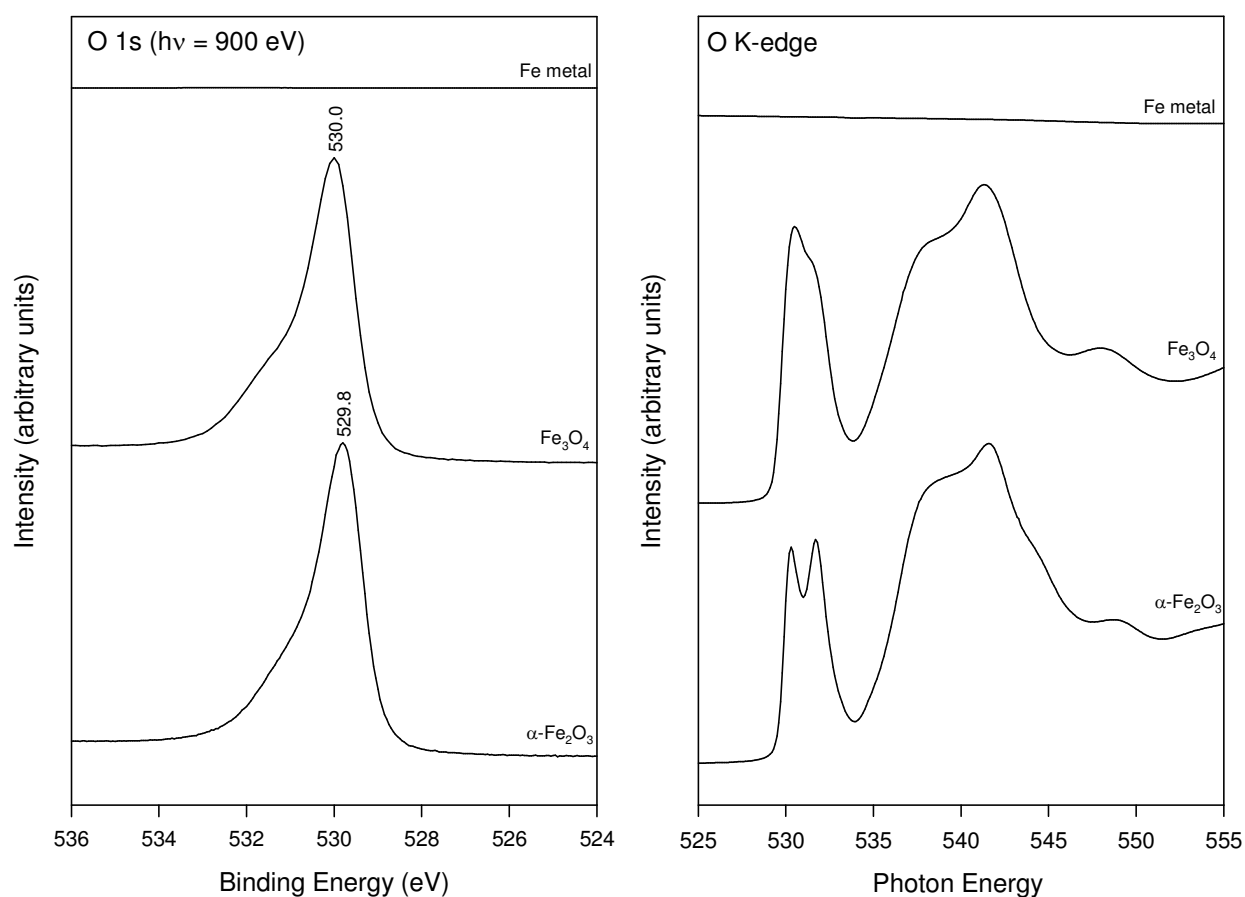
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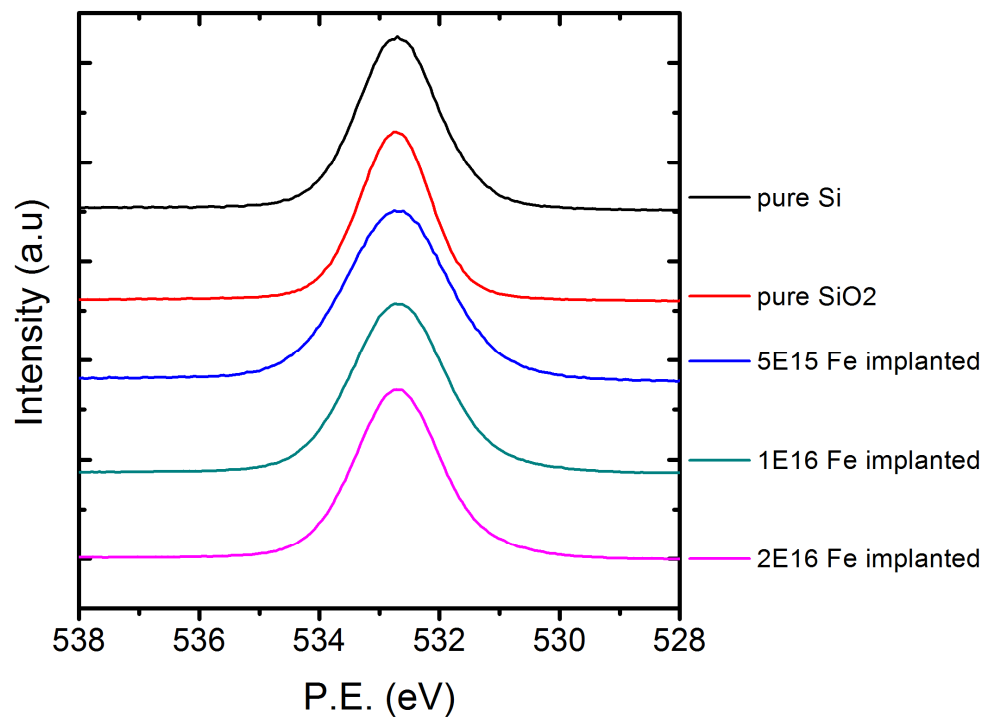
^{||} Australian Centre for Microscopy and Microanalysis, University of Sydney, NSW 2006, Australia.

O 1s XPS and O K-edge XANES data for reference materials.

O 1s XPS and O K-edge XANES spectra were also collected for the Fe, Fe₃O₄ and α -Fe₂O₃ samples. Fe metal gave no O 1s or O K-edge signals as expected for a sputter cleaned pure Fe surface. The main O 1s signals were observed at 530.0 eV for Fe₃O₄ and 529.8 eV for α -Fe₂O₃. The O K-edge spectra for the oxides showed crystal field splitting. Similar crystal field splitting is observed in the Fe L-edges (Figure 5). The crystal field splitting for the Fe₃O₄ sample was less well-defined compared to the splitting for α -Fe₂O₃. The crystal field splitting was 1.0 eV for Fe₃O₄ and 1.4 eV for α -Fe₂O₃.

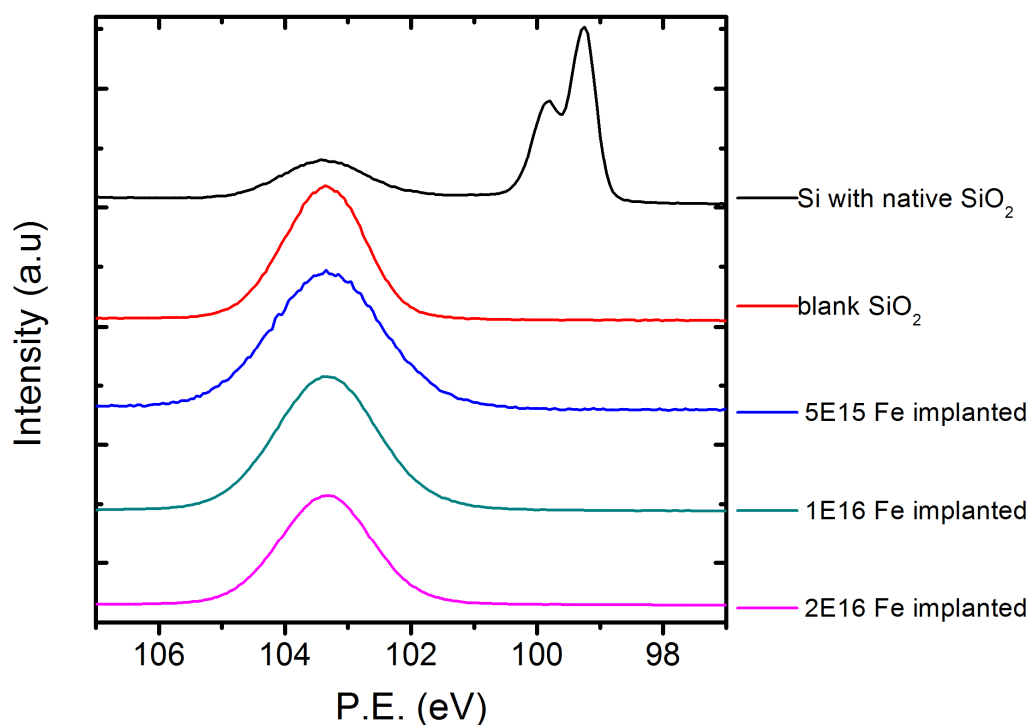


Supplementary Figure 1. O_{1s} (left) and K-edge (right) spectra for the reference Fe samples.



Supplementary Figure 2. O 1s XPS spectra for the reference silicon and silica samples compared to as-implanted samples with different fluences.

No significant variations were observed in the O 1s XPS spectra for iron implanted samples and the pure SiO₂ matrix.



Supplementary Figure 3. Si 2p XPS spectra for a reference silicon wafer with native oxide and silica samples implanted with iron at different fluences.

Si 2p XPS spectra collected for a silicon wafer, a blank 400 nm silica layer, and iron implanted silica samples. The silicon wafer spectrum shows peaks characteristic from Si⁰ (Si 2p_{3/2} = 99.3 eV) and Si⁴⁺ (103.4 eV). No significant variations were observed when measuring the implanted samples compared to pure SiO₂. This confirmed the absence of formation of iron silicides.

Details for the calculations of the probing depth of XPS and TEY-XANES.

The first principle of quantitative XPS¹ gives an indication of photoelectron current at the detector arising from the photoelectrons (PE) emitted in a material as a result of the interaction between an incident X-ray and an atom. For a homogeneous material with low surface roughness, it is proportional to the X-ray flux, number of atoms of a given element, total photoionization cross-section, total inelastic mean free path of photoelectron, efficiency of the detector, analyser transmission function and to a constant depending on the geometry of the measurement. To evaluate the number of PE emitted at a particular depth it is possible to simplify the relation. The number $N_{emitted}$ of emitted PEs emitted is then a function of the depth z and the incident photon energy E_p : $N_{emitted}(z, E_p) = N_{Fe}(z)\sigma(E_p)$ where $N_{Fe}(z)$ is in Fe at./cm², $\sigma(E_p)$ in cm/at. is the cross section for photoelectron emission at a photon energy E_p . It is assumed that the inelastic electron scattering is not considered. To evaluate the number of electrons leaving the surface of the material it is then necessary to multiply this number by the probability p for an electron with a kinetic energy E_K to leave the surface when emitted from a depth z . This value can be obtained from the literature. The number of PEs N leaving the surface is then $N(z, E_p) = N_{Fe}(z)\sigma(E_p)p(z, E_K)$. For the calculations, the silica density was taken at 2.26 g/cm³, the valence state was 4 and the band gap was 8.9 eV. The photoelectron kinetic energies were chosen at 190 and 780 eV respectively. Since the penetration depths of X-rays at the considered energies are much greater than the escape depth it is not necessary to normalise the results from different E_p with the X-ray distribution profile. At 40 nm, the distributions diverge by only 4% for energies between 700 and 1500 eV.

In total electron yield X-ray absorption near-edge spectroscopy (TEY-XANES), unlike XPS where the kinetic energy distribution of emitted PEs is measured, a drain current is measured as a function of photon energy. The photon energy is moved to different absorption edges. The measured current is obtained from the current drained to compensate electrons leaving the surface. These electrons result from Auger electron emission during the photo electric interaction and the secondary electrons resulting

from their cascade in the material. Consequently, the emitted Auger electrons will have different energies due to the different elements (actually different electron states). The escape profile of Auger and resulting secondary electrons will be significantly different when looking at O or Fe for instance. This was evidenced by Frazer et al.² who showed that the escaping depth of electrons through a Chromium layer during total electron yield X-ray absorption spectroscopy (TEY-XAS) was dependent on the Auger electron kinetic energy. The electron range is very different for different Auger electrons: 14.1 nm for 920 eV (Cu), 2.9 nm for 76 eV (Si). They also show that the probing depth is equivalent for TEY-XAS and X-ray Photoelectron Emission spectromicroscopy. Consequently we made the assumption that it was possible to approximate the probing depth of TEY-XANES with the probing depth of an XPS analysis using appropriate energies. In this study Fe L-edge signal will come from a maximum depth of about 7 nm with 50 % of the signal emitted from the first 4 nm. The compositional differences for the different depth probed by these analyses provides an insight into the distribution of Fe oxidation states in the implanted matrix. These values were obtained using the same formula as above, taking E_p as a photon energy in the measured range (710 eV) and the kinetic energy of Fe LMM Auger electron (651 eV). In Frazer et al's.² experiment the range obtained in Chromium was 7.64 nm.

Supporting information references.

- (1) Grant, J. T. *Surf. Interface Anal.* **1989**, *14*, 271-283.
- (2) Frazer, B. H.; Gilbert, B.; Sonderegger, B. R.; De Stasio, G. *Surf. Sci.* **2003**, *537*, 161-167.