

**Experiment title:**

EXAFS Study of Metal Inclusions into Silicon for Quantum Information Processing Applications

**Experiment****number:**

SI 1622

<b>Beamline:</b> ID26	<b>Date of experiment:</b> from: 26/09/07 to: 01/10/07	<b>Date of report:</b> 28/02/08
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Marcin Sikora	<i>Received at ESRF:</i>

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**Report:**

**In this experiment we performed a study of Mn atoms introduced into silicon from the ex-situ UV degradation of thin manganese phthalocyanine (MnPc) films [1].**

We have developed a novel method for the inclusion of metal dopants into silicon from organic precursors. Briefly, prior to arrival at the ESRF, an ordered array of MnPc molecules was formed on a HF-etched Si(100) surface and subsequently irradiated with 172nm UV light. Samples were characterised at UCL and Imperial College using Raman Spectroscopy, Atomic Force Spectroscopy (AFM) and Secondary Ion Mass Spectroscopy (SIMS). In particular, the SIMS analysis confirmed the presence of Mn in Si as a result of UV processing, with a Mn concentration of  $\sim 10^{20}$  atoms/cm<sup>3</sup>.

X-ray Absorption Near-Edge Fine Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) were used to both check the quality of the starting MnPc film and to determine the nature any Mn-rich residue at the sample surface. As can be seen in Figure 1, the spectra verify the integrity of the 5nm MnPc film, which is seen to match that of the starting material (MnPc powder). Furthermore, differences were observed in the XANES and EXAFS spectra of the film before and after UV exposure, suggesting a change in chemical composition. The x-ray absorption edge position (Figure 1(a)) suggests that the Mn is in the same oxidation state as it is in the MnPc molecule, namely Mn<sup>2+</sup>. A pre-edge is observed at

~6540eV and peaks at ~65543eV, ~6568eV and ~6598eV, in close agreement with the known spectrum of MnO [2, 3]. EXAFS fitting of the post-UV film was performed, although due to a low signal-to-noise ratio only the first shell was fitted. The modelling returned a Mn-O bond distance of 2.28Å, in reasonable agreement with the measured Mn-O bond distance of 2.22Å [4], and co-ordination number of 6 is found, confirming the formation of MnO at the surface.

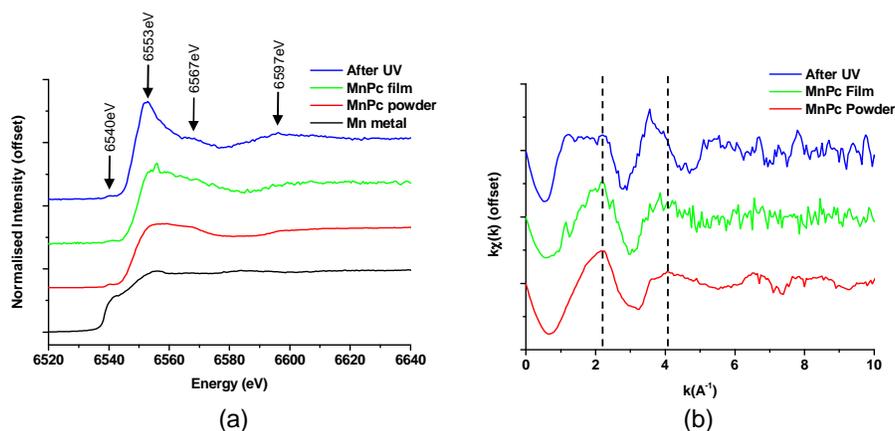


Figure 1. (a) XANES and (b) EXAFS spectra of Mn metal (black), MnPc powder (red), and a 5nm MnPc film before (green) and after (blue) UV irradiation. Data is offset for clarity.

In order to study Mn introduced into the bulk Si, some UV-treated samples were chemically cleaned prior to arrival at the ESRF (SIMS and XPS measurements confirmed the removal of MnO from the surface). Although measurements attempted at low temperature using a cryogenic flow stream were promising, owing to time constraints in optimising the experimental set-up, these were impractical and need to be repeated to obtain higher quality data. A typical room temperature XANES spectrum is shown in Figure 2(a) (top spectrum). Comparison of the magnitude of the x-ray absorption edge with that of bulk Mn (assuming similar x-ray penetration and escape depths) gives an approximate Mn concentration of  $\sim 5 \times 10^{20}$  atoms/cm<sup>3</sup>, in agreement with our SIMS-based estimates. The spectrum of the UV treated sample is vastly different to that of MnPc, with a different x-ray absorption edge position, demonstrating that the metal is no longer bound to the organic ligand. Comparison with the XANES profile of bulk manganese suggests a similar edge position, implying that the Mn is in a neutral oxidation state (as is also the case for the Mn silicide reference) and rules out the possibility that the metal species introduced into the bulk Si are in the form of an oxide. Commonly, small Mn clusters can form in Si, however, the edge features that we have measured are vastly different to the bulk metal case, demonstrating that this is not the case here. Instead, the features are very similar to those of the manganese silicide reference, suggesting that the Mn atoms are surrounded by silicon atoms. In fact, the XANES spectra are in excellent agreement with that observed for implanted Mn in Si systems [5], although the signal to noise ratio of our data is not sufficient to permit detailed comparisons with the theoretical lineshapes presented.

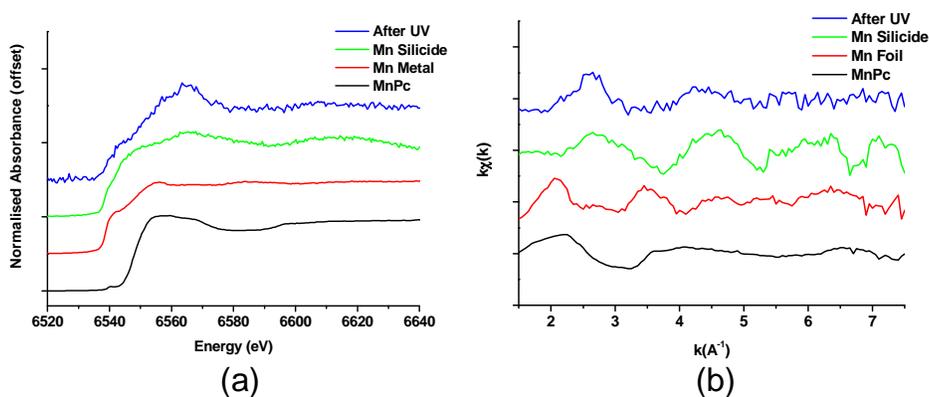


Figure 2. (a) XANES and (b) EXAFS oscillations of MnPc (black), Mn foil (red), Mn silicide (green) and a MnPc film after UV exposure and cleaning (blue). Data is offset for clarity.

Although the signal to noise ratio was also too low to permit the abstraction of the Mn-Si bond distance and co-ordination number, a direct comparison of the EXAFS oscillations is shown in Figure 2(b). Once again, the spectrum of the UV-treated MnPc film (after chemically cleaning) is different from that of the starting material (MnPc) and the bulk Mn foil. Instead, the closest agreement is seen between the data with that of the silicide reference, although slight variations are seen, suggesting a difference in the Mn-Si distance and/or co-ordination number. A very good agreement is seen with the EXAFS oscillations reported for implanted Mn in Si, which occur at  $\sim 2.7 \text{\AA}$  and  $\sim 4.5 \text{\AA}$  [5], further justifying our claim that the Mn has been introduced into the silicon lattice.

In summary, these experiments have allowed us to study the effect of UV irradiation on MnPc films onto silicon. The UV light ruptures to the organic molecule and introduces Mn into the bulk Si substrate, whilst MnO is also formed at the surface. In order to assess whether this method could be used for the nanofabriation of arrays of dopants, further experiments are necessary to determine both the depth profile of the implanted dopants and whether or not the order of the initial organic film is maintained upon introduction to the silicon.

## References:

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