Growth and Characterization of FeSi Nanowires by Chemical Vapor Deposition for Gas Sensing Applications.

By

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DEDICATED TO

My Parents and Siblings

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- The University of the Western Cape.
DECLARATION

I declare that

“Growth and Characterization of FeSi Nanowires by Chemical Vapor Deposition for Gas Sensing Applications”

is my own work and all the sources have been acknowledged by means of references.

Sibongiseni Stanley Thabethe

Signature:__________________________________

May 2013
“Growth and Characterization of FeSi Nanowires by Chemical Vapor Deposition for Gas Sensing Applications”

FeSi Nanowires
Chemical Vapor Deposition
Band Structures
Silicon Substrates
Vapor Solid
Scanning Electron Microscopy
Transmission Electron Microscopy
X-ray Diffraction
Raman Spectroscopy
Photoluminescence Spectroscopy
Fourier Transform Infrared Spectroscopy

May 2013
FeSi nanowires were synthesized via a chemical vapor deposition method. Anhydrous FeCl₃ powder in this case served as the Fe source and was evaporated at a temperature of 1100°C to interact with silicon substrates which served as the silicon source. The nanowires followed the vapor solid (VS) growth mechanism, which does not require the use of a metal catalyst; the native silicon oxide layer on the silicon substrates played the role of the catalyst in the growth of these nanostructures. A second growth mechanism, involving the use of a metal catalyst to assist in the growth of the nanowires was attempted by depositing a thin film of gold on silicon substrates. The reaction yielded SiOₓ nanowires; these results are discussed in detail in Chapter 5. All the nanostructures were characterized by X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Photoluminescence Spectroscopy (PL), Raman Spectroscopy and Fourier Transform Infrared Spectroscopy (FTIR).
LIST OF ABBREVIATIONS

BSE: Backscattered Electrons

SE: Secondary Electrons

CVD: Chemical Vapor Deposition

EDS: Energy Dispersive X-ray Spectroscopy

FC: Field Cooling

FIB: Focused Ion Beam

FTIR: Fourier Transform Infrared Spectroscopy

HF: Hydrofluoric Acid

HFS: Heavy Fermion Systems

MOSFET: Metal Oxide Semiconductor Field Effect Transistor

SEM: Scanning Electron Microscopy

TEM: Transmission Electron Microscopy

XRD: X-ray Diffraction

OAG: Oxide Assisted Growth

PL: Photoluminescence

PVD: Physical Vapor Deposition
VS: Vapor Solid
VLS: Vapor Liquid Solid

sccm: standard cubic centimeters

SAED: Selected Area Electron Diffraction

SE: Secondary Electrons

SQUID: Superconducting Quantum Interference Device
LIST OF SYMBOLS

$\lambda$: Wavelength

$h$: Planck's Constant

$m$: Mass of an Electron

$v$: Speed of an Electron

$cm$: Centimeter

$\theta$: Theta

$\alpha$: Alpha

$\beta$: Beta

$nm$: Nanometer

Fe: Iron

Si: Silicon

Ar: Argon

$^\circ C$: Degrees Celsius

K: Kelvin

$T$: Temperature

$\chi$: Magnetic Susceptibility
\( \rho(T) \): Resistivity

\( \rho \): Density

\( E_g \): Band Gap

\( \sigma \): Conductivity

\( k_B \): Boltzmann Constant

\( \omega \): Frequency

1D: One Dimensional

\( \mu A \): Micro Amperes

V: Voltage

Z: Atomic Number
LIST OF PUBLICATIONS AND CONFERENCES ATTENDED

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2. S. Thabethe, B. W. Mwakikunga, C.J Arendse, Conversion of FeCl₃ into Fe-Si nano-noodles at high temperature for gas sensing applications, nanoafrica conference, University of the Free State (UFS), South Africa.


4. S. Thabethe, D.E. Motaung, C.J. Arendse, B.W. Mwakikunga and J. Wesley-Smith, Growth of FeSi nanowires by chemical vapour deposition, MICROSCOPY SOCIETY OF SOUTHERN AFRICA FIFTIETH ANNUAL CONFERENCE, University of Cape Town (UCT), South Africa.
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CHAPTER 1

1. LITERATURE REVIEW (FeSi)

1.1 INTRODUCTION

By mass the four most abundant elements in the Earth are iron, oxygen silicon and magnesium, which together account for approximately 93% of the Earth’s mass. Nickel, sulfur, calcium and aluminum make up another 6.5%. The remaining 0.5% or so of the Earth’s mass is made up of the other naturally occurring elements. The relative abundance of Fe and Si offer major advantage to shifting research to iron silicides. Transition metal silicides form an important group of transition metal compounds, which possess very interesting properties. Within the Fe: Si binary systems, there are five well known compounds most likely to be formed between the two elements; these include FeSi, FeSi$_2$, Fe$_5$Si$_3$, Fe$_3$Si and Fe$_2$Si. The FeSi$_2$ phase, which has two phases namely: $\alpha$-FeSi$_2$ (metallic) and $\beta$-FeSi$_2$ (semiconducting) has also received a lot of attention, particularly the semiconducting phase with a band gap of 0.8 eV [1.1]. The iron rich phases Fe$_5$Si$_3$, Fe$_3$Si and Fe$_2$Si have also been studied and they have ferromagnetic properties and display metallic behaviour [1.2-1.4]. In recent years it has been found that nanowires can be used for various devices. For this reason some iron silicide nanowires of FeSi, FeSi$_2$ (both $\alpha$ and $\beta$), Fe$_5$Si$_3$ and Fe$_3$Si have so far been reported for the potential use in silicon based electronics [1.5]. In this study we focus on
one phase, the cubic FeSi phase, with some unique properties such as a metal to insulator transition (MIT) at temperatures near 250 K, a narrow band gap of 0.1eV, behaves like a dirty metal at higher temperatures i.e. the resistivity is relatively low and the temperature coefficient of the resistivity is positive, also a highly enhanced paramagnet or nearly a ferromagnet at high temperatures and has been classified as a Kondo insulator. The cubic \( \varepsilon \)-FeSi phase and the \( \beta \)-FeSi\(_2\) phase, are the most stable of all the mentioned Fe: Si compounds at room temperature \[1.6-1.8\]. The aim of this chapter is to familiarize the reader with the electrical, optical and magnetic properties of FeSi.
1.2 Crystal Structure

Crystal systems are usually classified with Strukturbericht designation and a Pearson symbol; FeSi has a B20 crystal structure, meaning that it is classified under a group of diatomics with an equal number of each type of atom in the crystal. It belongs to space group 198 and has Pearson symbol P2$_1\overline{3}$, both describe that it is a cubic crystal system. In a unit cell, there are four atoms of Fe and four atoms of Si and it has a lattice constant of 4.49 Å.

![Figure 1.1: Simplified representation of the simple-cubic unit cell for the FeSi structure: Fe (shaded circles) and Si (open circles) [1.9]](image-url)
The model of the FeSi crystal structure as described by Mattheiss *et al* [1.9] is shown in Figure 1.1. The local coordination at the individual Fe and Si sites is explained in terms of a pairing type distortion of an underlying rocksalt structure in which the individual constituents are displaced along the [111] directions so as to change the rocksalt third neighbours (i.e. those along cube diagonals) into FeSi nearest neighbours. This displacement reduces the space group from \( Fm\overline{3}m(\overline{O}h) \) to \( P\overline{2}_{1}3T^{1} \) in such a way that the Bravais lattice is simple cubic, but the overall point symmetry is tetrahedral. Both the Fe and Si atoms are situated at the 4(a)-type sites in the simple-cubic unit cell, with position coordinates: \((u,u,u), \left( \frac{1}{2} + u, \frac{1}{2} - u, \bar{u} \right), \left( \bar{u}, \frac{1}{2} + u, \frac{1}{2} - u \right) \) and \( \left( \frac{1}{2} - u, \bar{u}, \frac{1}{2} + u \right) \).

Similar models of the crystal structure of FeSi have also been calculated and used by Sharif *et al* [1.10] and Kulatov *et al* [1.11] for band structure calculations using density functional theory (DFT) related methods.
1.3 Band Structure

The band structure of a material is very important in material science, because it is intimately related to its electrical and optical properties. Different band structure and band gap calculations have been presented by using local density approximation (LDA) and linear augmented plane wave method (LAPW). Mattheiss et al [1.9] were able to calculate the band gap of FeSi to a value of 0.11 eV, which agreed very well to the empirical value of 0.13 eV that was obtained by Jaccarino et al [1.12].

![LDA band structure of FeSi along high-symmetry directions of the whole Brillouin zone, respectively, the Fermi level is positioned 0 eV [1.13].](image)

**Figure 1.2:** LDA band structure of FeSi along high-symmetry directions of the whole Brillouin zone, respectively, the Fermi level is positioned 0 eV [1.13].
Figure 1.2 shows band structure calculations reported by Zhao et al [1.13], where they used the Ab-initio code, which is based on first principles pseudopotentials and plane waves in the framework of the density functional theory. Their results also affirmed that FeSi has an indirect band gap of 0.13 eV in LDA. In order to demonstrate the reliability of their computational method they calculated the band structure for the generalized gradient approximation (GGA). Although the GGA revealed a smaller band gap, it was observed that in both LDA and GGA computations, there was no intersection of the bands with the Fermi level, which clearly indicated that the material has semiconducting properties. The calculations performed agreed well with previous band structure calculations that have been reported [1.12, 1.13].

Researchers have a number of reasons for using computational methods and modelling of materials as it plays a crucial role in material science. Phonon dispersion curves can help in determining active optical and acoustic modes in materials. For example in determining whether the material has Raman active or infrared active modes, thus it helps in the interpretation of some optical and thermal measurements. These types of computations help the material scientist to have an idea of what is happening before going to the lab and lets them know what to expect.

We have also carried out functional theory simulations using GGA and LDA for the exchange and correlation functional, as implanted in the Cambridge Serial Total Energy Package (CASTEP) code. The band structure calculations were used to explain photoluminescence properties of FeSi nanostructures by Thabethe et al [1.14]. Further details will be discussed in Chapter 3.
1.4 Electrical Properties

One of the most interesting properties of the iron monosilicide (FeSi) phase is its unique transport properties. The fact that this material has a transition from semiconducting to metallic (see Figure 1.3) on its own provides more reason as to why it has been studied for many years. Electrical measurements of FeSi thin films synthesized by pulsed laser deposition for different laser energies have been reported by Witanachchi et al [1.15].

Figure 1.3: Temperature dependence of the resistance of FeSi films deposited with laser fluencies in the range of 1-5 J/cm² [1.15].
Near room temperature, the carrier transport occurs through the conducting silicon substrate, which is enabled by impurity assisted tunneling across the SiO$_2$/Si interface. The diffusion of multivalent Fe ions formed interface states facilitate the impurity assisted hopping of carriers. For temperatures below 250 K, the carriers become localized due to the interaction between the tunneling electrons and magnetic moment of the Fe ions at the interface, which causes the resistance to increase. Below the transition temperature the carrier transport resembles that of variable range hopping [1.15].

Other transport measurements were reported by Lukenheimer et al. [1.16], where they wanted to clarify the question of hopping conductivity in FeSi. They determined the ac conductivity of polycrystalline FeSi and found that at higher temperatures, the ac response of the samples changed from capacitive (semiconducting) to inductive (metallic) behaviour. At the metallic side no sign of hopping conductivity is found; i.e. the dominant charge carriers behave like band-like states and at low temperatures the ac response is governed by hopping of localized charge carriers.

The room temperature value of the resistivity of 140 $\mu\Omega$cm, reported by Hunt et al. [1.17], is consistent with the description of FeSi as a dirty metal at this temperature. Figure 1.4 shows the resistivity as a function of temperature.
When the temperature falls, there is a rise in the resistivity through three and a half orders of magnitude at the lowest measured temperature of 1.5 K. On a linear scale there is a shoulder in the data at $T \approx 120$ K and a tendency for saturation below 10 K in between. Although the resistivity rises very steeply, it is never the less not possible, over any extended range of temperature, to describe the data with a usual activated behaviour using the relationship between the conductivity and temperature of a semiconductor: $\sigma \propto \exp\left(\frac{E_g}{2k_B T}\right)$. Instead a fit of the expression of the form:

![Figure 1.4: The resistivity $\rho(T)$ of FeSi between 1.5 and 300 K [1.17].](image)
\( \sigma \propto \exp \left( \frac{T_0}{T} \right)^{1/4} \) seemed more appropriate for variable range hopping, which is a plausible explanation for the observed behaviour in this region. The inset shows the conductivity below 10 K fitted by the sum of a constant and cubic temperature contribution. In this range the conductivity is given by: \( \sigma = \sigma_0 + aT^3 \), where \( a \) is the temperature coefficient. This shows saturation of the resistivity at very low temperatures [1.17].

All transport properties of this material have led researchers to classify it under a class of materials known as Kondo insulators. They are closely related to heavy fermion systems (HFS), which are characterized by a strong hybridization of the band states with localized magnetic moments leading to high effective masses of the conduction electrons. However, unlike in normal metallic HFS the Kondo insulators exhibit semiconducting behaviour at low temperatures [1.15,1.6,1.17].
1.5 Optical Properties

Another way of determining properties of a material, such as estimating the band gap, is through the use of spectroscopic techniques. An optical investigation in the far and mid infrared frequency range done by Schlesinger et al [1.18] suggested that FeSi is a dirty metal at higher temperatures, while at low temperatures its optical conductivity resembled that of a semiconductor. Degiorgi [1.19] et al investigated the optical conductivity and reflectivity of FeSi as a function of temperature over a large frequency range, extending from the far infrared region up to the ultraviolet spectral region.

![Figure 1.5](image)

Figure 1.5: (a) Optical reflectivity of FeSi at 10, 120, 200 and 300 K and (b) corresponding optical conductivity[1.19].
Figure 1.5 shows the results of the reflectivity and optical conductivity for the FeSi single crystal. The optical conductivity ($\sigma(\omega)$) was obtained by applying a Kramers-Kronig Transformation to the measured optical reflectivity. Appropriate extrapolations were used above the highest frequency limit, while from the far-Infrared (FIR) down to zero frequency the reflectivity was extrapolated with the Hagen-Ruben's law.

The relevant features that were observed, characteristic of FeSi, are that the reflectivity changes from metallic behaviour at temperatures higher than 100 K to an insulating at temperatures below 40 K. This can also be observed in the optical conductivity $\sigma_1(\omega)$ plot, whose DC limit drops continuously as the temperature decreases and below 40 K is very small. Other reflectivity and optical conductivity measurements performed from the far infrared to the visible region that have been reported [1.20, 1.21, 1.22] agree very well with the above mentioned study. Like infrared reflectivity, electronic Raman scattering is a powerful tool for probing charge excitations in metals and semiconductors. Raman scattering is particularly useful in that it not only couples optically inactive excitations that are inaccessible to other spectroscopic methods, but it can also provide important excitation symmetry information. Nyhus et al [1.23] showed that the electronic Raman spectrum of FeSi single crystals is dominated by a number of optical phonons, including strong E symmetry modes at 180 and 315 cm$^{-1}$, an A symmetry mode at 219 cm$^{-1}$, and T symmetry (infrared active modes at 193, 260, 311, 436 and possibly 333 cm$^{-1}$ (see Figure 1.6). They suggested two alternative interpretations for the electronic continuum in FeSi by (i) collision-limited scattering of carriers within the narrow $d$ band that cuts the Fermi surface in FeSi.
The large energies associated with the peaks in the electronic continua of FeSi are consistent with infrared evidence for dirty-limit carrier scattering at room temperature. While isotropic scattering of carriers (expected in cubic FeSi) should have a spectral response that is independent of scattering geometry, the electronic continuum in FeSi is strongly polarization dependent, with large $E+T$ symmetry and a small $A$ symmetry contributions. They concluded that the electronic Raman continua involve interband transitions within the narrow manifold of non-bonding $d$ levels that span the Fermi energy.

**Figure 1.6:** Solid line: The 340 K $A+E+T$ symmetry Raman-scattering intensity, $S(\omega)$, in FeSi, showing phonons below 500 cm$^{-1}$ and a broad electronic continuum with a peak near $\Delta_0$. Dashed line: Raman scattering response function derived from the 340 K spectrum of FeSi. Inset: A comparison of the 340 and 15 K Raman-scattering response function for CoSi [1.23].
1.6 Magnetic Properties

As mentioned earlier, in the low temperature region, FeSi behaves like a narrow gap semiconductor, whereas at high temperatures it exhibits properties of a dirty metal. Its magnetic properties are no less unusual as reported by Mihalik et al [1.24]. The ground state of the pure stoichiometric compound is non-magnetic. On the other hand, two temperature regions, where the magnetic susceptibility $\chi(T)$, follows the Curie-Weiss law:

$$\chi(T) = \frac{C}{T - \theta}$$

(1.1)

Where $C$ is the Curie constant, $T$ is the absolute temperature and $\theta$ is correction term and has unit of temperature. $\chi(T)$ is small ($\sim 100$ K) but increases rapidly until it reaches a maximum at 500 K.
Hysteresis loop measurement revealed a ferromagnetic contribution. The ferromagnetic contribution is usually attributed to ferromagnetic Fe ions which are present if crystal growth starts from stoichiometric composition [1.24].

The unusual high temperature properties of FeSi including the band gap, $E_g$ and the magnetic susceptibility, $\chi(T)$ on the temperature $T$ can be explained by the strong dependence of the spin density fluctuations as reported [1.25]. On the other hand, the low temperature Curie-Weiss behaviour of $\chi(T)$ may have two different reasons.
The first is connected with the presence of residual magnetic impurities in FeSi due to the deviation from the exact stoichiometry. Actually up to 1% of Fe excess could be possible in the FeSi range of inhomogeneity. The second postulates the intra-site interaction between the electrons localized in the sense of Anderson, such intra-site correlations give rise to the Curie-type behaviour at temperature at $T \ll U$, where $U$ is the correlation energy. The Anderson localization has been suggested in different papers [1.26-1.28] to interpret the variable range hopping conductivity (VRH) and the low temperature optical properties.
1.7 FeSi Nanowires

1.7.1 Introduction

Nanometer scale structures represent an exciting, intellectually challenging and rapidly expanding area of research that crosses the borders between many areas of the physical sciences and also in the field of engineering. Nanostructures can be defined as systems in which at least one dimension is ≤ 100 nm; that is, reducing 1, 2, or 3 dimensions (D) of a bulk material to the nanometer scale produces nanometer thick 2D layers, 1D nanowires or 0D nanoclusters, respectively. Silicide nanowires with various properties have been attracting a lot of interest due to the following unique properties: excellent crystal quality, generally single crystal structure and ease of fabrication and self-assembly. The most common and favoured method for the synthesis of FeSi nanowires is by chemical vapor deposition (CVD)/chemical vapor transport (CVT). It has been found to be the most viable route and easiest option in this regard. In wet chemistry methods, it is difficult to find solvents that are free from oxygen and other impurities [1.29-1.31]. To date the production of FeSi nanowires has been very successful; a lot work is yet to be done on the possible applications of these nanostructures. Since FeSi nanowires exhibit the same metallic behaviour at room temperature, they can be used in room temperature sensing devices.
1.7.2 Growth Mechanisms

1.7.2.1 Vapor-Liquid-Solid (VLS)

Amongst all direct vapor-based methods, the VLS process is one the most successful for the production of nanowires. A typical VLS process (see Figure 1.8) begins with the dissolution of gaseous reactants into nanosized liquid droplets of the catalyst metal deposited on the substrate. This is followed by the nucleation and growth of single crystalline nanowires. The 1D growth is mainly induced and dictated by the liquid droplets, their sizes remain unchanged during the entire process of nanowire growth. This model for explaining this growth mechanism was proposed by Wagner et al [1.32] for silicon nanowires synthesized using Au as a catalyst. They used a vapor-phase precursor SiCl$_4$, a liquid alloying as the mediating material (AuSi) and finally a solid one dimensional crystal which forms (Si nanowire).
The underlying basic principle is that an ideal liquid surface traps all the Si source atoms from thrusting outwards, while the solid surface of Si rejects all Si source atoms if the temperature is sufficiently high, the end result will be the nanowire growing from the substrate.

**Figure 1.8:** A representation of the VLS growth mechanism. (a) Metal seed particles are formed and/or deposited onto a substrate. (b) The sample is heated to a desired growth temperature and growth materials introduced, whichever alloy with the particle. (c) When an appropriate supersaturation of groth material is achieved, nucleation occurs at the particle-crystal interface. (d) Nanowire growth occurs at the particle-wire interface. [1.32].
1.7.2.2 Vapor-Solid (VS)

Instead of using metal catalysts, the vapor-solid or self-catalytic growth mechanism has been used mostly in the synthesis of metal oxide and some semiconductor nanomaterials. It is mainly referred to as the self-catalytic method because nanostructures grow directly from the vapor phases (see Figure 1.9). Another formation mechanism of 1D nanostructures is what is known as oxide assisted growth (OAG) of nanowires in which in most cases a thin oxide layer is formed around the semiconductor core [1.33,1.35].

Figure 1.9: A representation of the VS growth mechanism [1.32].
The oxide assisted growth method offers one major advantage compared to the VLS method in that it does not require any metal catalyst and thus eliminating metal contaminations on the nanostructures which can be detrimental in device applications [1.36, 1.37].

1.7.3 Properties of FeSi nanowires

1.7.3.1 Electrical properties of FeSi nanowires

In order to investigate the transport properties of single FeSi nanowires, Schmitt et al [1.38] fabricated a two-terminal device using a large scale statistical process with standard photolithography, followed by an acid etch in hydrofluoric acid (HF) to remove the native oxide layer formed on the surface of the nanowires and then the evaporation of Ti/Au metal films as contacts at the ends of the nanowires. The measurements were carried out at room temperature and as expected, they showed a linear current ($I_{sd}$) versus voltage ($V_{sd}$) relationship (see Figure 1.10) and thus confirming the metallic behaviour of FeSi at that temperature. Also, a value of the resistivity of 210 $\mu\Omega$cm was observed, which was found to be equal in magnitude to that of the bulk material.
They found that the current passing through each FeSi nanowire device of 20-50 nm diameter at a source-drain voltage of 1V was often about 100 $\mu$A, which was a remarkably high current that is indicative of the single crystal high quality of the nanowires. However, when an even higher source-drain voltage was applied to these devices, they eventually break down at currents generally above 200 $\mu$A and voltages between 1.5 and 4 V. Melting was attributed to be the main cause of the failure because the middle of the nanowire has the highest temperature under resistive self-heating.

**Figure 1.10:** Room temperature transport properties of FeSi NWs in two terminal devices [1.38].
Similar electrical properties of single FeSi nanowires were also observed by Hung et al [1.39], whereby the used a four terminal method instead of two at room temperature. Their measured value of the resistivity of 2650 $\mu \Omega \text{cm}$ was one order higher than the values reported by previous works. The much higher value of the resistivity was attributed to the surface scattering effect and rough interface induced in the nanodevice fabrication process (removal of surface silicon oxide) or deposition of the platinum contacts using focused ion beam (FIB). This increase was also attributed to contact resistance. These are some of the challenges facing researchers in fabricating nanowire based devices. The transition from semiconducting to metallic at higher temperatures is one interesting property of this material which cannot be avoided. However temperature dependence transport measurements on single FeSi nanowires from low to higher temperatures as has already been done for their bulk counterparts are yet to be reported.
1.7.3.2 Magnetic Properties of FeSi nanowires

Hung *et al* [1.39] investigated the magnetic properties of FeSi nanowires by using a superconducting quantum interference device magnetometer (SQUID). Temperature-dependent field cooling (FC) and zero field cooling (ZFC) magnetization measurements at various applied field directions were performed on the nanowires as shown in Figure 1.11.

![Figure 1.11: Magnetic properties of the as grown FeSi nanowires, M-T curves of the as-synthesized FeSi nanowires, showing the typical ferromagnetic behaviour with a Curie temperature above room temperature [1.39].](image-url)
Magnetization versus Temperature of the as synthesized nanowires shows typical ferromagnetic behaviour with a Curie temperature above room temperature. The FC and ZFC curves of the FeSi nanowires do not overlap at temperatures lower than room temperature, indicating the existence of large anisotropic in FeSi nanowire system. The specific room temperature ferromagnetic properties in FeSi nanowires can be accounted for by the interaction of charge carriers (electrons or holes) with localized dangling bond spins, which is significant when the system is reduced to the nanoscale.

1.8 Other FeSi Nanostructures

In the process of synthesizing nanostructures, it is often common for other nanostructure morphologies to be formed during the reaction as a result of different experimental conditions. Szczech et al [1.40] have reported on epitaxially hyper-branched nanowires, which have the potential to improve performance in many applications such as solar energy conversion. Other unique structures such as nanocombs, nanorods, nanoflowers and crystal clusters (see Figure 1.12) were also observed at temperatures ranging from 800 to 900 °C.
As in most cases using chemical vapor transport (CVT), because there might be non-equilibrium conditions, it makes it very difficult to predict the stoichiometry of the deposited material under such conditions. The other important factors which play a crucial role in chemical vapor transport synthesis of nanostructures are the choice of the precursor and substrate temperature. In most cases these two factors result in other phases in the Fe-Si diagram to be formed. CVT, despite some of its setbacks seems to be the most common and successful method for the synthesis of nanostructures.

Figure 1.12 Representative SEM images of unique morphologies observed under different substrate temperature conditions (a) Hyper-branched nanowires; (b) unbranched nanowires; (c) nanorods; (d) nanocombs; (e) nanoflowers; (f) crystal clusters [1.40].
1.9 Fe-Si Phase Diagram

The phase diagram of Fe-Si is shown in Figure 1.13; the formation of the FeSi phase occurs at temperatures around 1200°C.

**Figure 1.13:** Representation of the Fe-Si phase diagram [1.41].
1.10 Objectives

The main objectives of this project were to obtain stoichiometric FeSi nanowires by using the chemical vapor deposition (CVD) method and comparing nanostructure growth under different conditions such as substrate temperature, self-catalyzed growth and metal catalyzed growth. The following methods/techniques: Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-ray Diffraction (XRD), Photoluminescence spectroscopy (PL), Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy were used to characterize and study optical and structural properties of the nanostructures.
1.11 Thesis outline

Chapter 1  Introduction and Literature Review

This chapter introduces some of the key properties of FeSi as well as work already done in synthesizing FeSi nanowires and their possible applications.

Chapter 2  Procedures and Characterization Techniques

This particular chapter is dedicated to the characterization techniques used in this study and explains the theory behind every technique.

Chapter 3  Visible and IR photoluminescence of \( \varepsilon \)-FeSi/Si core-shell nano-fibres produced by vapor transport

This chapter explains the photoluminescence properties of FeSi nanofibers. This work has been published in the Journal of Luminescence.


Chapter 4  Synthesis and Characterization of FeSi nanowires

This chapter focuses on the synthesis of FeSi nanowires. Structural and optical properties of the nanowires are also discussed.
Chapter 5  Synthesis and Characterization of amorphous SiO\textsubscript{x} nanowires

This chapter discusses the formation of SiO\textsubscript{x} nanowires which were formed in an attempt to grow FeSi nanowires using a metal catalyst.

Chapter 6  Summary and Future Plans

This chapter gives an overview of the work done in this project.
1.11 References


2. Procedures and Characterization Techniques

In this chapter all the characterization techniques that have been employed in the current research endeavor and their respective data acquisition theories are reviewed. It was an important chapter for the researcher to include in order to ensure sound interpretation of results from these instruments. This exercise is also important, so that the reader understands the characterization results and outcomes. Many errors in conclusions about observations emanate from the lack of understanding of how characterization instruments are designed to work.
2.1 Characterization Techniques

2.1.1 Scanning Electron Microscopy (SEM)

2.1.1.1 Introduction

Material particles such as electrons possess a wavelike character, inspired by Einstein's photon description of electromagnetic radiation. Louis De Broglie proposed that their wavelength is given by

\[ \lambda = \frac{h}{mv} \]  

(2.1)

Where \( h \) is the Planck constant; \( m \) and \( v \) represent the mass and speed of the electron, respectively. Scanning electron microscopy is a powerful and popular technique for imaging the surfaces of almost any material with a resolution down to about 1 nm. The image resolution offered by SEM depends not only on the property of the electron probe, but also on the interaction of the electron probe with the specimen. The interaction of an incident electron beam with the specimen produces secondary electrons, with energies typically smaller than 50 eV. The emission efficiency of which sensitively depends on surface geometry, surface chemical characteristics and bulk chemical composition. The high resolution capability afforded by SEM makes it convenient for probing nano-materials of which the structural features on the nanoscale are critical to their properties and functionalities [2.1-2.2].
2.1.1.2 Theory

When accelerated electrons enter a solid they are scattered both elastically (by electrostatic interaction with nuclei) and in-elastically (by interaction with atomic electrons). Most of this interaction between the solid and electrons is forward scattering, which implies deflection angles less than $90^\circ$. However, a small fraction of the incident electrons are elastically backscattered ($\theta<90^\circ$) with a small fractional loss of energy. Due to their high kinetic energy, these back-scattered electrons have a high probability of leaving the specimen and re-entering the surrounding vacuum, in which they can be collected as a backscattered-electron (BSE) signal. Inelastic scattering involves relatively small scattering angles and so contributes little to the backscattered signal. However, it reduces the kinetic energy of the primary electrons until they are eventually brought to rest and absorbed into the specimen. The depth (below the surface) at which this occurs is called the penetration depth or electron range. The volume of the sample containing most of the scattered electrons is called the interaction volume and it is represented as pear-shaped volume in cross section, because scattering causes the beam to spread laterally as the electrons penetrate the specimen and gradually lose energy.

The electron range $R$ for electrons of incident energy $E_0$ is given by the following formula:

$$\rho R \approx a E_0^\beta$$  \hspace{1cm} (2.2)
Where $a$ and $r$ are constants and $\rho$ is the density of the specimen. Expressing the range as a mass-thickness $\rho R$ makes the coefficient $a$ roughly independent of atomic number $Z$. This implies that the distance $R$ itself decreases with $Z$ as the density of the specimen tend to increase with atomic number. This strong $Z$-dependence arises mainly because backscattering depletes the number of electrons moving forward into the specimen. The interaction volume is therefore smaller for materials of higher atomic number [2.2].

**Figure 2.1**: Dependence of the interaction volume and penetration depth as a function of incident energy $E_0$ and atomic number $Z$ of the incident electrons [2.2].
2.1.1.3 Data Analysis

In this study SEM was used to study the surface morphology of the nanostructures and also to estimate the particle size. Elemental composition of the nanowires was determined using energy dispersive x-ray spectroscopy (EDS) in TEM in section 2.2.2. Nanowire diameters were also measured using Image J software on the final images.
2.1.1.4 Setup

A stream of monochromatic electrons generated by an electron gun is condensed by the first condenser lens to both form the beam and limit the amount of current as well as in conjunction with the condenser aperture, to eliminate the high-angle electrons from the beam.

Figure 2.2: Typical setup of a SEM [2.1]
The second condenser lens focuses the electrons into a thin, tight, coherent beam and an objective aperture is used to further eliminate high-angle electrons from the beam. A set of coils is used to scan the beam in a grid fashion. The objective lens focuses the scanning beam onto the desired specimen, one point at a time. Interaction between the electron beam and the sample generates back scattered electrons (BSE), X-rays, secondary electrons (SE) and Auger electrons in a thick or bulk sample. These various electrons are detected and the signal detected contains information about the specimen under investigation. BSE is more sensitive to heavier elements than SE. The X-ray radiation can be detected in a technique called energy dispersive x-ray spectroscopy (EDS) that can be used to identify specific elements [2,2].
SEM imaging was done using an Auriga Cobra FIB FESEM at the Council for Scientific and Industrial Research (CSIR), South Africa. The accelerating voltage used when imaging ranged from 2 to 30 kV.

**Figure 2.3:** Electron-Specimen interaction in a SEM [2.2].
2.1.2 Transmission Electron Microscopy (TEM)

2.1.2.1 Introduction

The main difference between SEM and TEM is that TEM can detect transmitted electrons (see Figure 2.4). Transmission electron microscopy (TEM) uses high energy electrons to penetrate through a thin sample usually less than 100 nm. This offers increased spatial resolution in imaging as well as diffraction from small sample volumes. A modern TEM has the capability to directly image atoms in crystalline specimens at resolutions close to 0.1 nm, smaller than interatomic distance. An electron beam can also be focused to a diameter smaller than 0.3 nm, allowing quantitative chemical analysis from a single nanocrystal. This type of analysis is extremely important for characterizing materials at a length scale from atoms to hundreds of nanometers. TEM can be used to characterize nanomaterials to gain information about particle size, shape, crystallinity and inter-particle interaction [2.2].
Figure 2.4 Electron-Specimen interaction in a TEM [2.2].
2.1.2.2 Theory

An explanation of the basic theory of electron diffraction from a specimen in TEM, the appearance of lattice fringes on TEM images and EDS are provided and this theory is discussed as in reference [2.2]. One of the most important functions in a TEM is that it can be used to determine the crystal structure for a crystalline material. The high energy electrons used in a transmission electron microscope can penetrate through many planes of atoms and are diffracted within the crystalline regions of a solid, just like x-rays. However, their wavelength ($\approx 0.004 \text{ nm for } E_0 \approx 100 \text{ keV}$) is far below a typical atomic plane spacing (0.3 nm) so the Bragg angles are small, as required by Bragg’s law for when the wavelength ($\lambda$) of the x-rays is smaller than the distance between the atomic planes ($d$) as in section 2.2.3. Using small angle approximation Bragg’s law can be rewritten as:

$$\lambda \approx 2\theta_B d = \alpha d$$  \hspace{1cm} (2.3)

Where $\theta = 2\theta_B$ is the angle of scattering (deflection angle) of the electron resulting from the diffraction process.
Figure 2.5: (a) Geometry of x-ray or fast-electron from atomic planes, which are shown as parallel dashed lines; R is the radius of the diffraction ring at the recording plane. (b) Schematic cross section through a cubic lattice with an atom at each lattice point. The diagonal lines represent two sets of atomic planes whose spacings are $d_1$ and $d_2$ [2.2]
In addition to a diffraction (or scattering) contrast, features such as lattice fringes in some TEM images depend on the phase of the electron waves at the exit plane of the specimen. Although this phase cannot be measured directly, it gives rise to interference between electron waves that have passed through different regions of the specimen. Such electrons are brought together when a TEM image is defocused by changing the objective lens current slightly. Figure 2.6 shows a representation of a crystalline specimen with a single layer of atoms of equal spacing $d$, irradiated by a parallel electron beam with a uniform current density. The nuclei of the atoms elastically scatter the electrons through angles that depend inversely on the impact parameter $b$ of each electron. If the objective lens is focused on the atom plane and all the electrons are collected to form the image, the uniform illumination will ensure that the image contrast is zero. In the overfocus condition, the TEM will image a plane below the specimen, where the electrons are more numerous at positions vertically below the atom positions, causing the atoms to appear bright in the final image. In the underfocus condition, the TEM will image just above the specimen, the electrons appear to come from positions halfway between the atoms, and the image will show atoms that appear dark relative to their surroundings. The optimum amount of defocus $\Delta z$ can be estimated by considering a close collision with impact parameter $b \ll d$. Geometry of the right angled triangle in Figure 2.7 gives:

$$\Delta z = \frac{d - 2b}{2 \tan \theta} \approx \frac{d}{2\theta}$$

If the scattering angle $\theta$ is small. But for atoms of uniform spacing $d$, the scattering angle should satisfy Bragg law, therefore equation 2.3 implies $\theta = \lambda / d$ and
The chemical composition of the nanowires was determined by using energy dispersive x-ray spectroscopy (EDS). When an incident electron enters a TEM or SEM specimen, it has a small probability of being scattered inelastically by an inner shell electron causing it to undergo a transition to a higher energy orbit and leaving the atom with an electron hole in its inner shell. The scattering atom remains in this excited state for only a very brief period of time, one of the other atomic electrons fills the inner shell electron

\[ \Delta z \approx \frac{d}{2\theta} \approx \frac{d^2}{2\lambda} \] (2.4)

**Figure 2.6:** Equally spaced atomic nuclei that are elastically scattering the electrons within a broad incident beam [2.2].
hole by making a downward transition from a higher energy level. In this de-excitation process, energy can be released in the form of a photon whose energy is given by:

$$ E = hf \quad (2.5) $$

where $h$ is the Planck constant and $f$ is the frequency of the electromagnetic wave.

**Figure 2.7**: Bohr model of a carbon atom visualized in terms of the (a) electron orbits and (b) the equivalent energy levels [2.2].

In Figure 2.7 the orbits are described as electron shells and are designated as $K(n = 1), L(n = 2), M(n = 3)$ and so forth. The dashed arrows show a possible scenario for x-ray emission: a $K$-shell electron is excited to the empty $M$-shell and an $L$-shell electron fill the $K$-shell vacancy in the de-excitation process.
2.1.2.3 Data Analysis

Nanowire diameter sizes including the thickness of the oxide layer that formed around the nanowires were measured using Image J software on the final images, the selected area diffraction (SAED) of the nanowires showed that they have cubic crystal structure; this was proven by the fact that each spot was surrounded by four nearest spots. Indexing the SAED pattern could not be achieved as the lattice fringes on the nanowires are one dimensional and the resulting fast Fourier transform is a straight line of bright spots instead of a two dimensional one. The observed lattice fringes on the nanowires provided information about the growth direction of the nanowires. A line profile between bright and dark fringes was done to determine the spacing between the lattice fringes as they represent ordered planes of atoms. A value of 0.134 nm was obtained for most nanowires which corresponds to the d-spacing in the (110) plane for FeSi. The chemical composition of the nanowires was that of Fe and Si, the height of the peaks is the same, showing a 1:1 ratio of both elements present in the nanowires. The chemical composition of the layer showed a big peak for silicon and the oxygen peak could not be observed as a result of overlapping spectra.
2.1.2.4 Setup

Similar to SEM, a stream of monochromatic electrons produced by an electron gun is focused into a thin, coherent beam by two condenser lenses. The electron beam is restricted by the condenser aperture to remove high angle electrons before it reaches the specimen. It is thus important in this case that the specimen is thin enough to allow some electrons to transmit through the sample.

Figure 2.8: Typical setup of a TEM [2.1].
TEM imaging was done using a JEOL-JEM 2100 at the CSIR, South Africa at an accelerating voltage of 200 kV.

### 2.1.3 X-ray Diffraction (XRD)

#### 2.1.3.1 Introduction

Following the discovery of X-rays in 1895 by Wilhelm Conrad Rontgen, Max von Laue, after discussions with P.P Ewald, realized that crystals may act as diffraction gratings for X-rays. X-rays are an electromagnetic radiation of small wavelengths. Crystals are three-dimensional arrays of atoms or molecules with fixed positions that consist of a basic shape that is repeated in space by three non-coplanar vectors to produce the crystal. When a crystal containing regular repeating arrays of atoms is irradiated by a mono-chromatic X-ray beam, it generates a unique fingerprint in the form of diffraction peaks. By this diffraction process, a diffractogram is used to identify crystalline components of a sample.
2.1.3.2 Theory

X-ray diffraction was used to identify the crystal structure of the nanowires. The relevant theory behind X-ray diffraction is provided as in reference [2.3]. Consider a row or one dimensional lattice of scattering points and a parallel beam of monochromatic X-rays directed perpendicular to the row as shown in Figure 2.9. The rays are scattered at an angle $\alpha$, which is the acute angle between the row of points and the scattered beam and detected at some distance from the row. The wavelets are parallel and in phase at $FI$, but after being scattered, they travel different path length, one takes path $IJ$ while the other takes path $FG$. $IK$ is drawn perpendicular to FG from $I$ and it is parallel to $JG$. Therefore the path lengths of the scattered wavelets differ by $FK$. This distance must be an integral number of wavelengths since the waves are in phase. Thus $FK = n\lambda$, where $n$ is an integer. But $\cos \alpha = \frac{FK}{a}$ and therefore

$$n\lambda = a \cos \alpha$$

(2.6)
The actual meaning of equation (2.6) is that diffraction from a one dimensional lattice will occur at all angles $\alpha$, whose cosines are $n\lambda/a$ and $a$ is the distance separating the points. But in general a case of diffraction from a row of points, the incident beam will not be perpendicular to the row as shown in Figure 2.10.
The path length difference between the two wavelets is $OM - FK$ and the condition for diffraction is

$$n\lambda = a(\cos\alpha - \cos\alpha_0)$$

since

$$\cos\alpha_0 = \frac{OM}{a}$$

$$\cos\alpha = \frac{FK}{a}$$

If we now consider diffraction from a two-dimensional array of points in which additional rows of points identical to the first are placed at distances $b$ apart.
A series of cones will form coaxial patterns with every row of points. Equation (2.7) will hold for cones forming along the $a$ direction and so a similar equation is required for direction $b$. The conditions necessary for diffraction are:

$$m_1 \lambda = a(\cos \alpha - \cos \alpha_0) \quad (2.8a)$$

$$m_2 \lambda = b(\cos \beta - \cos \beta_0) \quad (2.8b)$$

$\alpha_0$ and $\beta_0$ are the angles the incident beam makes with the $a$ and $b$ directions and $\alpha$ and $\beta$ are the same angles for the diffracted beam, respectively. Any point in the lattice is part of both $a$ and $b$ rows and has sets of two coaxial cones given by equations (2.8a) and (2.8b) and as shown along directions $OA$ and $OB$ in Figure 2.11.
Figure 2.11: Cones of reflection in two dimensions [2.3].
In three dimensions, three sets of cones, coaxial with $a$, $b$ and $c$, respectively need to be considered. A third equation is now required so that:

$$m_1 \lambda = a(\cos \alpha - \cos \alpha_0) \quad (2.8a)$$
$$m_2 \lambda = b(\cos \beta - \cos \beta_0) \quad (2.8b)$$
$$m_3 \lambda = c(\cos \gamma - \cos \gamma_0) \quad (2.8c)$$

The condition for constructive interference or diffraction is that these three equations known as the Laue equations, be simultaneously satisfied.

Bragg’s law of diffraction, developed by father and son, William Henry Bragg and William Lawrence Bragg is a simplified version of the three dimensional theory developed by Laue by considering the diffraction as being reflected by sets of parallel planes of atoms. The condition for diffraction from a set of parallel planes of interlayer spacing $d$ is given by

$$n\lambda = 2d \sin \theta \quad (2.9)$$

Where $\theta$ is the angle of incidence of the X-rays to the planes and $\lambda$ is the X-rays wavelength.
When the wavelets of the X-ray beam leave the source, all the wavelets are in phase. As the wavelets enter the crystal they travel longer distances than the wavelet reflected from the surface. These distances are dependent on the interlayer spacing, \( d \). The wavelets are in phase at the line \( BJL \) drawn parallel to \( ADG \). The path length difference between the wavelets ABC and DEF is \( JE + EK \) and for the wavelet GHI, \( LH + HM \). The condition for diffraction is that the wavelets be in phase at BKM. This requires that the distance \( JE + EK = n\lambda \), that is, the path difference is an integral number of wavelengths.

\[
\begin{align*}
\sin \theta &= \frac{JE}{BE} \text{ also } \sin \theta = \frac{EK}{BE} \\
\text{Therefore } 2\sin \theta &= \frac{JE + EK}{BE} \\
BE &= d \\
2\sin \theta &= \frac{n\lambda}{d}
\end{align*}
\]

Figure 2.12 Illustration of Bragg’s reflection from a set of parallel planes [2.3].
2.1.3.3 Data analysis

The XRD results were compared to data for $\varepsilon$-FeSi from the Inorganic Crystal Structure Database (ICSD) with file number: ICSD PDF-01-086-0795. Crystallite sizes were calculated using the Williamson-Hall and Scherrer equations

2.1.3.3. (a) The Scherrer method

In 1918, P. Scherrer showed that, when parallel monochromatic radiation falls on an oriented mass of crystals, the diffracted beam is broadened when the particle size is small. By an approximation, he obtained an expression for the half-value breadth $B$ of the diffracted beam in the form:

$$B = K \lambda / \left( L \cos \frac{\chi}{2} \right)$$

(2.10)

In which $\lambda$ is the wavelength of the incident x-rays, $L$, the linear dimension of the particle, $\frac{\chi}{2}$ the Bragg angle and $K$ a numerical constant for which he obtained the value $2(\ln(2/\pi)^{1/2} = 0.93$ \text{[2.4]}.$]
2.1.3.3. (b) Williamson Hall method

This method for estimating crystallite size was developed by G.K Williamson and his student W.H Hall. It relies on the principle that the approximate formulae for size broadening $\beta_L$, and strain broadening, $\beta_s$, vary quite differently with respect to the Bragg angle, $\theta$. Broadening is produced by either lattice strains alone, or by lattice strains and small particle size simultaneously. If the integral breadth of the strain distribution is $\varepsilon$ the corresponding spectral integral line breadth $\beta_s$ due to strain is

$$\beta_s = 2\varepsilon \tan \theta$$  \hspace{1cm} (2.11)

Particle size broadening obeys the relation

$$\beta_L = \frac{\lambda}{L \cos \theta}$$  \hspace{1cm} (2.12)

where $\lambda$ is the X-ray wavelength and $L$ is a mean linear dimension of the particle. In general, considering both the strain and size components is given by

$$\beta = \beta_s + \beta_L = 2\varepsilon \tan \theta + \frac{\lambda}{L \cos \theta}$$  \hspace{1cm} (2.13)

The breadth is a linear function of $\tan \theta$ for any reflection (hkl) irrespective of the nature of the broadening [2.5].
2.1.3.4 Setup

X-rays are produced by the collision of high velocity electrons with a stationary or rotating metallic target. In practice, the metallic target is made of chromium (Cr), cobalt (Co), Copper (Cu) or Molybdenum (Mo). These metals produce X-rays in the 4-21 keV range while providing heat conduction and corrosion resistance. Most X-ray diffractometers are configured according to the Bragg-Brentano geometry. A combination of two or more angular movements of the goniometer arms attached to various components, namely: X-ray tube, specimen stage and the detector result in the Bragg condition producing the diffraction pattern.

Figure 2.13: Typical setup of an X-ray Diffractometer.
The common combinations are (1) θ-θ where both the X-ray tube and the detector synchronously move to a θ degree while the specimen stage is stationary and (2) θ-2θ, where the x-ray tube is stationary, specimen stage and the detector synchronously move in the angular ratio 1:2. X-ray diffraction was done using a PANalytical X'Pert Pro with a Cu Kα radiation with a wavelength of 0.154 nm was used as the X-ray source, operating voltage and current of 45 kV and 40 mA respectively. The spectra were measured from 2θ=5° to 2θ=70° at room temperature.
2.1.4 Photoluminescence Spectroscopy

2.1.4.1 Introduction

Optical spectroscopic techniques are widely used in the study of optical properties of different materials including nano-materials. At the fundamental level, the principle underlying photoluminescence (PL) spectroscopy is the measurement of light absorption due to electronic transitions. The electronic transition involved in a PL measurement is from a higher energy level or state to a lower energy level. Electrons are excited by fixed excitation energy from the valence band and are then ejected to the conduction band, when they return from their excited states, they release photons. This technique can help in estimating the band gap of a material [2.6-2.10].

![Schematic diagram of electronic transitions in PL.](image)

**Figure 2.14:** Schematic diagram of electronic transitions in PL.
2.1.4.2 Theory

Photoluminescence spectroscopy involves the electronic transition from a higher energy level to a lower energy level, which may cause the material to emit light. Energy is emitted or absorbed when an electron moves from a higher orbit $n$ to a lower one, or vice versa (where $n = 1, 2, 3, ...$). The energy of the electron can be shown by classical mechanics to be

$$E_n = -\frac{\mu e^4}{8h^2\varepsilon_0^2 \frac{1}{n^2}}$$  \hspace{1cm} (2.14)

Where $\mu$ equals to $m_em_p/(m_e + m_p)$, is the reduced mass of the system of electron $e$ plus proton $p$, $e$ is the electronic charge and $\varepsilon_0$ the permittivity of free space. The energy levels are discrete below $n = \infty$ but continuous above it since the electron can be ejected with any amount of energy. When the electron transfers from a lower $n''$ to an upper $n'$ orbit, the energy $\Delta E$ required for this is from equation 2.15.

$$\Delta E = \frac{\mu e^4}{8h^2\varepsilon_0^2 \left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)}$$  \hspace{1cm} (2.15)

Or since $\Delta E = hv$, we have in terms of frequency

$$\nu = \frac{\mu e^4}{8h^3\varepsilon_0^2 \left(\frac{1}{n''^2} - \frac{1}{n'^2}\right)}$$  \hspace{1cm} (2.16)
2.1.4.3 Data Analysis

When electrons are excited from a filled valence band to higher energy level conduction band, the de-excited electrons from the conduction to the valence band should give an estimate of the band gap of the material. The wavelength at which the material emits is directly linked to the band gap of the material. In nanomaterials, there are unavoidably trap states caused by defects or surface states in the band gap for a semiconductor or insulator material, therefore Photoluminescence spectroscopy is a useful tool for probing trap states besides the intrinsic electronic band structure. Photoluminescence features, observed between the visible and ultraviolet region were explained by calculated band structures of FeSi and were attributed to intraband transitions because the material is expected to emit in the far infrared region taking into account the value of its band gap
2.1.4.4 Setup

Basically, in a typical PL measurement, a specific wavelength of light is selected from a white light source by a monochromators and directed at the sample of interest. Light emitted from the sample is collected through lenses, dispersed by another monochromator and detected by a photo detector. The spectrum is displayed in terms of intensity of emitted PL light as a function of the wavelength of the emitted light.

Figure 2.15: Essentials of a luminescence experiment. The sample is irradiated at one wavelength and emission is observed over a range of wavelengths. The excitation monochromator selects the excitation wavelength and the emission monochromator selects one wavelength at a time to observe.
The PL spectra were obtained using a Jobin Yvon Nanolog FL3-22 at the CSIR, South Africa, with a double excitation monochromator and detects emission in the UV-VIS-NIR. The excitation wavelengths used were 300 and 330 nm.

2.1.5 Fourier Transform Infrared Spectroscopy (FTIR)

2.2.5.1 Introduction

Infrared spectroscopy is one of the most important analytical techniques available to today’s scientists. One of the great advantages of infrared spectroscopy is that virtually any sample in virtually any state can be studied. Liquids, solutions, pastes, powders, films fibres, gases and surfaces can all be examined with a judicious choice of sampling technique. Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule [2.11,2.12].
2.1.5.2 Theory

All light (including infrared) is classified as electromagnetic radiation and consists of alternating electric and magnetic fields and is described classically by a continuous sinusoidal wave like motion of the electric and magnetic fields. For IR and Raman spectroscopy, only the electric field component is considered and the magnetic field is neglected. The important parameters are the wavelength ($\lambda$, length of one wave), frequency ($\nu$), number of cycles per unit time and wavenumbers ($\tilde{\nu}$, number of waves per unit length) and are related to one another by the following expression:

\[
\tilde{\nu} = \frac{\nu}{c/n} = \frac{1}{\lambda}
\] (2.17)

Where $c$ is the speed of light and $n$ the refractive index of the medium it is passing through. In quantum theory, radiation is emitted from a source in discrete units called photons where the photon frequency, $\nu$, and photon energy, $E_p$

\[
E_p = h \nu
\] (2.18)

Where $h$ is Planck’s constant. Process of change, including those of vibration and rotation associated with infrared spectroscopy, can be represented in terms of quantized discrete energy levels $E_0, E_1, E_2$, etc.

The molecule absorbs energy from the IR source at each vibrational transition. The intensity of IR absorption is governed by the Beer-Lambert law:

\[
I = I_0 e^{-\alpha d}
\] (2.19)
Where, $I$ and $I_0$ denote the intensities of the incident and transmitted beams, respectively, $\varepsilon$ is the molecular absorption coefficient, and $c$ and $d$ are the concentration of the sample and the cell length, respectively. In IR spectroscopy it is customary to plot the percentage transmission, $T$, versus wave number:

$$T(\%) = \frac{I}{I_0} \times 100 \quad (2.20)$$

$T(\%)$ is not proportional to $c$. For quantitative analysis, the absorbance, $A$, is defined as:

$$A = \log \frac{I_0}{I} = \varepsilon cd \quad (2.21)$$

### 2.1.5.3 Data Analysis

Transmittance of the FeSi powder was measured to investigate the absorption infrared radiation at specific wave numbers as it passes through the sample. Observed absorption peaks were related to bending vibrations, stretching mode phonons and the band structure results.
2.1.5.4 Setup

Fourier-transform infrared spectroscopy (FTIR) is based on the idea of interference of radiation between two beams to produce an interferogram. An interferogram is a signal produced as a function of the change of the pathlength between the two beams. The basic components of an FTIR spectrometer are shown in figure 2.16. The radiation emerging from the source is passed through an interferometer to the sample before reaching the detector. Upon amplification of the signal, in which high-frequency contributions have been eliminated by a filter, the data is converted to digital form by an analog-to-digital converter and transferred to the computer for Fourier-transformation.

**Figure 2.16:** Basic components of an FTIR spectrometer.
FTIR spectra were obtained using a Perkin Elmer Spectrum 100 FTR spectrometer at the CSIR, South Africa.

**2.1.6 Raman Spectroscopy**

**2.1.6.1 Introduction**

In 1928, when Sir Chandreska Venkata Raman discovered the phenomenon that today bears his name, only crude instrumentation was available. He used sunlight as the source and a telescope as the collector and the detector was his eyes. That such a feeble phenomenon as the Raman scattering was detected was indeed remarkable. Raman and infrared spectroscopy are complementary techniques and usually both are required to completely measure the vibrational modes of a molecule. Infrared and Raman Spectroscopy involve the study of the interaction of radiation with molecular vibrations but differs in the manner in which photon energy is transferred to the molecule by changing its vibrational state. IR spectroscopy measures transitions between molecular vibrational levels as a result of the absorption of IR radiation. This interaction between light and matter is a resonance condition where the electric dipole mediated transition between vibrational energy levels. Raman spectroscopy is a two-photon inelastic scattering event. Here, the incident photon is of much greater energy than the vibrational quantum energy and loses part of its energy to the molecular vibration with the remaining energy scattered as a photon with reduced frequency. In the case of Raman spectroscopy, the interaction between light and matter is an off resonance condition involving the Raman polarizability of the molecule [2.12, 2.13].
2.1.6.2 Theory

In Raman spectroscopy the vibrational frequency $\nu_m$ is measured as a shift from the incident beam frequency $\nu_0$. According to classical theory, Raman scattering can be explained as follows: The electric field (E) of the electromagnetic wave (laser beam) fluctuates with time ($t$) as shown by equation

$$E = E_0 \cos 2\pi \nu_0 t \quad (2.22)$$

Where $E_0$ is the vibrational amplitude and $V_0$ is the frequency of the laser. If a diatomic molecule is irradiated by this light, an electric dipole moment $P$ is induced:

$$P = \alpha E = \alpha E_0 \cos 2\pi \nu_0 t \quad (2.23)$$

Where, $\alpha$ is a proportionality constant and is called polarizability. If the molecule is vibrating with a frequency $\nu_m$, the nuclear displacement $q$ is written:

$$q = q_0 \cos 2\pi \nu_m t \quad (2.24)$$

where $q_0$ is the vibrational amplitude. For a small amplitude of vibration, $\alpha$ is a linear function of $q$. Thus, it can be written as

$$\alpha = \alpha_0 + \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 + \ldots \ldots \quad (2.25)$$

Here, $\alpha_0$ is the polarizability at the equilibrium position and $(\partial \alpha / \partial q)_0$ is the rate of change of $\alpha$ with respect to the change in $q$, evaluated at the equilibrium position.
Combining 2.23 with 2.24 and 2.25

\[ P = \alpha E_0 \cos 2\pi \nu_0 t \]
\[ = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q E_0 \cos 2\pi \nu_0 t \]
\[ = \alpha_0 E_0 \cos 2\pi \nu_0 t + \left( \frac{\partial \alpha}{\partial q} \right)_0 q E_0 \cos 2\pi \nu_0 t \cos 2\pi \nu_m t \]
\[ = \alpha_0 E_0 \cos 2\pi \nu_0 t + \frac{1}{2} \left( \frac{\partial \alpha}{\partial q} \right)_0 q_0 E_0 \left[ \cos \{2\pi (\nu_0 + \nu_m) t \cos [2\pi (\nu_0 - \nu_m) t] \] \]

according to classical theory, the first term represents an oscillating dipole that radiates light of frequency \( \nu_0 \) (Rayleigh scattering), while the second term corresponds to the Raman scattering of frequency \( \nu_0 + \nu_m \) (anti-Stokes) and \( \nu_0 - \nu_m \) (Stokes). If \( (\partial \alpha/\partial q)_0 \) is zero, the vibration is not Raman active. In other words, to be Raman active, the rate of polarizability (\( \alpha \)) with the vibration must not be zero.

### 2.1.6.3 Data Analysis

Raman spectroscopy was used as a fingerprint method and it was used to identify the presence of amorphous and crystalline silicon phases in the nanostructures. The peak for amorphous Si appears at 480 cm\(^{-1} \) and for crystalline Si appears at 520 cm\(^{-1} \) and results were verified by comparing with results in literature.
2.1.6.4 Setup

Four major components make up the commercially available Raman spectrometer. These consist of the following:

- An excitation source, which is generally a continuous-wave (CW) laser.
- Sample illumination and collection system.
- Wavelength selector.
- Detection and computer control/processing systems

Figure 2.17: Schematic diagram of the major components in a Raman Spectrometer [2.13].
Raman spectra were obtained using a Jobin Yvon LabRAM HR 800 UV-VIS-NIR Raman Spectrometer, equipped with an Olympus microscope and excitation wavelengths 488 nm, 514 nm, 647 nm, 785 nm and 1064 nm.

2.2 Sample Preparation

Silicon substrates were cut into approximately 2 cm×2 cm pieces using a diamond knife, then dipped in a 5% Hydrofluoric acid (HF) and distilled water solution in order to remove the native oxide layer on the silicon substrates. After dipping in the HF solution, the samples were rinsed thoroughly in three beakers containing pure distilled water. The samples were left to dry in air.

In most of the experiments conducted the silicon substrates were not pre-treated and were used as received.

To prepare samples for metal or catalyst assisted growth, a thin layer of gold was deposited on silicon substrates by an ultra-high vacuum sputtering system. The deposition time was set for 5 minutes and the system was allowed to cool down before the samples were taken out for examination.
2.3 Deposition Systems

2.3.1 Chemical Vapor Deposition (CVD)

2.3.1.1 Introduction

Chemical vapor deposition may be defined as the deposition of a solid on a heated surface from a chemical reaction in the vapor phase. It belongs to the class of vapor-transfer processes which are atomistic in nature, i.e. the deposition species are atoms or molecules or a combination of both. Besides CVD, other physical vapor deposition (PVD) methods such as evaporation, sputtering, molecular beam epitaxy and ion plating exist. CVD is widely used in materials processing technology. The majority of its applications involve applying solid thin film coatings to surfaces, but it is also used to produce high-purity bulk materials, powders and fibers [2.14,2.15].

In this study FeCl₃ powder was used as a precursor and pieces cut from a silicon wafer used as substrates and the silicon source. The starting materials i.e. FeCl₃ and Si substrates were heated in a quartz horizontal quartz tube furnace at a temperatures ranging from 200°C to 1100°C. The main objective of the experiment was to form FeSi alloy nanowires.
2.3.1.2 Setup

The thermal chemical vapor deposition system (see Figure 2.18) used in this study was set up at the Council for Scientific and Industrial Research (CSIR). It offers convenience in the synthesis of nanostructures and it can also be used to anneal samples.

The setup consists of horizontal quartz tube situated in a three stage hot wall furnace. A gas inlet is connected at one end of the furnace to serve as a carrier for the precursor vapors during the reaction. A quartz boat containing the FeCl$_3$ powder and the silicon substrates are pushed inside the tube using a rod. Gases in the quartz tube go out through the exhaust.

Figure 2.18: A schematic representation of the thermal CVD system.
2.3.1.3 Deposition Procedures

After the starting materials are loaded into the tube, gas supply is switched on. This is done to ensure that there is constant gas flow before the furnace is turned on. The gases used for deposition were Argon and Nitrogen. The furnace is then switched on and allowed to ramp to a temperature of 1100°C. Deposition is done in atmospheric pressure. The reaction is allowed to run for 1 hour 40 minutes and then the furnace is switched off and allowed to cool. Then the substrates were taken out for further examination.
2.3.2 Physical Vapor Deposition (PVD)

2.3.2.1 Introduction

Physical Vapor Deposition (PVD) processes (often just called thin film processes) are atomistic deposition processes in which a material is vaporized from a solid or liquid source in the form of atoms and molecules, then transported in the form of a vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. Sputter deposition is one of the common PVD methods used to deposit thin films. Sputter deposition is the deposition of particles vaporized from a surface (target), by the physical sputtering process. Physical sputtering is a non-thermal vaporization process where surface atoms are physically ejected from a solid surface by momentum transfer from an atomic-sized energetic bombarding particle which is usually a gaseous ion accelerated from plasma. Sputtering deposition is usually done in vacuum using an ion gun, because of the vacuum, the sputtered particles suffer few or no gas phase collisions in the distance between the target and the substrate [2.16].

In this study, we used sputtering to deposit thin films of gold on silicon substrates to act as catalysts during nanostructure growth.
2.3.2.2 Setup

The system used is an ultra-high vacuum (UHV) magnetron sputtering system. It is equipped with five sputtering sources, only one is shown for demonstration purposes (see Figure 2.19) situated at the bottom of the chamber (sputter up deposition). The system uses a magnet below the electrode to trap free electrons in a magnetic field directly above the target surface. It has a rotating sample holder with heating capability. The deposition chamber and the loading chamber are isolated from each other by a shutter (load lock system), where one can insert a sample in the deposition chamber without breaking the vacuum. The deposition chamber is connected to an Argon gas supply, for introducing neutral gas atoms in the chamber. The loading chamber is connected to a Nitrogen gas supply for breaking the vacuum.
The system works by ionizing neutral Argon gas atoms, the process is as follows: The ever present free electrons will be immediately accelerated from the negatively charged electrode. These accelerated electrons will approach the outer shell electrons of the neutral gas atoms in their path, being of like charge they will drive away the outer electrons from the gas atoms, this leaves the gas atom electrically unbalanced since it will have more protons than electrons and this ionizes the gas atom, at this stage it is no longer a neutral gas atom but a positively charged ion (Ar⁺). These positively charged ions are then accelerated to the negatively charged electrode and knock off atoms from the target which will condense on the substrate.
2.3.2.3 Deposition procedures

In order to load the sample, the vacuum in the small chamber (loading chamber) is broken and the sample holder is taken out. The sample is then mounted onto the sample holder. The sample holder is placed back in to the loading chamber and the pressure is pumped down to the initial vacuum (~10\(^{-7}\) mTorr). Before loading the sample into the main chamber (deposition chamber), a desired vacuum for deposition (~10\(^{-8}\) mTorr) must be reached. The sample is then pushed from the small chamber to the main chamber for deposition. Computer software connected to the system is then used to select the target, deposition time and deposition rate.
2.4 References


CHAPTER 3

3. Visible and IR photoluminescence of ε–FeSi/Si core-shell nano-fibres produced by vapor transport

3.1 Abstract

The procedures for the synthesis of amorphous ε-FeSi / Si core-shell nanofibres by vapor transport in a CVD configuration are reported. Crystallite studies by the Williamson-Hall method show the sizes to be typically about 8.0 nm which agrees with TEM value of 7.9 nm fibre diameter with a compressive strain of about 0.04. Features in the photoluminescence of these FeSi core-shells in both visible and IR are at 410, 1062, 1414 and 1772 nm and absorption feature at 1000 cm\(^{-1}\) from FTIR are explained from density functional theory (DFT) ab initio calculations. PL confirms the intra-band transition whereas FTIR agrees perfectly with the band-to-band transition whose band gap energy is 0.13 eV for FeSi. FTIR also unveils inter-band transition which DFT calculation could not predict. Raman spectroscopy data confirm FeSi and nano-Si presence.
3.2 Introduction

One-dimensional (1-D) inorganic nanowire materials have enjoyed prominent attention in the research community in the past decade because they can be rationally and controllably synthesized and have found many promising applications in electronics, photonics, spintronics, sensing, photovoltaics and thermo-electrics. These nanostructures exhibit fascinating physical and chemical properties distinct from those of bulk or thin film materials [3.1-3.4]. Experimental conditions such as reaction time and temperature play an important role in the morphology of the reaction products. Unique morphologies of FeSi nanostructures such as nanocombs [3.4], nanoflowers [3.5] and hyperbranched nanowires [5] have been reported. For the synthesis of 1-D nanowires, metal-catalyzed chemical vapor deposition (CVD) has proven to be one of the most successful growth methods as it offers convenience compared to wet chemical methods. CVD here works well since the object was to obtain the alloy of Fe and Si. In wet chemistry methods, it is difficult to find solvent that are free from oxygen and other impurities. The temperatures used here may be similar to those used in other reports; however, synthesis of FeSi from the Fe containing FeCl₃ precursor and the heated Si substrate is new. However, metal contaminations are often detrimental to their applications. Growth by a spontaneous chemical vapor transport method without the use of a catalyst is favoured if the method proves to be a viable alternative [3.5-3.6]. Silicides form an important group of transition metal compounds with interesting physical properties. The majority of silicides turn out to be metallic, some of them, including the B20 cubic phase of iron mono-silicide (FeSi) have been found to exhibit semiconducting properties (E₉ =0.1eV) below room temperature and a metal to insulator
transition (MIT) around 300 K [3.7-3.11]. Its transition temperature makes this material a good candidate in the field of gas sensing as well as in thermo-chromism where the material could keep homes warm in winter and cool in hot summer when coated on window glass as is the case for vanadium dioxide (VO$_2$) [3.12-3.15]. The disadvantage with VO$_2$ is that its MIT is at 340K [3.16-3.18] which is 40 °C above room temperature, and it requires doping with metals such as W, Cr and Nb for its MIT to shift to room temperature. The doping of VO$_2$ comes at the expense of its switching contrast. FeSi has its MIT already at room temperature, naturally, and the relative abundance of Fe and Si are the major advantages of shifting research attention to FeSi.

In this paper, we report on the noodle-like nanofibres of FeSi obtained by vapor transport in a chemical vapor deposition (CVD) configuration. In addition we report on the luminescent properties of FeSi nanofibres which appear in the IR through blue to UV regions and IR absorption properties which reveal other transitions in FeSi that a standard photoluminescence spectrometer could not give.
3.3 Experimental Details

FeCl₃ powder (97% Purity) and Si (111) wafers were purchased from Sigma-Aldrich and were used as received. The other 3% of the FeCl₃ powder (97% Purity) is documented in the suppliers (Sigma-Aldrich) which are trace elements of Na, K and Ca. For the synthesis of FeSi nanostructure, Fe source precursor FeCl₃ was placed at the centre of the horizontal quartz tube furnace in quartz boat. Si (111) substrates were placed 1-2 cm away from the Fe source. The temperature of the furnace was adjusted from room temperature to 1100°C. N₂ gas was used a carrier gas to transport the precursor vapors from the FeCl₃ to the silicon substrates and the reaction was performed for 1 hour 40 minutes. After cooling down to room temperature in air, the Si substrates were taken out for further analysis.

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 = 0.154nm) monochromated radiation source.

The photoluminescence (PL) properties of the nanostructures were investigated using a spectro-fluorometer (Jobin Yvon Nanolog FL3-22) at room temperature. The emission was detected with Jobin-Yvon PMT detector. In order to explain the new features in the
PL spectra of these FeSi nano-structures, band structure and density of states (DOS) calculations were undertaken.

We carried out density functional theory simulations using the generalized gradient approximation (GGA) and the local density approximation (LDA) [3.19] for the exchange and correlation functional, as implemented in the CASTEP code [3.20]. The interaction between the ionic cores and the valence electrons is described using ultra soft pseudo potential of Vanderbilt [3.21]. The Brillouin zone of FeSi is sampled using the scheme of Monkhorst and Pack [3.22]. This kind of k-point sampling method gives a good convergence to the total energy calculations. A kinetic energy cut-off of 300 eV was used for the plane wave expansion of the wavefunctions. The positions of all atoms in the defective nanotubes were relaxed using the conjugate gradient algorithm with a tolerance of $2 \times 10^{-5}$ eV for maximal change in total energy. Calculations converged when the value of residual force was less than the value of 0.05 eVÅ$^{-1}$. The electronic states were occupied in accordance with the Fermi distribution function using a Fermi smearing parameter of $k_B T = 0.20$ eV.
3.4 Results and Discussions

3.4.1 Morphology and Structural Properties of FeSi nanofibres

Figure 3.1 shows a scanning electron microscopy (SEM) image of the bundles of interwoven fibrous nanostructures. The diameter of a single strand ranged from 20-100 nm with a single strand composed of 7-8 single FeSi fibres. The mingling of the FeSi nanofibres could be a result of an indeterminate growth direction and the presence of many growth nuclei at the surface of the Si substrate. The other reason for non-directionality is that the nanofibres have a diameter of about 8 nm. This is too thin compared to the roughness of the Si surface which of the order of 100’s of nm. This roughness influences the meandering morphology of the subsequent FeSi/Si core-shell nanofibres. Because no catalyst was used, Si is inevitably one of the candidates in the fibres. Previous synthesis of FeSi without catalysis reports presence of amorphous SiO$_2$ [3.5]. One notes that the nanofibres in Figure 3.1 appear outstandingly bright against the substrate background. This over-brightness could be due to electron charging effect owing to the loose attachments of the fibres to the grounded substrate. However, if the secondary electron detector also detected photons as a result of the electron-FeSi phonon interaction and if the fibres are well attached to the ground, the over-brightness could be due to cathodoluminescence (CL) from the FeSi nano-fibres. CL spectra could not be performed due to the limitations of the instrument.
Figure 3.1: Representative SEM image of the interwoven FeSi fibres. Note that the fibres are outstandingly bright against the background. This could be due to electron charging effects as well as cathodoluminescence.
A high resolution transmission electron microscopy (HRTEM) micrograph is shown in Fig 3.2. The nanostructures appeared to have core-shell structures and are semi-crystalline indicating that the nanostructures composed of an amorphous network and crystalline region. The core is dense and crystalline, whereas the shell is amorphous. Szczech et al [3.1] found that when they performed surface characterization of the individual FeSi nanowires with X-ray Photoelectron Spectroscopy (XPS), that the surface oxide layer formed on the nanowires was in fact not Fe$_2$O$_3$, but SiO$_2$, which was consistent with the fact that FeSi will develop a thin silicon oxide layer during exposure to air. In our case, the amorphous shell is in fact Si as shown in the localized energy dispersive spectroscopy (EDS) performed at the core and around the shell in Figure 2 (c) and (d). The few peaks of Fe in the local EDS for the shell could be small contributions from core.
Figure 3.2: (a) TEM image of a single core-shell FeSi nanofiber; a dense and crystalline FeSi core surrounded by Si-rich amorphous shell and (b) TEM image of the tangled FeSi nanofibers. (c) local EDS of the core and (d) local EDS of the shell.
X-ray diffraction was performed on the deposited nanostructures. All the observed diffraction peaks are indexed to FeSi [Figure 3], which has a cubic structure with a lattice constant of 4.496 Å (space group P2\(_1\)3, Pearson symbol cP8, structure type FeSi, Z=4, ICSD PDF-01-086-0795). In order to estimate the crystallite size, the Debye-Scherrer [3.23] method is employed, which states that the peak width B(2\(\theta\)) is inversely proportional to the crystal size (L) i.e.

\[
B = \frac{0.94\lambda}{L \cos \theta}
\]

where \(\lambda\) is the x-ray wavelength and \(\theta\) is the Bragg angle for the individual peaks starting from 2\(\theta\)=28° to 2\(\theta\)=61°, the crystallite sizes were found to range from 13.9 to 131.1 nm (Table 1). In addition to the Debye-Scherrer method, a second method for estimating the crystal size was used, namely the Williamson-Hall Method [3.24], This method accounts for both strain and crystallite size of the material i.e.

\[
B = (C\varepsilon) \tan \theta + \frac{0.94\lambda}{L \cos \theta}
\]

where \((C\varepsilon)\) is the strain component. This calculated crystallite size differs significantly from the Debye-Scherrer crystallite size as shown in Table 1, but the Williamson-Hall calculation agrees with the HRTEM measurements. For all the planes the estimated crystallite size is 1.93 nm but when only the FeSi main peaks are considered, the crystallite diameter by the Williamson-Hall plot, is 7.75 nm compared to HRTEM measurement of about 8.00 nm. The Williamson-Hall provided a more accurate estimation of the crystallite sizes, which agrees with our TEM results, thus proving to be a more reliable method.
Figure 3.4 shows that the 110 plane is an outlier and does not follow a pattern similar to the other planes. The observed 110 plane might be resulting from contributions from the silicon substrates.

**Figure 3.3:** XRD of the FeSi nanofibers.
Figure 3.4: Williamson-Hall plot
<table>
<thead>
<tr>
<th>$2\theta$ (Degrees)</th>
<th>Miller planes</th>
<th>Debye-Scherrer (L) (nm)</th>
<th>Williamson-Hall (L) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>110</td>
<td>83.6</td>
<td>L, $\varepsilon$ values when all peaks are considered</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>L, $\varepsilon$ values when (110) peaks is excluded</td>
</tr>
<tr>
<td>34.5</td>
<td>111</td>
<td>65.1</td>
<td>L</td>
</tr>
<tr>
<td>40</td>
<td>200</td>
<td>48.9</td>
<td>1.93</td>
</tr>
<tr>
<td>45</td>
<td>210</td>
<td>68.1</td>
<td></td>
</tr>
<tr>
<td>49.6</td>
<td>211</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>61.9</td>
<td>221</td>
<td>131.1</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.1:** Results from Debye-Sherrer model and the Williamson-Hall plot for crystallite sizes and strain in the nano-fibres.
3.4.2 Photoluminescence of the FeSi/Si core-shell nanofibres

The FeSi$_2$ phase’s photoluminescence properties have been studied and it has been reported that the material, with a band gap of 0.8 eV, emits at a wavelength of 1.54 $\mu$m (0.81 eV) [3.25-3.31]. To the best of our knowledge photoluminescence properties of the FeSi have never been reported. Therefore, in this study we report for the first time on the photoluminescence properties of FeSi. By using the excitation energy of 325 nm (3.8 eV), we observe an emission peak around 410 nm (3.02eV), 1062 nm (1.16 eV), 1414 nm (0.88 eV) and 1717 nm (0.70 eV). There is a strong PL peak between 600 and 700 nm. This peak may be as a result of (1) quantum confinement due to the typical crystallite size of about 8 nm of the FeSi core as well as the thinner than 5 nm Si shell and (2) intra-band transitions due to impurity and vacancy defect states in the FeSi structure.

On the nano-Si shell, it is known that bulk Si with a band gap of 1.1 eV emits at a wavelength of 1100 nm in conformity with band-to-band transition in Si. Nano-Si has been observed to show a blue shift. However the blue shift from 1100 nm to between 600 and 700 nm was calculated to be too big for a crystallite size of 5 nm. For instance, from Efros and Efros [3.32], the change of energy of the emitted photons due to strong, moderate and weak quantum confinement are respectively given as

\[
\Delta E = \frac{\hbar^2 \pi^2}{2 \mu R^2} \quad \text{(strong confinement)} \tag{3}
\]

\[
\Delta E = \frac{\hbar^2 \pi^2}{2MR^2} \quad \text{(weak confinement)} \tag{4}
\]
\[
\Delta E = \frac{h^2 \pi^2}{2 \mu R^2} \quad \text{(very small nanoclusters)}
\]

\[
\Delta E = \frac{h^2 \pi^2}{\mu R^2} - \frac{1.786e^2}{\epsilon_r R} + 0.284 \frac{13.606m_p}{\epsilon_r^2 \left(1/m_e^* + 1/m_h^* \right)}
\]

(5)

where \(\mu^*\) is the reduced mass of the electron-hole pair (exciton) which is usually taken to be \(2m_e\) (with \(m_e\) being the mass of the electron), \(R\) is the crystallite radius, \(M = m_e + m_h\), is the relative dielectric constant of the medium and \(m_p\) is the mass of the proton in Hydrogen. Performing a simple calculation for the typical nano-fibres presented here, one find that the 1100 nm peak for bulk Si should shift by 0.1 eV (112 nm) for strong quantum confinement and much less than that value for moderate and weak confinement. The quantum confinement theoretical equations therefore are not able to singly account for the major shift of the 1100 nm peak down to between 600 and 700 nm. It is possible therefore that the second reason of intra-band transitions due to defects is an added attribute to this blue shift.
Figure 3.5: (a) Visible range photoluminescence spectrum for FeSi nano-fibres excited by a light source of wavelength 325 nm (b) Visible and IR photoluminescence spectra showing the quality of IR spectra compared to the visible range against high background noise.
We therefore explain this using the band structures of FeSi calculated using LDA and GGA. Band structure and electron density of states calculations performed on the FeSi system are presented in Figure 6. We attribute the energy dispersion curves of \( E > 3 \text{ eV} \) to Si \((3p)\) and \(-6 \text{ eV} < E < -3 \text{ eV}\) to Fe-Si hybridization, those curves of energy in the range \((-3 \text{ eV} < E < +3 \text{ eV})\) to Fe \((3d)\) electrons and those below \(-6 \text{ eV}\) to Si \((3s\) and \(3p)\) electronic states. The Fe and Si labels are clearly marked in Figure 3.6 (a) and (b). This assignment is in agreement with the previous calculations [3.33]. The density of states in (b) show that while most of the electrons belong to Fe \((3d)\) close to the Fermi level, a good proportion are in the valence band confirming the Kondo insulator behaviour in FeSi. For clarity, we have labelled the energy levels differently in this paper and these appear in Figure 3.6 (c). Those bands with predominant Fe \(3d\) are identified by our labels Fe \(3d^2\) to Fe \(3d^2\) where positive exponent refers to conduction band and negative refers to valence band and those of Si \(3s\), \(3p\) orbital character are specified by our label Si \(3s^6+3p^6\), Si \(3s^5+3p^5\), Si \(3s^6+3p^6\), and Si \(3s^5+3p^5\). The lowest grouping of four bands evolves essentially from the Si \((3s)\) states (Si \(3s^6+3p^6\), Si \(3s^5+3p^5\), Si \(3s^6+3p^6\), and Si \(3s^5+3p^5\)). The bands above these at slightly higher \((\sim -6 \text{ to } -3 \text{ eV})\) energies reflect Si-Fe hybridization effects and their mixed character has been distinguished by labels Si \(3s^4+3p^4\), Si \(3s^3+3p^3\), Si \(3s^4+3p^4\), and Si \(3s^3+3p^3\). The Fe \(3d\) bands span the adjoining energy range from about \(-3 \text{ to } +3 \text{ eV}\), while hybridized bands with enhanced Si \(3p\) character reappear at higher energies near the top of Figure 3.6 with our labels Si \(3p^3\) to above Si \(3p^6\).
Figure 3.6: Assignments of the band structure (a) and DOS (b) to the Si (3p), Fe (3d), Fe-Si hybridization and Si (3s and 3p) electron states. In (c) we consider the gamma, G, symmetry line and introduce our labels for explanation of our PL results in Figure 5. In (d) the 3.11 eV (410 nm) photon emission is due to the de-excitation from Si (3p) electron states down to the Fe (3d) level.
In as far as the new photoluminescence feature appearing at 410 nm, we consider the gamma, G, line of symmetry which we have zoomed-in in Figure 3.6 (c) and our corresponding labels. The gamma point (where $\pi a / \lambda = 0$) being the centre of the Brillouin zone is appropriate when the photon wavelength, $\lambda$, of excitation (in this case 325 nm) is much longer than the lattice parameter of the FeSi system ($a \sim 0.47$ nm). One of the transitions extracted from the band structure in Figure 3.6 to explain the luminescence feature at a wavelength of 410 nm is one of those electrons de-exciting from Si (3p) level down to the Fe (3d) as shown in Fig 6 (d). The other IR features at 1062 nm (1.16 eV), 1414 nm (0.88 eV) and 1772 nm (0.70 eV) are assigned to the transition $<\text{Fe} 3d^1|\text{Fe} 3d^0|\text{Fe} 3d^{-1}>$, $<\text{Fe} 3d^1|\text{Fe} 3d^0>$, and $<\text{Fe} 3d^0|\text{Fe} 3d^{-1}>$ respectively. The probability that these transitions will occur are defined as the square of each operation respectively written as $|<\text{Fe} 3d^1|\text{Fe} 3d^0|\text{Fe} 3d^{-1}>|^2$, $|<\text{Fe} 3d^1|\text{Fe} 3d^0>|^2$, and $|<\text{Fe} 3d^0|\text{Fe} 3d^{-1}>|^2$ where the state Fe $3d^0$ is equivalent to the Fermi level, $E_F$. These data compared to the amplitudes of the individual peaks in the PL spectra along with all the possible transitions that have been observed by our PL spectrometer in Table 2. This table shows that the most probable emission from FeSi is the IR emission at 1062 nm which seems equivalent to the YAG emission at 1064 nm.
<table>
<thead>
<tr>
<th>Wavelength, $\lambda$(nm)</th>
<th>Transition Description</th>
<th>Transition Probability (theory)</th>
<th>Amplitude, $A_i$, (Expt)</th>
<th>Probability (Expt) $A_i/\Sigma_i A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>410 nm (3.02 eV)</td>
<td>$&lt;\text{Si }3p^5</td>
<td>\text{Fe }3d^6&gt;$</td>
<td>$</td>
<td>&lt;\text{Si }3p^5</td>
</tr>
<tr>
<td>484 nm (2.56 eV)</td>
<td>$&lt;\text{Si }3p^5</td>
<td>\text{Fe }3d^6&gt;$</td>
<td>$</td>
<td>&lt;\text{Si }3p^5</td>
</tr>
<tr>
<td>1062 nm (1.16 eV)</td>
<td>$&lt;\text{Fe }3d^1</td>
<td>\text{Fe }3d^0</td>
<td>\text{Fe }3d^1&gt;$</td>
<td>$</td>
</tr>
<tr>
<td>1414 nm (0.88 eV)</td>
<td>$&lt;\text{Fe }3d^0</td>
<td>\text{Fe }3d^1&gt;$</td>
<td>$</td>
<td>&lt;\text{Fe }3d^0</td>
</tr>
<tr>
<td>1772 nm (0.70 eV)</td>
<td>$&lt;\text{Fe }3d^1</td>
<td>\text{Fe }3d^1&gt;$</td>
<td>$</td>
<td>&lt;\text{Fe }3d^1</td>
</tr>
</tbody>
</table>

Table 3.2: A summary of the transitions in FeSi from DFT and the measured amplitudes from PL with their associated probabilities.

As already noted about the density of states, the photoluminescence feature at a wavelength of 410 nm, however, seems not to come from the majority of the electrons but from only those that are above the Fermi energy level. More reliable assignment has been accomplished via the band structure in (a); the DOS in (b) only gives an idea of how many electron in a single atom are involved and this can give an indication of the probability of luminescence and hence the magnitude of intensity expected in a typical experimental measurement. In this case one can clearly see why the 410 nm feature has not been reported to date. The features around Fermi level and those just below that level, being contributed from the majority of the electrons, which leads to an emission at around 1540 nm for FeSi$_2$, has been widely reported. In the present case, FeSi shows peaks at 1062 nm, 1414 nm and 1772 nm in this same range. Given large
excitation intensities, FeSi can then be employed in UV sources and IR lasers apart from the microwave generators that have so far been reported.

The above intra-band transition assignments have been carried for FeSi for the first time; however similar work has been performed on gold [3.34]

### 3.4.3 Fourier transform infrared spectroscopy and Raman spectroscopy of the FeSi core-shell nanofibres

It must be mentioned that the band to band transitions reveal a band gap of 0.13 eV as an average between 0.21 eV from GGA approximation and 0.04 eV from the LDA approximation. These band to band transitions could not be measured from the PL due to the limitations of the detector as 0.13 eV translates to 12 μm. In order to observe these band to band absorptions, FTIR was performed on the ε-FeSi/Si fibre sample. The FTIR spectrum is given in Figure 7. Immediately one sees two major absorption peaks at 783 cm\(^{-1}\) (0.09 eV) and 1067 cm\(^{-1}\) (0.13 eV). The former is a bending vibration of the Fe-Si bond technically referred to as the transverse-optical (TO) phonon whereas the latter can be assigned to the longitudinal optical (LO) FeSi (stretching mode) phonon. The latter absorption at 0.13 eV agrees perfectly with the band gap energy from our calculations (0.13 eV) as averaged from GGA and LDA as well as in agreement with previous observations as stated in the preceding Introduction section. The FTIR spectrum also reveals other minor inter-band absorptions which could be due to small defects and vacancies in the FeSi lattice.
Figure 3.7: (a) Typical Fourier transform infrared spectrum of c-FeSi/Si nanofibre sample showing the two major IR absorptions by TO and LO phonon at 783 cm⁻¹ and 1066 cm⁻¹ wave-numbers respectively. The latter agrees perfectly with the band gap of FeSi as calculated by DFT. (b) Raman spectrum for the ε-FeSi/Si nano-fibres grown on a Si substrate.
The Si that forms the shell material is not amorphous. This fact has been confirmed by Raman spectroscopy as shown in Fig 3.7 (b). Amorphous Si shows a peak at 480 cm\(^{-1}\) while crystalline Si has a peak at 520 cm\(^{-1}\) [35]. The Raman spectrum from our FeSi/Si fibres show a broad peak between these two extremes centered 490 cm\(^{-1}\). Therefore we can conclude that this peak signifies nano-crystalline Si rather than amorphous Si.
3.4.4 Conclusions

We have successfully obtained new FeSi core-shell nanofibres. TEM confirms the shell to be somewhat amorphous while the core is dense and largely crystalline. XRD does point to the stoichiometric FeSi with the usual peaks indexed to FeSi which has a cubic structure with a lattice constant of 4.496 Å (space group P2₁₃, Pearson symbol cP8, structure type FeSi, Z=4, ICSD PDF-01-086-0795). We have employed both the Debye-Scherrer model and the Williamson-Hall method to determine the crystallite sizes and the strain in the fibres. The Debye model suggests the crystallite size ranges from 13 nm to 130 nm where the Williamson-Hall plot yields a size of about 8 nm and a strain of 0.04. The latter is more agreeable with HRTEM of a single core-shell nano-fibre whose core is 4 nm in diameter and a shell of about 10 nm from edge to edge.

Photoluminescence has revealed new features at a wavelength of about 410 nm, 1062 nm, 1414 nm and 1772 nm. This has been ascribed by ab initio calculation of electronic band structure and density of states to the de-excitation of the Si (3p) electron to the Fe (3d) ground state. The DOS has helped explain why this feature has not been observed to date. By the DOS calculation, we have found that this feature comes from minority electrons. We then have shown that FeSi can not only be used in infrared application but also can be a UV emitter.
3.5 References


CHAPTER 4

4. Synthesis and Characterization of FeSi nanowires

4.1 Abstract

In this chapter we report on the successful synthesis of stoichiometric FeSi nanowires by chemical vapor deposition (CVD) without the assistance of a metal catalyst. Synthesis temperatures were varied from 200 to 1100°C under Argon gas ambience. No nanostructure growth was observed at substrate temperatures below 800°C. FeSi nanowires with a 1:1 stoichiometry were obtained at 1100°C. Transmission electron microscopy (TEM) studies of the nanowires showed that they have core-shell structures. The growth of these FeSi nanowires is described by a vapor solid mechanism known as oxide assisted growth (OAG). New photoluminescence features were observed in the ultraviolet (UV), visible (Vis) and near infrared regions for the FeSi nanowires.
4.2 Introduction

The key to one dimensional (1D) nanostructure formation is about crystallization; a process that has been investigated for hundreds of years. The transformation of a solid from a vapor, liquid or solid phase involves two fundamental steps: nucleation and growth. As the concentration of the building blocks (atoms, ions or molecules) of a solid becomes sufficiently high, they aggregate into small clusters (or nuclei) through homogenous nucleation. With a constant supply of these building blocks, these nuclei can act as seeds for further growth to form larger structures [4.1]. Vapor-phase synthesis is definitely the most extensively used method for the formation of 1D nanostructures such as whiskers, nanorods and nanowires. In principle, it is therefore possible to process any solid material into 1D nanostructures by controlling the supersaturation at a relatively low level. Although the exact mechanism responsible for 1D growth in the vapor phase is still not clear, it is the most extensively explored approach in the field of material science to synthesize whiskers and derivatives from a variety of materials. Although most of products synthesized using vapor methods are oxides, with the reason being that oxidation is seemingly unavoidable due to trace amounts of oxygen in the reaction systems. The major advantage of using a vapor-phase method is its simplicity and accessibility. In a typical thermal chemical vapor deposition (CVD) setup, the vapor species is firstly generated by evaporation, followed by chemical reduction and other gaseous reactions. These species are then subsequently transported and condensed onto the surface of a solid substrate [4.2-4.8].
4.3 Experimental Details

The synthesis of the nanostructures was done using a horizontal quartz tube furnace (see section 2.3).

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 analyzed. The structural properties were examined using Panalytical X'pert PRO PW 3040/60 x-ray diffractometer (XRD) with a Cu Kα (λ = 0.154nm) monochromated radiation source.

Raman spectra were obtained using a Jobin Yvon LabRAM HR 800 UV-VIS-NIR Raman Spectrometer, equipped with an Olympus microscope and excitation wavelengths 488 nm, 514 nm, 647 nm, 785 nm and 1064 nm.
4.4 Results and Discussions

4.4.1 Morphology and Structural Properties

Figure 4.1(a) shows a scanning electron microscope image of circular structures obtained at substrate temperature below 300°C. At this substrate temperature, the final reaction products were not solid and were in the form of liquid droplets. The samples had to be annealed in order to dry the products on the substrates. For reactions in the temperature range of 400-700°C, the structure sizes which formed were in the range of a several micrometres in diameter and did not resemble the targeted material i.e. nanowires with diameters more or less than 100 nm. The other notable problem which featured quite often at low substrate temperatures was the presence of chlorine impurities; this was confirmed by an energy dispersive x-ray spectroscopy (EDS) spectrum (see Figure 4.1(b)).
Figure 4.1: (a) Representative SEM of reaction products obtained at low substrate temperature and (b) Local EDS of the structures.
In general, we started observing nanostructure growth at substrate temperatures of 800°C-900°C. Figure 4.2 shows a representative SEM image of the nanostructures grown in these temperature ranges. The morphology of these nanostructures shows that they are branched and have dendritic structures.

![Representative SEM image of the branched nanostructures at 800-900°C.](image)

**Figure 4.2:** Representative SEM image of the branched nanostructures at 800-900°C.
The diameter of the branches ranged from 90 to 100 nm, whereas the diameters of the stems were in the range of 485 to 500 nm. Lattice fringes were observed on the surface of the nanostructures; showing their high crystallinity (see Figure 4.3).

The chemical composition of these nanostructures was determined in HRTEM. The resulting EDS performed on the branched nanostructures showed that they contained a significant amount of Fe and a small amount of Si as shown in Figure 4.4. Chlorine traces were also present in the nanostructures; which is a major problem in the purity of the nanostructures and their future application thereof. This meant that the chlorine in the gas phase was not completely eliminated with the gases going out the exhaust during the reaction. This imbalance between Fe and Si peaks showed that the FeSi phase stoichiometry of 1:1 was far from being reached at these substrate temperatures. This result is supported by the XRD spectra (not shown here), which contain unidentified peaks which do not belong to FeSi.
Figure 4.3: Representative TEM image of the branched nanostructure.
Figure 4.4: Local EDS of the branched nanostructure.
Nanowires were successfully synthesized when substrate temperature ranged from 1000-1100°C. We found this to be the optimized growth temperature for obtaining nanowires and no traces of chlorine were found in the nanowires. At high temperature the chlorine is eliminated in the as it is converted to the vapor phase, the reaction that produces FeSi nanowires may follow these two plausible reaction paths:

\[
\begin{align*}
2\text{FeCl}_3 & \leftrightarrow \text{Fe}_2\text{Cl}_6(g) \\
2\text{Fe}_2\text{Cl}_6(g) + 7\text{Si}(s) & \rightarrow 4\text{FeSi}(s) + 3\text{SiCl}_4(g)
\end{align*}
\]

Or

\[
\begin{align*}
\text{Fe}_2\text{Cl}_6(g) & \leftrightarrow 2\text{FeCl}_2(s) + \text{Cl}_2(g) \\
\text{FeCl}_2(s) + \text{Cl}_2(g) + 2\text{Si}(s) & \rightarrow \text{FeSi}(s) + \text{SiCl}_4(g)
\end{align*}
\]

The vapor pressure of the Fe precursor is important in the formation of nanowires. Higher temperatures in the precursor vapors will result in high vapor pressures of the Fe precursor and FeSi product in the reaction area in the process creating a large super-saturation ratio [4.9].

Control experiments were done on silicon substrates treated in HF and untreated silicon substrates. These experiments were carried out to study the effect which the thickness of the surface silicon oxide layer has on the growth and morphology of the nanowires.
Figure 4.5 (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 maximum of 38 μm. Figure 4.5 (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, they grow and extend to about 60 μm in length and have a tendency of bending because of their length (see Figure 4.5 (d)). The diameters of the nanowires varied from 50 to 160 nm for different samples.
Figure 4.5: 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.
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 are shown Figure 4.6 (a), (b) and (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 Figure 4.6 (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 (110) lattice inter-planar spacing of the FeSi structure [4.10]. 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 Figure 4.6 (d)) showed a diffraction pattern with a cubic crystal structure, which was indexed to cubic $\varepsilon$-FeSi. The brightest spot in the pattern can be compared to the most intense peak in the XRD; which is the (210) plane.
Figure 4.6: TEM images of a nanowire showing a core shell structure at (a) lower magnification and (b) higher magnification. (c) Lattice fringes on the core and (d) SAED of nanowire.
The elemental composition of both the core and the shell were determined by energy dispersive x-ray spectroscopy (EDS). The EDS spectra for the core showed two major peaks belonging to Fe and Si (see Figure 4.7(a)) with equal intensity. The chemical composition of the shell (see Figure 4.7 (b)) was also determined and the most intense peak belonged to silicon. The small Fe peaks in the EDS spectra of the shell might be small contributions from the core. It is possible that the Fe peak between 0 and 1 keV might also be that of oxygen as the two peaks are overlapping on each other. Since we cannot quantify elements depending only on an EDS spectrum; we can only speculate that the chemical composition of this shell is that of amorphous SiO$_x$. X-ray diffraction was done on the nanostructures to prove that they were indeed FeSi nanowires (see Figure 4.8).

In similar studies done by Szczech et al [4.10], the question of the chemical composition of the shell was answered by doing XPS measurements on the layer. They had hoped that the layer formed on their nanowires would contain a significant amount of Fe$_2$O$_4$. They discovered that the amorphous layer was entirely silicon oxide.
Figure 4.7: Local EDS of the (a) core and (b) shell of a nanowire.
Figure 4.8 (a) shows an XRD spectrum of the nanowires from $2\theta=24^\circ$ to $2\theta=60^\circ$. All 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$_1$3, 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 (210) plane at $2\theta=45^\circ$.

![Figure 4.8: (a) XRD spectrum of the FeSi nanowires and (b) ICDD.](image_url)
There were no catalyst particles at the ends of the nanowires as confirmed by both SEM and TEM. This indicated that the metal catalyzed vapor liquid solid (VLS) was an unlikely growth mechanism for this nanowires. These nanowires follow the vapor solid (VS) growth mechanism; it is often called self-catalytic growth because nanostructures are directly generated from the vapor phase in the absence of a metal catalyst. The growth of these FeSi nanowires is assisted by the native oxide layer that exists on the silicon substrates; this type of growth is known as oxide assisted growth (OAG). This formation mechanism of one dimensional nanostructures happens when a thin oxide shell is formed around the semiconductor core. The key to a successful CVD growth of FeSi nanowires is to use silicon substrates covered with a thin layer of silicon oxide of thickness between 1 and 2 nanometers [4.11]. Several experimental observations suggest that FeSi nanowires grow by a vapor solid mechanism under a relatively low super-saturation ratio. Large super-saturation ratios in the reaction area can lead to FeSi nanowires with branched morphologies (see Figure 4.9). These branched nanostructures have been found to be promising materials in solar energy conversion and 3-D electronics by improving performance in those areas [4.12, 4.13].
Crystallite sizes were calculated from the XRD spectrum. The two methods used to estimate the crystallite sizes were Debye-Scherrer and Williamson-Hall method. Crystallite sizes were calculated and estimated using the Debye-Scherrer equation and the size ranged from 22 to 151 nm as shown in table 4.1.

**Figure 4.9:** SEM image of a branched nanowire formed at 1100°C
Table 4.1: Scherrer calculated crystallite sizes.

<table>
<thead>
<tr>
<th>Miller indices</th>
<th>2θ (Degrees)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>28.042</td>
<td>47.02</td>
</tr>
<tr>
<td>111</td>
<td>34.522</td>
<td>39.55</td>
</tr>
<tr>
<td>200</td>
<td>40.074</td>
<td>21.78</td>
</tr>
<tr>
<td>210</td>
<td>45.048</td>
<td>37.57</td>
</tr>
<tr>
<td>211</td>
<td>49.623</td>
<td>37.35</td>
</tr>
<tr>
<td>220</td>
<td>57.966</td>
<td>151.42</td>
</tr>
</tbody>
</table>

The full width at half maximum (FWHM) for each individual peak was determined by fitting a Gaussian function, the x-ray wavelength is known and has a value of 0.154 nm, therefore the crystallite sizes can be calculated using equation 2.10 as described in section 2.1.4.4.

The Williamson-Hall method was also used to calculate the crystallite sizes and it is defined by equation 2.13, it accounts for both strain and the crystallite size, the Williamson-Hall plot (see Figure 4.10) is a straight line graph and we observed an unusual behaviour in the plot as shown in Figure 4.10. The 110 is an outlier and does not follow the same trend when compared to the 110, 200, 210, 211 and 220 planes which follow the same pattern, this might be resulting from the presence of other phases.
and also contributions from the silicon substrate. The y-value of the 110 at that point is $1.45 \times 10^{-2}$ and putting this value into the constant part of the equation, crystallite size (L) has a value of 9.98 nm at the (110) plane. The y-value for the other remaining planes has a value of $1.59 \times 10^{-4}$ and the calculated crystallite size for all these planes was found to be 914.16 nm. Comparing the values of the crystallite size between the two methods; the Scherrer method is the one which proved to be the most reliable with the average particle size of 151.42 nm for all the planes. The strain component was determined by fitting a linear curve and calculating the slope and a negative value of 0.02 was obtained which meant that there was compressive strain.

**Figure 4.10:** Williamson Hall plot for all the peaks.
4.4.2 Raman and Photoluminescence spectroscopy

Raman spectroscopy was performed on the nanostructures (see Figure 4.11). It was used as a fingerprint method to identify the presence of amorphous and crystalline silicon in the nanostructures. The results showed only the presence of crystalline silicon which has a peak at 520 cm$^{-1}$. There was no presence of amorphous silicon in the nanostructures which has a peak at 480 cm$^{-1}$ [4.14]. Only crystalline Si peak was observed; this contradicted TEM results as they showed an amorphous shell around the nanowires. Electrons have higher energy when compared to photons, this might be a plausible explanation for the discrepancy.

![Raman spectrum of the FeSi nanostructures.](image)

**Figure 4.11:** Raman spectrum of the FeSi nanostructures.
To the best of our knowledge, the FeSi$_2$ phase photoluminescence properties have been reported; not much work has been done for FeSi [4.15-4.21]. Photoluminescence studies were done on the FeSi nanowires. By using an excitation energy of 325 nm (3.8 eV); we observed photoluminescence peaks in the ultraviolet (UV), visible (Vis) and near infrared (NIR) regions (see Figure 4.12). There were emissions around 399 nm (3.1 eV), 427 nm (2.9 eV), 448 nm (2.8 eV), 464 nm (2.7 eV), 751 nm (1.7 eV) and 783 nm (1.6 eV). These photoluminescence features cannot be attributed to band to band transitions; FeSi has a small band of 0.13 eV. These band to band transitions could not be measured from the PL due to the limitations of the detector as 0.13 eV translates to 12 µm. These results are due to intraband transitions and were explained by band structure calculations as in Chapter 3.
**Figure 4.12:** UV-Vis-NIR photoluminescence spectra of the FeSi nanowires.
4.5 Conclusions

Successful growth of single crystalline FeSi nanowires has been achieved by using chemical vapor deposition method without the use of a metal catalyst at substrate temperature of 1100°C. Synthesis temperatures were varied from 200 to 1100°C under Argon gas ambience. There was no nanostructure growth in the low temperature regions of 200 to 700°C. Nanostructures which were synthesized at temperatures less than 1000°C had big diameters and were not FeSi. It was observed that pretreatment of the silicon substrates with an HF acid solution had an effect on the length of the nanowires. XRD results showed that the nanowires were highly crystalline and corresponded very well with TEM results. SAED, performed in TEM, showed that the nanowires were single crystalline and had a cubic structure. The nanowires had core shell structures; a crystalline FeSi core covered by an amorphous SiO\textsubscript{x} shell. The growth of these FeSi nanowires was described by a vapor solid mechanism known as oxide assisted growth (OAG), where the nanowires are characterized by having a thin oxide layer covering them. New photoluminescence features were observed between the UV and near IR region and were attributed to intra-band transitions. Raman results indicated that there was no amorphous silicon present, only crystalline silicon peak was observed. The nature of the crystallinity of the shell formed around the nanowires as shown by TEM to be amorphous contradicted this result.
4.6 References


5.1 Abstract

In this chapter we report on the growth of amorphous SiO$_x$ nanowires via CVD in an attempt to grow FeSi nanowires using a metal catalyst on silicon substrates. A 60 nm thin film of gold was deposited on silicon substrates by sputtering. Anhydrous FeCl$_3$ powder was evaporated on to the silicon substrates at a temperature of 1100°C. Transmission electron microscopy (TEM) revealed that the nanowires do not have core shell structures; they are amorphous throughout the entire surface. The growth of these nanowires did not follow the vapor liquid mechanism (VLS). The growth is explained by the formation of SiO$_x$ clusters which act as nucleation centers for the growth of these nanowires. Fourier transform infrared spectroscopy (FTIR) and Raman spectroscopy showed that there was amorphous silicon present in the nanostructures.
5.2 Introduction

Nano-structured materials, in particular, nano-tubes 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. 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, chemical vapor deposition, carbothermal reduction of oxides and chemical vapor deposition (CVD). However most of the results were crystalline nanowires with a thin oxide outer layer [5.1-5.9].
5.3 Experimental Details

Gold (Au) thin films were deposited on silicon substrates in an ultra-high vacuum (UHV) sputtering system, which is a physical vapor deposition (PVD) 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.

The synthesis of the nanostructures was done using a horizontal quartz tube furnace with three hot zones at a temperature of 1100°C. The choice of the catalytic metal (Au-melting point of 1064°C) used was solely based on the melting temperature of the material compared to the other metals such as Ni, Fe etc. which have higher melting temperatures. It is a requirement that the catalyst metal melt during the reaction in a typical VLS reaction [5.9]. The gold coated silicon substrates, after being exposed to a temperature of 1100°C; were covered by a hard greyish layer. These reaction products were then scrapped off from the silicon substrates using a spatula for further examination.
5.4 Results and Discussion

5.4.1 Morphology and Structural Properties

Figure 5.1 (a) shows a scanning electron microscopy image (SEM) of a vast network of nanowires, with lengths extending into several microns. The nanowires have uniform diameters and are spread over a wide area. Figure 5.1 (b) shows spherical structures in the vicinity of the nanowires. These spherical structures formed a lot of clusters or agglomerates and some were in the vicinity of the nanowires. Observations made from these SEM micrographs suggest that the VLS growth was unlikely to be the growth mechanism for these nanowires. The clusters were not attached to the nanowires. The diameters of the clustered spheres were not uniform; the clusters with the smallest diameters had the same shade as the nanowires whereas the bigger clusters appeared darker.
Figure 5.1: Representative SEM image of the (a) nanowires with spheres and (b) clustered spheres.
High resolution transmission electron microscopy (HRTEM) was used to examine the crystallinity, morphology and elemental composition of the nanostructures. We observed that there were no catalyst tips or heads at the ends and on the surfaces of the nanowires (see Figure 5.2 (b)). The nanowires had reasonably smooth and clean surfaces. Also the spherical nanostructures were not attached to the nanowires. These results contradicted the expected results for the well-known VLS mechanism in which catalyst drops are usually found on the tips of the nanowires. This was a clear indication that the metal catalyst did not play any role in the growth of these nanowires. The VLS growth is based on the three step mechanism (i) diffusion of Si/SiO\textsubscript{x} vapors into the metal particles, (ii) formation of a liquid droplet of the metal and Si/SiO\textsubscript{x} and (iii) the precipitation in the form of solid nanowires after supersaturation of liquid metal Si/SiO\textsubscript{x} droplet at the liquid-solid interface. Thus a metal particle at one end of the nanowire is usually considered as evidence for the successful operation of the VLS model [5.9].
Figure 5.2: Representative TEM image of (a) network of nanowires and (b) nanowires with spheres.
The chemical composition of a single nanowire was determined by EDS as shown in Figure 5.3. There exists an intense peak, which belonged to silicon. The EDS spectrum did not reveal any traces of the metal catalyst in the nanowires. There are three peaks of Fe, two small ones and one bigger peak. The bigger Fe peak between 0 and 1 keV also belongs to oxygen. It thus possible that the two peaks are overlapping on each other as the k-shell value for both Fe and O are equal. The chemical composition of the spheres was also determined by EDS. The EDS spectrum of these spheres was identical to that of the nanowires (see Figure 5.3 (b)). Since an EDS spectrum is not enough to quantify the elemental composition of these nanostructures; we can speculate that these nanostructures are SiO$_x$. 
Figure 5.3: Local EDS spectrum of (a) nanowire and (b) sphere.
HRTEM analysis on the surface of the nanowires did not reveal any lattice fringes. The nanowires became sensitive to the electron beam in higher magnification; as a result little spots appear on their surfaces (see Figure 5.4 (a)). Nevertheless, it could be clearly seen that the nanowires do not have core shell structures; they are amorphous throughout the entire surface. Selected area diffraction on the surface of the nanowires did not reveal any diffraction spots and thus proving that the nanowires are entirely amorphous as shown in Figure 5.4 (a) and (b). The HRTEM analysis on these nanostructures suggests that they are amorphous SiO$_x$ nanowires. There was no sign of the gold catalyst used in the nanostructures. X-ray diffraction (XRD) was done on the nanowires to in order to validate the TEM results (see Figure 5.5).
Figure 5.4 (a) and (b): Representative selected area electron diffraction on a bundle of silicon oxide nanowires.
Figure 5.5 shows XRD results of the SiO$_x$ nanostructures; the spectrum confirmed that the nanostructures are amorphous. There is a large bump distributed over a wide range of the diffraction angle (2$\theta$); showing that the crystal structure is not well ordered. There were only a few peaks which were indexed to Au, Fe and Fe$_2$O$_3$ [5.10-5.12]. EDS has its detection limits and XRD was able to detect the Au peak, this might be attributed to traces of gold left on the silicon substrates which did not melt completely during the reaction.

**Figure 5.5**: XRD of the nanostructures of the amorphous nanostructures.
According to our TEM observations; the growth of these SiO<sub>x</sub> nanowires cannot be explained using the VLS mechanism and the oxide assisted growth (OAG) mechanism used to grow crystalline SiO<sub>x</sub> nanowires. The OAG process presumes an oxide cluster rather than a metal particle to assist the formation of nanowires wherein an outer oxide shell is essential to prevent the lateral direction that results in 1-D Si-SiO<sub>x</sub> core shell nanowire formation for most semiconductor nanowires [5.13]. However, these nanowires are amorphous across the entire diameter instead of a crystalline Si core and an amorphous SiO<sub>x</sub> outer shell as confirmed by TEM. Liu et al [5.14] observed similar nanowires and suggested the reason behind the absence of an amorphous shell/layer on the surface of the nanowires might be due to the Si-rich SiO<sub>2</sub> layers on the silicon substrates. Inside the SiO<sub>2</sub>, there are a lot of dangling bonds of silicon in the Si-rich layer. It catches the oxygen from the surrounding atmosphere and thus causing the absence of oxygen in the nanowire growth process. Therefore no silica layers are formed on the surface of the nanowires. There were no Fe nanoparticles among the nanowires; which could have suggested that Fe nano-particles, with known catalytic properties might have played a role in the growth of these nanostructures as it was the case with work done by Qu et al [5.15]. They developed a method for producing SiO<sub>x</sub> nanowire assemblies using a floating catalyst method, where anhydrous FeCl<sub>3</sub> was used as the precursor and silicon wafers as both the silicon source and substrate. FeCl<sub>3</sub> was sublimated and reduced in the gas phase to produce Fe nanoparticles with high catalytic activity and allowed growth of SiO<sub>x</sub> nanowires to grow via the vapor liquid solid (VLS) mechanism.
The following mechanism proposed by Srivastava et al [5.16] can be used to explain the observed growth of the nanowires. The SiO vapors, generated at temperature around 1200°C, are transported downstream towards the substrates by the carrier gas and during traversal they get converted into SiO$_2$ molecules directly by reacting with O$_2$ according to the following equation:

$$2\text{SiO(g)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{SiO}_2\text{(s)}$$

It must be stated that the synthesis was done at atmospheric pressure; traces of residual oxygen could have been present in the reaction tube. The SiO$_2$ molecules formed condense on the substrate in the lower substrate region (~1000°C) to form SiO$_2$ nanoclusters that then act as nucleation centers for the growth of SiO$_x$ nanowires.
5.4.2 Fourier Transform Infrared Spectroscopy of the SiO$_x$ nanowires

The IR absorption characteristic of amorphous SiO$_2$ has been studied before and three major absorption peaks centered at 460, 810 and 1070 cm$^{-1}$ have been confirmed by many researchers. These three absorption peaks reflect the rocking of an oxygen atom about an axis through the two silicon atoms, the symmetrical stretching of stretching of an oxygen atom along a line bisecting the axis through the two silicon atoms and asymmetrical stretching of an oxygen atom along a line parallel to the axis through the two silicon atoms, respectively [5.17,5.18]. FTIR measurements were done on the silicon oxide nanowires at room temperature in the range of 500-4000 cm$^{-1}$. Figure 5.6 shows the transmittance and absorbance of the nanostructures, with major absorption peak at 558 and 1075 cm$^{-1}$, which can be attributed to Si-O-Si and Si-O stretching vibrations respectively. The other major absorption expected at 810 cm$^{-1}$ was not observed this might be directly related to the purity of the nanostructures. The most intense peak at 1075 cm$^{-1}$ is characterized by Si-O asymmetric stretching mode, whereby the adjacent O atoms execute the asymmetric motion in phase [5.19, 5.20].
Figure 5.6: FTIR spectra of SiO$_x$ nanowires.
5.4 Conclusions

A 60 nm thin film of gold was deposited on silicon substrates by sputtering to act as a catalyst and assist in the growth of FeSi nanowires; this was done to observe the VLS growth mechanism. There nanowires that were produced from the reaction were not FeSi nanowires; instead amorphous SiO$_x$ nanowires resulted in the final reaction products. XRD and TEM results showed that the nanowires were amorphous and there was no FeSi present in the nanowires. Raman and FTIR also revealed signatures for amorphous silicon in the nanostructures. The absence of Fe and Au particles in the nanostructures provided proof that Fe and Au did not play any catalytic role in the growth of the SiO$_x$ nanowires. No catalyst tips were found on the tips of the nanowires, which should be a typical scenario if the nanowires followed the VLS growth mechanism. The growth mechanism for these nanowires was explained by the formation of SiO$_x$ clusters which acted as nucleation centers for the growth of the nanowires.
5.5 References


6. Summary

Synthesis of stoichiometric FeSi nanowires and nanofibers was done successfully by means of a chemical vapor deposition method at an optimized temperature of 1100°C. We have optimized the synthesis conditions, specifically temperature; experiments were done in the temperature range of 200°C to 1100°C. We found that at substrate temperatures lower than 1000°C, the nanostructures which result from those reactions have big diameters with values up to 600 nm and often contain chlorine impurities. When doing reactions at very low temperatures, in most instances, no nanowire growth was observed. However FeSi nanowires synthesized at temperatures above 1000°C had smaller diameters. The preferred growth method/mechanism for these nanowires was through the oxide assisted or self-catalytic growth method, which does not require a metal catalyst. The nanowire growth was simply aided by the native silicon oxide layer on the substrates. The nanowires have a crystalline core and an amorphous shell covering them. Characterization of the nanowires was done using the following techniques: XRD, SEM, TEM, FTIR, PL and Raman spectroscopy.
Photoluminescence studies were done on the nanostructures on the FeSi nanowires and fibers. There were observed features between the UV and the near infrared region (410 nm to 1772 nm), which could not be assigned to FeSi, with its band gap value of 0.1 eV, the material is expected to emit in the far infrared region and could not be observed due to instrument limitation. These results were attributed to intraband transitions and were explained by using band structure calculations using local density approximation (LDA) and generalized gradient approximation (GGA).

Attempts made to grow FeSi nanowires via the assistance of metal catalyst proved to be unsuccessful. Thin films of gold were deposited on silicon substrates and placed in a quartz tube furnace at a temperature of 1100°C. Instead of single crystalline FeSi nanowires with gold catalyst tips, as would be expected from a VLS reaction, amorphous SiO\textsubscript{x} nanowires were obtained. The growth mechanism was explained by the formation of clusters which act as nucleation centers for the formation of the nanowires. The SiO\textsubscript{x} nanowires were characterized by XRD, SEM, TEM, FTIR and Raman spectroscopy.
6.1 Future Plans

Figure 6.1 shows preliminary gas sensing results of a powder that was collected from the wall of the quartz tube. The powder was tested for hydrogen sensing at 300°C and showed good response for different concentrations. We would like to establish more reliable contact between the powder and electrodes because of noise in the results.

Figure 6.1: Hydrogen sensing at 300°C of a Fe$_x$Si$_x$Cl$_x$O$_x$ ceramic.
The other preliminary work involved dropping nanowires that were dispersed on ethanol on an interdigitated device (see Figure 6.2). The dropping method has its shortcomings as nanowires and other structures fall anywhere on the device. The future plan is to weld the nanowires using FIB-SEM in order to have more accurate electrical and gas sensing measurements.

Figure 6.2: Nanowire between two electrodes of the interdigitated device.
Visible and IR photoluminescence of c-FeSi@a-Si core-shell nano-fibres produced by vapour transport

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ABSTRACT

The procedures for the synthesis of amorphous FeSi@a-Si core-shell nanofibres by vapour transport in a CVD configuration are reported. Crystalline studies by the Williamson–Hall method show the sizes to be typically about 8.0 nm which agrees with TEM value of 7.9 nm fibre diameter with a compressive strain of about 0.04. Features in the photoluminescence of these FeSi core-shells in both visible and IR are at 410 nm, 686 nm, 1484 nm and 1722 cm−1 and absorption feature at 1000 cm−1 from FTIR are explained from density functional theory (DFT) ab initio calculations. PL confi rms the intra-band transition whereas FTIR agrees perfectly with the band-to-band transition whose band gap energy is 0.13 eV for FeSi. FTIR also unveils an inter-band transition which DFT calculation could not predict. Raman spectroscopy data confrms FeSi and nano-a-Si presence.

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1. Introduction

One-dimensional (1-D) inorganic nanowire materials have enjoyed prominent attention in the research community in the past decade because they can be rationally and controllably synthesized and have found many promising applications in electronics, photonics, spintronics, sensing, photovoltaics and thermoelectrics. These nanomaterials exhibit fascinating physical and chemical properties distinct from those of bulk or thin film materials [1–4]. Experimental conditions such as reaction time and temperature play an important role in the morphology of the reaction products. Unique morphologies of FeSi nanomaterials such as nanocorns [4], nanoflowers [5] and hyper-branched nanowires [5] have been reported. For the synthesis of 1-D nanowires, metal-catalyzed chemical vapour deposition (CVD) has proven to be one of the most successful growth methods as it offers convenience compared to wet chemical methods. CVD here works well since the object was to obtain the alloy of Fe and Si. In wet chemistry methods, it is difficult to find solvents that are free from oxygen and other impurities. The temperatures used here may be similar to those used in other reports; however, synthesis of FeSi from the Fe containing FeCr precursor and the heated Si substrate is new.

However, metal contaminants are often detrimental to their applications. Growth by a spontaneous chemical vapour transport method without the use of a catalyst is favoured if the method proves to be a viable alternative [5,6]. Silicides form an important group of transition metal compounds with interesting physical properties. Most of the silicides turn out to be metallic, some of them, including the B2-phase of iron monosilicide (FeSi) have been found to exhibit semi-conducting properties (τ = 0.1 eV) below room temperature and a metal to insulator transition (MIT) around 300 K [7–11], its transition temperature makes this material a good candidate in the field of gas sensing as well as in thermochromism where the material could keep homes warm in winter and cool in hot summer when coated on window glass as is the case for vanadium dioxide (VO2) [12–15]. The disadvantage with VO2 is that its MIT is at 340 K [16–18] which is 40 °C above room temperature, and it requires doping with metals such as W, Cr and Nb for its MIT to shift to room temperature. The doping of VO2 comes at the expense of its switching contract. FeSi has its MIT already at room temperature, naturally, and the relative abundance of Fe and Si are the major advantages of shifting research attention to FeSi.

In this paper, we report on the noodle-like nanofibres of FeSi obtained by vapour transport in a chemical vapour deposition (CVD) configuration. In addition we report on the luminescence properties of FeSi nanofibres which appear in the IR through blue to UV regions and IR absorption properties which reveal other transitions in FeSi that a standard photoluminescence spectrometer could not give.

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2. Experimental

FeCl₃ powder (97% Purity) and Si (1 1 1) wafers were purchased from Sigma-Aldrich and used as received. The other 3% of the FeCl₃ 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 FeCl₃ 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, N₂ gas was used as a carrier gas to transport the precursor vapours from the FeCl₃ 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.

The morphology of the products formed on the silicon substrates was examined using focused ion beam (FIB) field emission scanning electron microscopy (FE-SEM) (Tescan Lyra FIB FESEM). The crystallinity of the nanostructures was analyzed using high resolution transmission electron microscopy (HR-TEM) (FEI Tecnai G2 F20). Nanostuctures removed from the Si substrates were dispersed in ethanol, and TEM copper grids were dipped into the solution and analyzed. The structural properties were examined using Nanalytical Xpert PRO PW 3040/60 X-ray diffractometer (XRD) with a Cu Kα (λ = 0.154 nm) monochromated radiation source.

The photoluminescence (PL) properties of the nanostructures were investigated using a spectrometer (Jobin Yvon NanoLog FLS-32) at room temperature. The emission was detected with a Jobin-Yvon PMT detector. In order to explain the new features in the PL spectra of these FeSi nanostructures, band structure and density of states (DOS) calculations were undertaken.

We carried out density functional theory simulations using the generalized gradient approximation (GGA) and the local density approximation (LDA) [19] for the exchange and correlation functional, as implemented in the CASTEP code [20]. The interaction between the ionic cores and the valence electrons is described using a pseudo potential of Vanderbilt [21]. The Brillouin zone of FeSi is sampled using the scheme of Monkhorst and Pack [22]. This kind of 8-point sampling method gives a good convergence to the total energy calculations. A kinetic energy cut-off of 300 eV was used for the plane wave expansion of the wavefunctions. The positions of all atoms in the defective nanowires were relaxed using the conjugate gradient algorithm with a tolerance of 2 x 10⁻⁵ eV for maximal change in total energy. Calculations converged when the residual forces were less than 0.05 eV/Å. The electronic states were occupied in accordance with the Fermi distribution function using a Fermi smearing parameter of kF = 0.20 eV.

3. Results and discussion

3.1. Morphology and structural properties of FeSi nanowires

Fig. 1 shows a scanning electron microscopy (SEM) image of the bundles of interfiber fibrous nanostructures. The diameter of a single strand ranged from 20 nm to 100 nm with a single strand composed of 7–8 single FeSi fibres. The mingling of the FeSi nanowires could be a result of an indeterminate growth direction and the presence of many growth nuclei at the surface of the Si substrate. The other reason for non-directionality is that the nanowires have a diameter of about 8 nm. This is too thin compared to the roughness of the Si surface which of the order of 1000 nm. This roughness influences the meandering morphology of the subsequent FeSi/UiO core–shell nanowires. Because no catalyst was used, Si is inevitably one of the candidates in the fibres. Previous synthesis of FeSi without catalyst reports presence of amorphous SiO₂ [5]. One notes that the nanofibres in Fig. 1 are outstandingly bright against the substrate background. This over-brightness could be due to electron charging effect owing to the loose attachments of the fibres to the grounded substrate. However, if the secondary electron detector also detected photons as a result of the electron-FeSi photon interaction and if the fibres are well attached to the ground, the over-brightness could be due to cathodoluminescence (CL) from the FeSi nano-fibres. CL spectra could not be performed due to the limitations of the instrument.

A high resolution transmission electron microscopy (HRTEM) micrograph is shown in Fig. 2. The nanostructures appear to have core-shell structures and are semi-crystalline indicating that the nanostructures composed of an amorphous network and crystalline region. The core is dense and crystalline, whereas the shell is amorphous. Szczep et al. [1] found that when they performed surface characterization of the individual FeSi nanowires with X-ray Photoelectron Spectroscopy (XPS), that the surface oxide layer formed on the nanowires was in fact not Fe₂O₃, but SiO₂, which was consistent with the fact that FeSi will develop a thin silicon oxide layer during exposure to air. In our case, the amorphous shell is in fact Si as shown in the localised energy dispersive spectroscopy (EDS) performed at the core and around the shell in Fig. 2(c) and (d). The few peaks of Fe in the local EDS for the shell could be small contributions from core.

X-ray diffraction was performed on the deposited nanostructures. All the observed diffraction peaks are indexed to FeSi (Fig. 3), which has a cubic structure with a lattice constant of 4.486 Å (space group P4₃, Pearson symbol cP8, structure type FeSi, Z = 4, JCPDS PDF 36-1488, 89-1298 and 89-2077). In order to estimate the crystallite size, the Debye-Scherrer [23] method is employed, which states that the peak width 2θ(2θ) is inversely proportional to the crystallite size (L) i.e.

\[
B = \frac{0.94\lambda}{L \cos\theta}
\]

where λ is the X-ray wavelength and θ is the Bragg angle for the individual peaks starting from 2θ = 28° to 2θ = 61°. The crystallite sizes were found to range from 13.9 nm to 131.1 nm (Table 1). In addition to the Debye-Scherrer method, a second method for estimating the crystallite size was used, namely the Williamson-Hall Method [24]. This method accounts for both strain and crystallite
size of the material i.e.

$$B = \frac{C}{\tan \theta} - \frac{C}{\cos \theta}$$

where \(C\) is the strain component. This calculated crystallite size differs significantly from the Debye-Scherrer crystallite size as shown in Table 1, but the Williamson-Hall calculation agrees with

the HRTEM measurements. For all the planes the estimated crystallite size is 1.93 nm but when only the FeSi main peaks are considered, the crystallite diameter by the Williamson-Hall plot, is 7.75 nm compared to HRTEM measurement of about 8.00 nm. The Williamson-Hall provided a more accurate estimation of the crystallite sizes, which agrees with our TEM results, thus proving to be a more reliable method.

Fig. 4 shows that the 110 plane is an outlier and does not follow a pattern similar to the other planes. The observed 110 plane might be resulting from contributions from the silicon substrates.

3.2. Photoluminescence of the FeSi/Si core-shell nanofibres

The FeSi2 phase's photoluminescence properties have been studied and it has been reported that the material, with a band gap of 0.8 eV, emits at a wavelength of 1.54 nm (0.81 eV) [25-31]. To the best of our knowledge photoluminescence properties of the FeSi have never been reported. Therefore, in this study we report for the first time on the photoluminescence properties of FeSi. By using the excitation energy of 325 nm (3.8 eV), we observe an emission peak around 410 nm (3.02 eV), 1062 nm (1.16 eV), 1414 nm (0.88 eV) and 1717 nm (0.70 eV). There is a strong PL peak between 600 nm and 700 nm. This peak may be as a result of (1) quantum confinement due to the typical crystallite size of about 8 nm of the FeSi core as well as the thinner than 5 nm Si shell and (2) intra-band transitions due to impurity and vacancy defect states in the FeSi structure.

On the nano-Si shell, it is known that bulk Si with a band gap of 1.1 eV emits at a wavelength of 1100 nm in conformity with band-to-band transition in Si. Nano-Si has been observed to show a blue
Table 1
Results from Debye–Scherrer model and the Williamson–Hall plot for crystallite sizes and strains in the nano-fibres.

<table>
<thead>
<tr>
<th>2θ (Degrees)</th>
<th>Miller planes</th>
<th>Debye–Scherrer (L) (nm)</th>
<th>Williamson–Hall (L) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>110</td>
<td>83.6</td>
<td>L e values when all peaks are considered</td>
</tr>
<tr>
<td>34.5</td>
<td>111</td>
<td>62.1</td>
<td>L e values when (1 1 0) peaks is excluded</td>
</tr>
<tr>
<td>40</td>
<td>200</td>
<td>48.9</td>
<td>e</td>
</tr>
<tr>
<td>45</td>
<td>210</td>
<td>68.1</td>
<td>e</td>
</tr>
<tr>
<td>49.6</td>
<td>211</td>
<td>13.9</td>
<td>e</td>
</tr>
<tr>
<td>51.8</td>
<td>221</td>
<td>13.1</td>
<td>e</td>
</tr>
</tbody>
</table>

![Figure 4: Williamson–Hall plot.](image)

The blue shift from 1100 nm to between 600 nm and 700 nm was calculated to be too big for a crystallite size of 5 nm. For instance, from Efros and Efros [32], the change of energy of the emitted photons due to strong, moderate and weak quantum confinement are respectively given as

\[ \Delta E = \frac{\hbar^2}{2m_e R^2} \]  

(strong confinement)  

(3)

\[ \Delta E = \frac{\hbar^2}{2m_e R^2} \]  

(weak confinement)  

(4)

\[ \Delta E = \frac{\hbar^2}{2m_e R^2} \]  

(very small nanoclusters)  

(5)

\[ \Delta E = \frac{\hbar^2}{2m_e R^2} \left( \frac{1}{R} + 0.264 \right) \]

where \( \mu^* \) is the reduced mass of the electron-hole pair (exciton) which is usually taken to be 2m_e (with m_e being the mass of the electron), R is the crystallite radius, \( M = m_p + m_e \) is the relative dielectric constant of the medium and m_p is the mass of the proton in hydrogen. Performing a simple calculation for the typical nanofibres presented here, one finds that the 1100 nm peak for bulk Si should shift by 0.1 eV (112 nm) for strong quantum confinement and much less than that value for moderate and weak confinement. According to quantum confinement theories, the new peak should shift from 1100 nm to 988 nm. The quantum confinement theoretical equations therefore are not able to singly account for the major shift of the 1100 nm peak down to between 600 nm and 700 nm. It is possible therefore that the second reason for intra-band transitions due to defects is an added contribution to this blue shift.

![Figure 5: (a) Visible range photoluminescence spectrum for FeSi nano-fibres excited by a light source of wavelength 325 nm. (b) Visible and IR photoluminescence spectra showing the quality of IR spectra compared to the visible range against high background noise.](image)

We therefore explain the second contribution using the band structures of FeSi calculated using LDA and GGA. Band structure and electron density of states calculations performed on the FeSi system are presented in Fig. 6. We attribute the energy dispersion curves of \( E > 3 \text{ eV} \) to Si (3p); and \( -6 \text{ eV} < E < +3 \text{ eV} \) to Fe–Si hybridization; those curves of energy in the range \( -3 \text{ eV} < E < +3 \text{ eV} \) to Fe (3d) electrons and those below \(-6 \text{ eV}\) to Si (3s and 3p) electronic states. The Fe and Si labels are clearly marked in Fig. 6(a) and (b). This assignment is in agreement with the previous calculations [33]. The density of states in (b) show that while most of the electrons belong to Fe (3d) close to the Fermi level, a good proportion are in the valence band confirming the Mott insulator behaviour in FeSi. For clarity, we have labelled the energy levels differently in this paper and these appear in Fig. 6(c). Those bands with predominant Fe 3d are identified by
Fig. 6. Assignments of the band structure (a) and DOS (b) to the Si (3p), Fe (3d), Fe–Si hybridization and Si (3s and 3p) electron states. In (c) we consider the gamma, G symmetry line and introduce our labels for explanation of our PL results in Fig. 5. In (d) the 3.2 eV (410 nm) photon emission is due to the 3s excitation from Si (3p) electron states down to the Fe (3d) level.

Table 2
A summary of the transitions in FeSi from DFT and the measured amplitudes from PL with their associated probabilities.

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Transition description</th>
<th>Transition probability (theory)</th>
<th>Amplitude, A (inset)</th>
<th>Probability (inset)A(0)=A</th>
</tr>
</thead>
<tbody>
<tr>
<td>488 nm (3.02 eV)</td>
<td>&lt;Si 3p Fe 3d^2&gt;</td>
<td>&lt;i&lt;Si 3p Fe 3d^2&gt;^2&gt;</td>
<td>1.000</td>
<td>0.025</td>
</tr>
<tr>
<td>514 nm (2.96 eV)</td>
<td>&lt;Si 3p Fe 3d^2&gt;</td>
<td>&lt;i&lt;Si 3p Fe 3d^2&gt;^2&gt;</td>
<td>0.864</td>
<td>0.018</td>
</tr>
<tr>
<td>588 nm (2.59 eV)</td>
<td>&lt;Si 3p Fe 3d^2&gt;</td>
<td>&lt;i&lt;Si 3p Fe 3d^2&gt;^2&gt;</td>
<td>4.966</td>
<td>0.019</td>
</tr>
<tr>
<td>1062 nm (1.18 eV)</td>
<td>&lt;Si 3p Fe 3d^2&gt;</td>
<td>&lt;i&lt;Si 3p Fe 3d^2&gt;^2&gt;</td>
<td>1.048</td>
<td>0.031</td>
</tr>
<tr>
<td>1414 nm (0.88 eV)</td>
<td>&lt;Si 3p Fe 3d^2&gt;</td>
<td>&lt;i&lt;Si 3p Fe 3d^2&gt;^2&gt;</td>
<td>0.440</td>
<td>0.019</td>
</tr>
</tbody>
</table>

our labels Fe 3d^2 to Fe 3d^2 where positive exponent refers to conduction band and negative refers to valence band and those of Si 3s, 3p orbital character are specified by our label Si 3s^1-3p^1, Si 3s^1-3p^1, Si 3s^1-3p^1, and Si 3s^1-3p^1. The lowest grouping of four bands evolves essentially from the Si (3s) states (Si 3s^1+3p^1, Si 3s^1+3p^1, Si 3s^1+3p^1, and Si 3s^1+3p^1). The bands above these at slightly higher (~6 to ~3 eV) energies reflect Si–Fe hybridization effects and their mixed character has been distinguished by labels Si 3s^1+3p^1, Si 3s^1+3p^1, Si 3s^1+3p^1, and Si 3s^1+3p^1. The Fe 3d bands span the adjoining energy range from almost ~3 to ~3 eV, while hybridized bands with enhanced Si 3p character reappear near higher energies near the top of Fig. 5 with our labels Si 3p^3 to above Si 3p^3.

In as far as the new photoluminescence feature appearing at ~410 nm, we consider the gamma, G line of symmetry which we have zoomed-in to Fig. 6(c) and our corresponding labels. The gamma point (where k||=0) being the centre of the Brillouin zone is appropriate when the photon wavelength, l, of excitation (in this case 325 nm) is much longer than the lattice parameter of the FeSi system (~0.274 nm). One of the transitions extracted from the band structure in Fig. 6 to explain the luminescence feature at a wavelength of 410 nm is one of those electrons de-exciting from Si (3p) level down to the Fe (3d) as shown in Fig. 6(d). The other IR features at 1062 nm (~3.4 eV), 1414 nm (~0.88 eV) and 1772 nm (~0.71 eV) are assigned to the transition ~Fe 3d^2 Fe 3d^2 Fe 3d^1>, ~Fe 3d^2 Fe 3d^1>, and ~Fe 3d^2 Fe 3d^1> respectively. The probability that these transitions will occur are defined as the square of each operation respectively written as ~i<Fe 3d^2 Fe 3d^2 Fe 3d^1>^2, ~i<Fe 3d^2 Fe 3d^1>^2, and ~i<Fe 3d^2 Fe 3d^1>^2 where the state Fe 3d^3 is equivalent to the Fermi level, E_F. These data compared to the amplitudes of the individual peaks in the PL spectra along with all the possible transitions that have been observed by our PL spectrometer in Table 2. This table shows that the most probable emission from FeSi is the IR emission at 1032 nm which seems equivalent to the YAG emission at 1064 nm.
As already noted about the density of states, the photoluminescence feature at a wavelength of 410 nm, however, seems not to come from the majority of the electrons but from only those that are above the Fermi energy level. More reliable assignment has been accomplished via the band structure in (a); the DOS in (b) only gives an idea of how many electron in a single atom are involved and this can give an indication of the probability of luminescence and hence the magnitude of intensity expected in a typical experimental measurement. In this case one can clearly see why the 410 nm feature has not been reported to date. The features around Fermi level and those just below that level, being contributed from the majority of the electrons, which leads to an emission at around 1540 nm for FeSi, has been widely reported. In the present case, FeSi shows peaks at 1062 nm, 1414 nm and 1772 nm in this same range. Given large excitation intensities, FeSi can then be employed in UV sources and IR lasers apart from the microwave generators that have so far been reported.

The above inter-band transition assignments have been carried for FeSi for the first time; however similar work has been performed on gold [34].

3.3. Fourier transform infrared spectroscopy and Raman spectroscopy of the FeSi core-shell nanofibres

It must be mentioned that the band to band transitions reveal a band gap of 0.13 eV as an average between 0.21 eV from GGA approximation and 0.04 eV from the LDA approximations. These band to band transitions could not be measured from the PL due to the limitations of the detector as 0.13 eV translates to 12 µm. In order to observe these band to band absorptions, FTIR was performed on the FeSi/Si fibre sample. The FTIR spectrum is given in Fig. 7. Immediately one sees two major absorption peaks at 783 cm⁻¹ (0.09 eV) and 1067 cm⁻¹ (0.13 eV). The former is a bending vibration of the Fe-Si bond, as theoretically referred to as the transverse-optical (TO) phonon whereas the latter can be assigned to the longitudinal optical (LO) FeSi (stretching mode) phonon. The latter absorption at 0.13 eV agrees perfectly with the band gap energy from our calculations (0.13 eV) as averaged from GGA and LDA as well as in agreement with previous observations, as stated in the preceding introduction section. The FTIR spectrum also reveals other minor inter-band absorptions which could be due to small defects and vacancies in the FeSi lattice.

The Si that forms the shell material is not amorphous. This fact has been confirmed by Raman spectroscopy as shown in Fig. 7(b). Amorphous Si shows a peak at 480 cm⁻¹ while crystalline Si has a peak at 520 cm⁻¹ [36]. The Raman spectrum from our FeSi/Si fibres show a broad peak between these two extremes centred 400 cm⁻¹. Therefore we can conclude that this peak signifies nano-crystalline Si rather than amorphous Si.

4. Conclusions

We have successfully obtained new FeSi core-shell nanofibres. TEM confirms the shell to be somewhat amorphous while the core is dense and largely crystalline. XRD does point to the stoichiometric FeSi with the usual peaks indexed to FeSi which has a cubic structure with a lattice constant of 4.496 Å (space group P2₁₃, Pearson symbol pPb, structure type FeSi, Z=4, CPDF PDF 76-1748, 88-1297 and 89-2677). We have employed both the Delye-Scherer model and the Williamson-Hall method to determine the crystallite sizes and the strain in the fibres. The Delye model suggests the crystallite size ranges from 13 nm to 130 nm, where the Williamson-Hall plot yields a size of about 8 nm and a strain of 0.04. The latter is more agreeable with HRTEM of a single core-shell nano-fibre whose core is 4 nm in diameter and a shell of about 10 nm from edge to edge.

Photoluminescence has revealed new features at a wavelength of about 410 nm, 1062 nm, 1414 nm and 1772 nm. This has been ascribed by ab initio calculation of electronic band structure and density of states to the de-excitation of the Si (3p) electron to the Fe (3d) ground state. The DOS has helped explain why this feature has not been observed to date. By the DOS calculation, we have found that this feature comes from minority electrons. We then have shown that FeSi cannot only be used in infrared application but also can be a UV emitter.

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References
