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Influence of substrate treatment on the growth of advanced core–shell alloys and compounds of FeSi@SiO_2 and SiO_2 nanowires

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ABSTRACT

Advanced core–shell FeSi@SiO_x nanowires are observed when $FeCl_3$ vapour is made to flow over a SiO_2/Si substrate at 1100 °C. The thickness of the SiO_x sheath (δ') is found to depend inversely as the period of time of HF etching of the SiO_2/Si substrate. When such substrates are overlaid with a thin film of Au, the nanowires obtained are found to be pure SiO_2. The Au layer disappears as vapour of $AuCl_3$ as its melting point is at 298 °C. Proposed mechanisms of growth in all the various scenarios are identified to be governed by self-catalyzed vapour–solid (VS) mechanism.

1. Introduction

Nanostructured materials, in particular, nanotubes and nanowires are of important technological interest because of their unique electronic, optical and magnetic properties and their potential applications in emerging technology. Among the numerous types of nanowires, silicon oxide nanowires were reported to be good candidates for the fabrication of noble nanodevices such as scanning near-field microscopy probes, lower dimensional waveguide and blue light sources. FeSi and Si nanowires have received considerable attention because of their potential applications. For silicon, it is possible to emit visible light by reducing its dimension, in which the motion of carriers is confined, causing a possible transformation of the electronic band structure from indirect band gap to a direct band gap.

This has stimulated a lot of interest in preparing silicon oxide nanowires. Until now controlling the size and length of these synthesized nanomaterials has practical problems, which seriously restrict future applications. To date; silicon oxide nanowires have been successfully prepared through different ways, such as excimer laser ablation, carbothermal reduction of oxides and chemical vapour deposition (CVD). However, most of the results were crystalline nanowires with a thin oxide outer layer [1–9]. FeSi nanowires have also received considerable interest as they have potential applications in nanowire devices and have already been used in memory device applications. These nanowires have been mainly synthesized by CVD [10–15, 25].

In this paper, we report on the noodle-like nanofibres of FeSi, Si and SiO_2 obtained by vapour transport in a CVD configuration by treating substrates variously.

2. Experimental

Detailed procedure for synthesis of FeSi nano-structures can be found in our recent paper [16]. However, briefly, $FeCl_3$ powder (97% Purity) and Si (1 1 1) wafers were purchased from Sigma–Aldrich and were used as received. The other 3% of the $FeCl_3$ powder (97% Purity) is documented in the suppliers (Sigma–Aldrich) which are trace elements of Na, K and Ca. For the synthesis of FeSi nanostructures, Fe source precursor $FeCl_3$ was placed at the centre of the horizontal quartz tube furnace in quartz boat. Si (1 1 1) substrates were placed 1–2 cm away from the Fe source. The temperature of the furnace was adjusted from room temperature to 1100 °C. N_2 gas was used a carrier gas to transport the precursor vapours from the $FeCl_3$ to the silicon substrates and the reaction was performed for 1 h 40 min. After cooling down to room temperature in air, the Si substrates were taken out for further analysis.

Control experiments were done to compare the effect of etching Si substrates in a 5% Hydroflouric (HF) acid and distilled water solution.

Gold (Au) thin films of 60 nm were deposited on silicon substrates in an ultra-high vacuum (UHV) sputtering system. It contains multiple magnetron sputtering sources that are arranged in a specific circular pattern and aimed at a common focal point. The substrates are placed in the vicinity of this focal point and rotated, which makes it possible to deposit highly uniform single layers, multi-layers and deposit layers simultaneously from a single power supply.

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The morphology of the products formed on the silicon substrates was examined using focused ion beam (FIB) field emission scanning electron microscopy (FE-SEM) (Auriga Cobra FIB FESEM). The crystallinity of the nanostructures was analyzed using high resolution transmission electron microscopy (HR-TEM) (JEOL-JEM 2100). Nanostructures removed from the Si substrates were dispersed in ethanol, and TEM copper grids were dipped into the solution and analysed. The structural properties were examined using Panalytical X'pert PRO PW 3040/60 X-ray diffractometer (XRD) with a Cu Kα (λ = 0.154 nm) monochromated radiation source.

3. Results and discussion

3.1. Morphology and structural properties of FeSi nanofibres

Fig. 1(a) and (b) shows representative SEM images of nanowires grown on the HF treated silicon substrate. The nanowires appear to have smooth surfaces and straight shapes, with lengths which only went up to a few micrometers. Fig. 1(c) and (d) shows representative SEM images of nanowires grown on the untreated silicon substrates. The differences immediately noticed in these nanowires were that; the nanowires were longer than the ones in the HF tread samples by several orders of magnitude, they grow and extend to several tens of microns and have a tendency of bending because of their length (see Fig. 1(d)). The diameters of the nanowires varied from 50 to 160 nm for different samples.

High resolution transmission electron microscopy (HRTEM) was used to study the morphology, crystallinity and the elemental composition of the nanowires. TEM micrographs of a single nanowire from the untreated sample are shown Fig. 2(a)–(c). It can be clearly seen that, the nanowires have core–shell structures. The noticeable differences between the two were that; the core appeared darker and the shell appeared lighter. The visibility of lattice fringes (see Fig. 2(c)) on the core of the nanowire showed that it was highly crystalline.

There were no lattice fringes on the shell; this suggested that the shell was amorphous. The lattice fringes along the nanowire appeared to have the same direction. The measured lattice spacing had a value of 3.14 Å which corresponded very well with the (1 1 0) lattice interplanar spacing of the FeSi structure [17]. The thickness of the shell layer that forms on the walls of these nanowires was in the range of 20–100 nm, for different nanowires. The selected area diffraction (SAED) on the nanowires (see Fig. 2(d)) showed a diffraction pattern with a cubic crystal structure, which was indexed to cubic ε-FeSi. The brightest spot in the pattern can be compared to the most intense peak in the XRD; which is the (2 1 0) plane. In our case, the amorphous shell is in fact Si/SiO_2 as shown in the localised energy dispersive spectroscopy (EDS) performed at the core and around the shell in Fig. 2(e) and (f) respectively. The peaks of Fe in the local EDS spectrum for the shell could be small contributions from core. From the two nanowires in the HRTEM images in Fig. 2(a) and (b), one can conclude that large-diameter nanowires tend to have proportionately thinner sheath or shell thicknesses than their core. The opposite observation is seen for small-diameter nanowires which tend to have larger shell thicknesses.

Fig. 3 shows an XRD spectrum of the nanowires, where the observed diffraction peaks were indexed to the FeSi phase, which has a cubic structure with a lattice constant of 4.496 Å (space group $P2_13$, Pearson symbol cP8, structure type FeSi, Z = 4, ICSD PDF-01-086-0795).The FeSi XRD spectrum is characterized by a unique fingerprint; with the most intense peak occurring at the (2 1 0) plane at $2\theta = 45°$.

3.2. Silicon nanostructures

3.2.1. Morphology and structural properties

Fig. 4(a) shows a scanning electron microscopy image (SEM) of a vast network of nanowires. The nanowires have uniform diameters and have high density. Fig. 4(b) shows spherical structures in the vicinity of the nanowires, which agglomerate into larger structures. Observations made from these SEM micrographs suggest that the VLS growth was unlikely to be the growth mechanism for these nanowires since the clusters were not attached to the

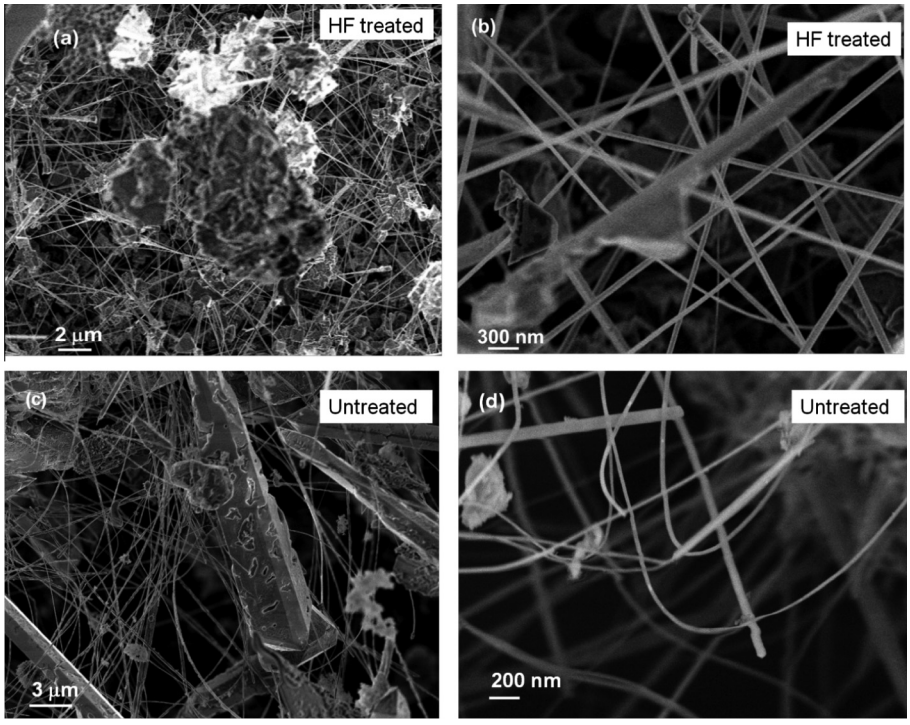

Fig. 1. Representative SEM images of nanowires at (a) lower magnification and (b) higher magnification for HF treated samples. (c) SEM image at lower magnification and (d) higher magnification for untreated samples.