Structural properties of iron disilicide nanocrystals from the gas phase investigated by advanced electron microscopy

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Beta-phase iron disilicide (β-$FeSi_2$) is a promising material for applications as a result of its thermoelectric and semiconducting properties, as well as the abundance of iron and silicon in earth's crust. However, the fabrication of β-$FeSi_2$ nanostructures is challenging due to its complex crystallographic structure. Here, we report on the structural and chemical properties of β-$FeSi_2$ nanocrystals synthesized from the gas phase by the thermal decomposition of silane (SiH_4) and iron pentacarbonyl ($Fe(CO)_5$) in a hot wall reactor. The as-prepared material typically consists of crystals between 10 and 30 nm in diameter sintered into aggregates of a few hundred nanometres in size.

Conventional, analytical, spherical and chromatic aberration-corrected transmission electron microscopy (TEM) are employed to investigate the structures and chemical compositions of β-$FeSi_2$ nanocrystals. The structure of the β-phase was confirmed using both X-ray and electron diffraction. However, the intensities of the (221) and the (312) reflections differ from those expected for single phase β-$FeSi_2$. A reduction in the intensities of (hkl) reflections for which $k+l \neq 2n$ can be modelled by (100)[011]/2 planar defects [1]. Such planar defects have previously only been observed in β-$FeSi_2$ layers [2]. High-resolution TEM images of the nanocrystals acquired in the [012] direction confirm the presence of planar defects perpendicular to [100] (Fig. 1a), while both three-dimensional electron diffraction patterns acquired using automated diffraction tomography [4] and nano beam electron diffraction patterns show streak-like arrays of spots centred on the positions of (hkl) reflections for which $k+l \neq 2n$ (Fig. 1). These observations are consistent with the presence of (100)[011]/2 planar defects in β-$FeSi_2$ nanocrystals.

Each crystalline particle is surrounded by an amorphous shell. Closer inspection of the amorphous shell results in decomposition by the electron beam, with dose of ~1000 electrons per pm^2 at 200 kV reducing the shell thickness from 2 to ~0.7 nm. Since SiO_2 is known to be stable under electron beam illumination, the initial amorphous shell is not thought to consist of stoichiometric SiO_2. Figure 2 shoes a chromatic aberration (Cc) corrected energy filtered TEM image of a nanocrystal recorded at 80 kV, showing an enrichment in oxygen at the position of the shell. The iron and silicon distribution was investigated using low dose electron energy-loss spectroscopy (EELS) linescans at 300 kV using the StripeSTEM technique [4]. Figure 3a shows that the shell is rich in silicon, whereas the iron signal is detected only in the core region. In Fig. 3b, different Si $L_{2,3}$ edge onset energies are compared between different positions on the nanocrystal. In the shell region, the Si $L_{2,3}$ edge onset starts at 105 eV, which is characteristic for SiO_4 tetrahedra. In the core region, an edge onset at 99 eV is observed, which is characteristic of covalently bonded Si. These observations provide additional evidence that the shell is rich in silicon and oxygen.

References

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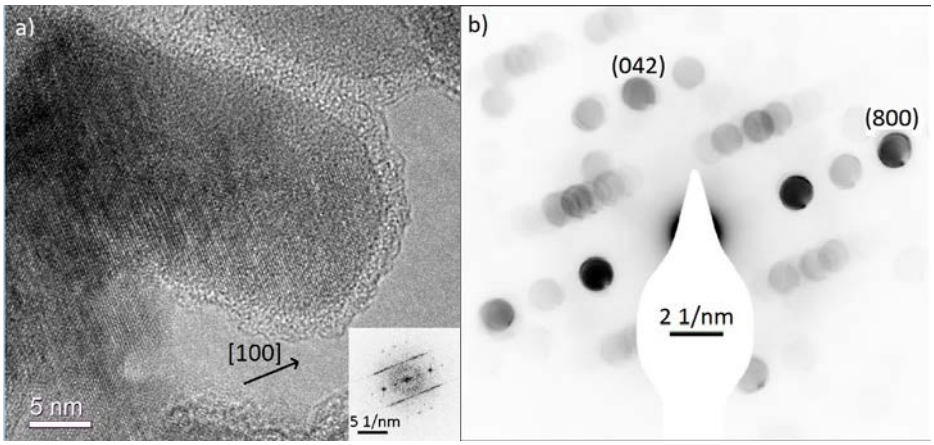

Figure 1. *a) High-resolution TEM image of a β-$FeSi_2$ nanocrystal in [012] zone axis. b) Nano beam electron diffraction pattern recorded from the same crystal in an FEI Tecnai F20 TEM at 200 kV.*

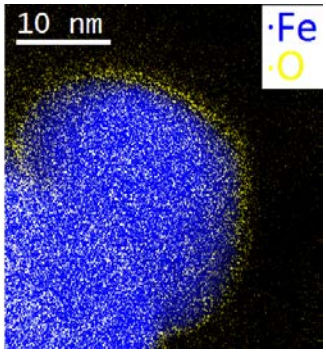

Figure 2. *Cc corrected background-substracted EFTEM maps of a β-$FeSi_2$ nanocrystal recorded using an FEI PICO TEM at 80 kV obtained from an energy-loss series of images recorded over an energy range of 450 to 780 eV with a window size of 20 eV and a step size of 20 eV. The colour map shows the Fe and O distribution in blue and yellow, respectively.*

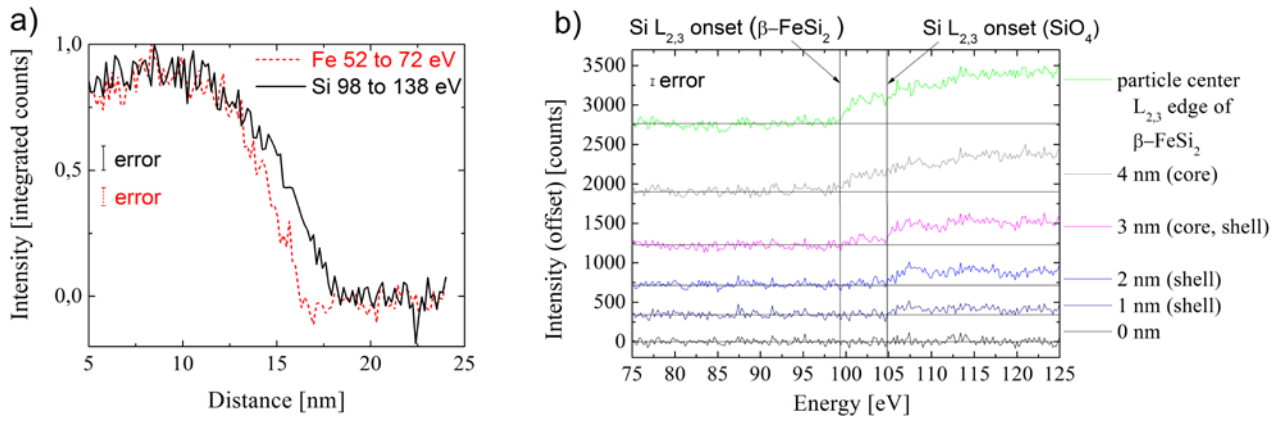

Figure 3. *EELS linescans acquired in a probe corrected FEI Titan TEM at 300 kV using the StripeSTEM technique [6] showing a) the Fe and Si integrated intensity at the edge of a β-$FeSi_2$ nanocrystal and b) background-subtracted EEL spectra of the Si $L_{2,3}$ edge recorded from the edge of an individual nanocrystal. In each plot, 2σ error bars are shown.*