CHAPTER 1

INTRODUCTION

1.1 Background

One dimensional (1D) semiconductor nanostructures such as nanowires and nanorods, have attracted more and more attention recently, due to their applications in mesoscopic physics and in the building blocks of nanoscale devices [1-3]. These 1D semiconductor nanostructure materials mostly Si based nanorods and nanowires, have had showed their excellent structural [4-6], optical [7-9] and electrical [10] properties. These superior properties have made the Si based nanowires achieved excellent performance in solar cells, lithium ion batteries and thermoelectric devices [11-13]. However, due to their intrinsic material properties such as weak mechanical stability and associated side reactions due to un-protected surfaces, single-phased nanomaterials could not fulfil the requirements [14, 15]. Hot-wire (HW) CVD is one of the most promising techniques for low temperature, high deposition rate and large-area deposition for SiC based thin films materials [16-18]. The HWCVD has demonstrated a low-temperature deposition (around 300 °C) of cubic SiC thin films [19, 20]. In the HWCVD process, decomposition of SiH₄/CH₄ molecules on the filament surfaces at a filament temperature above 2000 °C sufficiently generates higher densities of growth precursors (SiH₃ and CH₃) than plasma processes. Moreover, decomposition of high density of H radicals plays an important role in the low-temperature growth of nanocrystalline SiC thin films [21, 22]. Recent studies on the growth of Si nanowires by HWCVD demonstrated that HWCVD is a promising technique for the growth of novel one-dimensional Si based nanostructures owing to the lower production cost and largescale production capability [23-25]. The HWCVD has also been proven to enhance the

growth rate of Si nanowires [26, 27]. Deposition by HWCVD when compared to plasma enhanced CVD (PECVD) does not utilized high energy ions leads to a better crystallinity of the nanowires [28, 29]. In this work, we studied a low temperature growth of the nickel (Ni)-catalyzed NiSi/SiC core-shell nanowires prepared by HWCVD at different deposition pressures. The effects of the deposition pressure on the growth and structural property of these core-shell nanowires were investigated mainly using field emission scanning electron microscopy (FESEM) + energy dispersive X-ray (EDX), high resolution transmission electron microscopy (HRTEM) + scanning transmission electron microscopy (STEM), micro-Raman scattering spectroscopy, Xray diffraction (XRD) and photoluminescence (PL) spectroscopy. The morphological change of the nanowires was found to be significant for the samples prepared at 3 mbar. The effects of the deposition pressure on the growth and structural properties of these core-shell nanowires are also reported.

1.2 Motivation of this work

SiC are wide band gap semiconductor, high electric field at breakdown, high electron velocity, high thermal stability and high thermal conductivity. Therefore, silicon carbide (SiC) nanowires would be favourable for high temperature, high power, and in harsh environments applications [30]. This leads to a motivation incorporate the SiC nanostructures or nanowires into the Si nanowires as a core-shell nanowire. Hybrid nanostructures such as core-shell nanowires have advantages to overcome the limitations of single-phased nanomaterials. NiSi/SiC, a hybrid core-shell nanowire is expected to further enhance the properties of the core-shell nanowires in their mechanical, chemical resistivity, thermal stability and in a wide range of optical properties [31, 32].

Furthermore, highly metallic properties of single crystalline NiSi nanowires could be used as a 1D electrode to enhance the efficiencies of electron transfer between current collector support and individual electrode material, and ion transport to the electrode [33-36].

1.3 Objectives

The objectives of this work are as follows:

1) To study the effects of deposition pressure on the growth of NiSi/SiC core-shell nanowires by HWCVD,

2) To study the growth mechanism of the NiSi/SiC core-shell nanowires by HWCVD.

1.4 Report overview

This report is organized into five chapters:

| Chapter | Details |
|---------|--|
| 1 | Provides an introduction of NiSi/SiC core-shell nanowires, objectives, |
| | motivation of this work and also an outline of the report. |
| 2 | Focuses on some review of other works. The advantages of nickel |
| | silicide, silicon carbide and also hybrid structure of nanowires. Also |
| | discuss the importance of using Hot-Wire Chemical Vapour |
| | Deposition system. |
| 3 | Experimental procedure and setup is further presented. A clearer view |
| | of how the system works is also discussed. |
| 4 | Results, analysis and also discussion are presented here in chapter 4. |

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| | Here, the more thorough and further analysis is discussed. Clarified |
|---|--|
| | result can be seen here in this chapter. |
| 5 | Summarizes the work done in this project. A conclusion of this work is |
| | described here. |
| | |

CHAPTER 2

LITERATURE REVIEW

2.1 Nanotechnology and Nanomaterials

The fabrication, design and application of nanomaterials and nanostructures are known as nanotechnology. It includes study of the basic principals of physical properties and phenomena of nanostructures and nanomaterials (nanoscience). Besides that, it also covers the processing of their applications [37]. Nanostructures sizes are ranging from several to several hundred nanometers $(10^9 - 10^7 \text{ m})$. The dimensions of the nanostructures extend from zero dimensional (nanoparticle and quantum dot) to one dimensional (nanowire and nanotube), and two dimensional thin film structures. Metal nanoparticles, SiNWs, carbon nanotubes, metal oxide nanorods and also graphene are some examples of nanomaterials which have generated a huge amount of research. Nanomaterials exhibit structural, optical and electrical properties which are distinctively different from their bulk or even micron-scaled of the materials that causes interest in them. Au nanoparticles for examples reveal surface plasmon resonance [38] and Si quantum dots emit visible light [39], which are totally absent in their bulk materials. Nanomaterials study is always aimed at discovering their unique properties and behaviours to build up the fundamental understanding of these materials. The research on these nanomaterials is further developed to design and integrate them into devices to merge the nanomaterials into nanotechnology development.

2.2 Nickel Silicide

Silicide is a compound of Si with an electropositive component [40]. They are commonly used in silicon-based microelectronics since they can reduce the resistivity of gate and local interconnect metallization. Some popular silicide candidates, such as CoSi₂ and TiSi₂, however have some limitations. TiSi₂ for example showed line width dependent sheet resistance and has difficulty in transformation from C49 phase to the low resistive C54 phase. Compared to TiSi₂, CoSi₂ consumes more Si [41]. Low resistivity, lower Si consumption and lower formation temperatures are some advantages that present in nickel silicide. It is a promising material to replace those silicde materials [42]. Recently, Ni silicide has appeared as an ideal electrical contact materials to the source and provide drain and gate in complementary metal oxide silicon devices. They also exhibit an excellent scaling down performance [43].

Several NiSi nanowire growths have been reported. A unique nanowire growth mechanism that the NiSi nanowire follows is the metal-induced growth (MIG) method [40]. By sputtering method, the highly linear nanowires were grown by solid-state reaction of Ni and Si at 575 °C. For applying nanowires as nanoscale interconnections with little or no damage on the fabricated structures, low-temperature process is desirable. Growing an epitaxial Si film, which adopts the concepts of solid phase crystallization and solid phase epitaxy is one of the great advantages of MIG. As a seed layer, the deposited metal catalyst film, will interacts with sputtered Si to form a silicide layer, which grow Si film above it. In MIG method, Ni and Co are common metal catalysts. The small lattice mismatch of CoSi₂ or NiSi₂ provides an excellent precursor layer to grow an epitaxial Si film as well as to render a spontaneously formed good ohmic contact layer. MIG method is a fast Si crystallization method at a low

temperature processing and would nurture versatile approaches in Si application. Figure 2.2.1 presented NiSi nanowire by MIG growth from Scanning Electron Microscopy (SEM) results. In Figure 2.2.2, we can see the XRD spectrums of the Ni silicide nanowires grown on a Si substrate and a tungsten plate.



Figure 2.2.1 Scanning electron microscopy (SEM) observation of the nanowire growth. (a) Ni layer was grooved by heating. The concave and convex regions were formed. (b) Ni silicide clusters were formed by reaction of Ni and Si. (c) Ni silicide fibers were formed. (d)Nanowires were grown. Some nanowires were segregated from a fiber. (Kim et al., 2005b. 2005)



Figure 2.2.2 XRD spectrums of the Ni silicide nanowires grown on a Si substrate and a tungsten plate. (Kim et al., 2008b. 2008)

2.3 Silicon Carbide

The study of one-dimensional nanomaterials, since the introduction of carbon nanotubes in 1992, that includes metallic, magnetic, semiconducting and oxide compounds has drawn considerable interest, especially the nanowires (NW), nanobelts and nanorods [43]. Silicon nanowires (SiNWs) are the most explored among the numerous nanomaterials, since its discovery by Wagner and Ellis in 1964 [44].

Silicon carbide (SiC) is a wide band gap semiconductor. Some great features that silicon carbide possesses are high saturation drift velocity, high breakdown field strength, and high thermal conductivity [44]. These superb physical properties make

SiC a favourable semiconductor material for the fabrication of electronic devices [45]. Moreover, as an important wide band gap semiconductor with high electron mobility, cubic silicon carbide (3C-SiC) nanowires would be suitable for applications in high power, high temperature, and high frequency nanoelectronic devices [46]. Besides, SiC wires reveal good field-emitting properties [47].

A lot of techniques have been developed to synthesize SiC nanorods or nanowires. SiC nanorods were first synthesis by Dai et al. [48] and succeeded in 1995 through the reaction of carbon nanotubes with SiO or Si + I₂. Synthesis of h-SiC by Meng et al. [49] nanorods using carbothermal reduction reaction, and Zhou et al. [50] fabricated SiC nanowires by the hot filament CVD method. Recently, Li et al. [51] synthesized SiC nanowires by using a SiC rod as the anode to arc-discharge. Despite that, because these methods use various reactants and require high temperatures reactions (usually above 1200 °C), there are several difficulties at reaction process to synthesized SiC nanowires at low temperatures, but are applying high pressure [52]. Syntheses of SiC nanowires using metal as a catalyst have also been reported [53, 54]. Figure 2.3 shows an example of SEM image of the SiC nanowires grown on a SiC thin film also XRD spectrum of SiC nanowires grown on a Si (111) substrate.



Figure 2.3 a) SEM image of the SiC nanowires grown on a SiC thin film. b) XRD spectrum of SiC nanowires grown on a Si (111) substrate. (J.P. Alper et al., 230. 2013)

2.4 Hybrid Nanostructure

The optical, electrical, and chemical properties of semiconductor nanostructures over the last two decades have been studied intensively. Semiconductor nanostructures have been shown to have unique properties, compared to bulk. Due to their large surface to volume ratio, they strongly influence the properties of the materials, effects at the surfaces, and/or interfaces in multi-component nanomaterials. For a better control over exciton creation, charge separation, and recombination, the energy levels within the materials can be modified. By transport, it helps in controlling the composition of these materials, its size, and also the shape of the materials.

It is desirable to have the combination of different functionalities, by the assembly of two or more nanostructured components with precise control over the size, shape, composition, and also spatial orientation. For advanced properties that can arise independent of the single-component materials, they are highly demanded. Engineering hybrid multi component nanostructures draws on the vast array of synthetic techniques now at our disposal to assemble nanocrystals with very different properties such as a

semiconductor nanocrystal can be combined with a metal in such a way that the hybrid structure can be tailored to a specific application.

2.5 Hot –Wire Chemical Vapor Deposition (HWCVD)

To develop Si/SiC core-shell nanowires, low pressure chemical vapour deposition (LPCVD) method has widely been used [55]. However, low pressure chemical vapour deposition (LPCVD) has some disadvantages that include lower deposition rates and needed high temperature usually above 600 °C for the process. The deposition rate is controlled by pressure and temperature [56]. Hence, other techniques such as hot-wire chemical vapour deposition (HW-CVD) also can be used in producing Si/SiC core-shell nanowires.

Hot Wire Chemical Vapor Deposition (HWCVD) is a deposition technique that encompasses thermal decomposition of precursor gases at the surface of resistively heated filament (usually Tungsten) to form radicals. These radicals form other classes and get adsorbed on the heated substrate [57].

Hot-Wire Chemical Vapor Deposition (HWCVD) are currently being preferred for the fabrication of Si/SiC core-shell nanowires due to the lower production cost and large –scale production capability making these methods more attractive for industrial applications.These techniques also have been proven to enhance the growth rate of SiNWs besides have advantages of low-temperature growth processess [19]. In addition, HWCVD provides an ion-free deposition by catalytical decomposition of the source gas using a catalyzer usually tungsten [18] is comparatively a better technique for the growth of Si/SiC core- shell (NWs).

CHAPTER 3

METHODOLOGIES

3.1 Hot-Wire Chemical Vapour Deposition Setup

The schematic of the home-built hot-wire CVD system is illustrated in Figure 3.1(a). The system consists of six parts; the CVD reactor, plasma generator, hot-wire power supply, vacuum system, gas line management and heating elements.



(a)



(b)



(c)

Figure 3.1 (a) Schematic diagram of the dual modes of plasma and hot-wire assisted CVD system. (b) Photograph of the home-built hot-wire CVD system. (c) Substrate place in the home-built hot-wire CVD system.

3.1.1 CVD Reactor

Figure 3.1.1 shows the photograph of CVD reactor. The CVD reactor of this deposition system consists of a cylindrical stainless steel chamber. The CVD reactor is well-sealed with Viton o-rings and is directly connected to a vacuum pump for evacuation. The connecting tube has an air admittance valve for venting purposes. A glass viewport on the body of the reactor is used for viewing interior of the reactor. It also acts as a window for the optical pyrometer used to determine the filament temperature. A stainless steel made substrate holder is designed to hold substrates with dimensions of 2.5 x 2.5 cm. The heater rod and thermocouple are attached to the substrate holder which is grounded to the earth and isolated from the body of the reactor by Quartz stands.



Figure 3.1.1 Photograph of the CVD reactor.

3.1.2 Plasma Generator

In the CVD reactor, a stainless steel electrode-cum-gas showerhead is installed with the gas inlet tube and is placed at a distance of 5 cm from the substrate holder. The thickness and diameter of the electrode is 1 cm and 10 cm, respectively. The electrode is decorated with cone-shaped holes. The inlet and outlet diameter of the hole is 2.2 mm and 1.0 mm, respectively, while the distance between holes is 1.0 cm. Precursor gas can be dispersed uniformly from these holes. The electrode is powered for plasma generation. It is connected to the rf generator via an impedance matching network. The plasma is generated between the powered electrode and grounded substrate holder by applying rf power. An impedance matching network is employed to match the load impedance of plasma to the impedance of the DC generator, so that the reflected power from plasma to rf generator can be minimized.



Figure 3.1.2 Photograph of rf generator used.

3.1.3 Hot-Wire Power Supply

Tungsten wire (purity of 99.95 %) is coiled to form a solenoid shaped filament with ~30 coils of diameter 2 mm and length of ~2 cm. This filament coil serves as the hot filament for the evaporation of metal catalyst and decomposition of source gas. The tungsten filament is placed on a filament holder, which is connected to a power supply. The power supply consists of a voltage regulator (IBC voltage regulator 1P-1kVA) with voltage ranging from 0 – 250 V and a step down transformer. The transformer steps down the output voltage to a range of 0 – 20 V and maximum current of 60 A. By regulating the voltage supplied to the tungsten filament, different filament temperatures, T_f can be controlled for deposition. An ammeter is connected with the voltage supply to measure the current flow through the tungsten filament. T_f is measured by a pyrometer (Reytek, Raynger, 3i). The detector of the pyrometer is stimulated by the incoming infrared energy and produces a signal to the circuitry, which will process the signal and compute the T_f . The tungsten filament is pre-heated to remove surface contaminations such as carbon and other metallic elements before deposition. Pre-heat treatment is carried out for 10 minutes at T_f ~1600 °C in H₂ with flow rate of 100 sccm.





(a)

16



(b)



(c)

Figure 3.1.3 (a) Photograph of (a) plasma treatment and hot-wire decompose silane process. (b) Pyrometer used to measure filament temperature. (c) Temperature of filament taken using pyrometer during deposition process.

3.1.4 Vacuum System

A vacuum pump is a device that removes gas molecules from a sealed volume in order to leave behind partial vacuum. Rotary pump is to expand the volume of a container. To continue evacuating a chamber indefinitely without requiring infinite growth, a compartment of the vacuum can be repeatedly closed off, exhausted, and expanded again. The simplest rotary pump is a circular rotor rotating inside of a larger circular cavity. The centres of these two circles are offset, causing eccentricity. Vanes are allowed to slide into and out of the rotor and seal on all edges, creating vane chambers that do the pumping work. On the intake side of the pump, the vane chambers are increasing in volume and are filled with fluid forced in by the inlet pressure. On the discharge side of the pump, the vane chambers are decreasing in volume, forcing fluid out of the pump. Rotary vacuum pumps can attain pressures as low as 10⁻³ mbar.

3.1.5 Gas Supply

Highly purified SiH₄ (99.9995 %) is used as the precursor gas for the synthesis of SiNWs. H₂ gas with purity of 99.999 % is used to dilute the SiH₄ gas in deposition. In addition to it, H₂ gas also serves as a precursor in H₂ plasma treatment and pre-heating of coiled tungsten filament process. Purified nitrogen (N₂) gas (99.999 %) is mainly used for gas line cleaning, purging and SiH₄ diluting in vacuum pump. The source gas tanks are stored in a gas room. The SiH₄ gas tank is kept in a secured gas cabinet equipped with a control panel. The source gases are introduced into the CVD reactor through the gas line, which is constructed using 316 L stainless steel tubing (outside diameter of 1/4 in). A check valve is installed in each gas line to prevent the backflow of the source gas. Ball valves are used to open or close the gas line, while metering

valves are used to roughly control the amount of gas flow. The gas flow rate is accurately controlled by using a mass flow controller (MFC) with unit reading of standard cubic centimeters per minute (sccm). The SiH₄ gas flow rate is controlled by an AALBORG MFC in a flow rate range of 0 - 10 sccm. H₂ gas flow rate can be varied from 0 - 200 sccm using an Aalborg Mass Flow Controller GFC with its display meter. Figure 3.1.5 below shows the photograph of gas line in which it is use for the process of deposition. Gas use for deposition process is SiH₄, CH₄ and H₂.



Figure 3.1.5 Photograph of the gas line.

3.1.6 Heating Supply

In order to prepare SiNWs samples, relatively higher substrate temperatures than film deposition are required to melt the metal catalyst or form a metal-Si alloy. Substrate temperature of 450 °C is used. The heating element of the CVD system is constructed based on this temperature requirement. A Watlow Fire Rod SFMH80 A-4183 heater cartridge is employed for substrate heating, which operates within temperature limit of <500 °C. The heater cartridge is clamped in between of the substrate holder, so that heat can be transferred from the stainless steel substrate holder to the substrate. The heater cartridge is connected to a voltage regulator (IBC voltage regulator 1P-1kVA) and a temperature controller (Taishio temperature controller TS-501) in a loop. The electrical power is supplied by the voltage regulator and the substrate temperature is set and controlled by the temperature controller. The temperature controller is connected to a thermocouple (Maltec-T type K thermocouple), installed at the bottom of the substrate in the CVD reactor. The thermocouple is used to directly measure the temperature of the substrate.



Figure 3.1.6 Photograph of voltage regulator

3.2 Substrates Cleaning

Prior to the substrate cleaning, the tools such as tweezers, beakers and Petri disc were cleaned using acetone and dried under N₂ purging. The solvents involved hydrochloric acid (37% HCl, M = 36.49 g/mol, diluted in H₂O₂ and deionized (DI) water in a ratio of 1:1:6), ammonia (25% NH₄OH, M = 17.03 g/mol, diluted in H₂O₂ and DI water in a ratio of 1:1:5). HCl can be used to remove residual metal contaminations, such as Al, Mg and Zn. NH₄OH can be used to remove organic contaminations and dissolved metal (Au, Ag, Cu, Ni, Cd, Co and Cr) contaminations.

Glass substrates were cleaned using decon 90, acetone (C_3H_6O , M = 58.08 g/mol), ethanol (C_2H_5OH , M = 46.07 g/mol). The glass substrates were immersed in a beaker containing decon 90 solution and sonicated in ultrasonic bath for 20 minutes to remove oil and gross dirt contaminations. This was followed by rinsing in acetone; ethanol and DI water subsequently to remove organic impurities such as the hydrocarbon dried by N₂ purging.



Figure 3.2 Photograph of glass substrate that has been cleaned

3.3 Pre-Heating of Filament

The tungsten filament is pre-heated to remove surface contaminations such as carbon and other metallic elements before deposition. Pre-heat treatment is carried out for 10 minutes at $T_f \sim 1600$ °C in H₂ with flow rate of 100 sccm. Both for Ni evaporation and deposition process required a pre-heated tungsten filament. Figure 3.3 (a) shows the pre-heated tungsten filament and Figure 3.3 (b) shows the setup of the filament, hold by the filament holder.



Before pre-heating



After pre-heating

Figure 3.3 Photograph of (a) Filament before and after heated. (b) Setup filament for pre-heating of filament. Filament is place in a filament holder.



Figure 3.3 (b) Photograph of setup of filament for nickel evaporation and deposition processes. Filament is place in a filament holder.

3.4 Ni Evaporation

Samples were prepared by Ni evaporation using heated tungsten filament. Ni foil (1 mm x 4 mm) which was tightly hung on a coiled filament is used as a source of evaporation. The Ni was evaporated at a filament temperature ~ 1600 °C in a H₂ flow rates of 100 sccm on a heated substrate temperature of 150 °C. The HW voltage supply used for Ni evaporation is 150 V for 5 minutes. Figure 3.4 (a) shows the substrate holder where all the substrate is place for Ni evaporation process while Figure 3.4 (b) shows the Ni coated on glass substrates.



(a)



(b)

Figure 3.4 Photograph of (a) Substrate holder, where substrate is place for Ni evaporation process and also deposition process. (b) Ni coated on glass substrate.

3.5 Deposition Process

NiSi/SiC core-shell nanowires were prepared on Ni coated glass substrates by a home-built HWCVD system. The Ni film thickness about 30 ± 5 nm was deposited on the heated glass substrates in a vacuum condition. Prior to deposition, the Ni films were treated by atomic hydrogen plasma for 10 minutes in order to form metal nano-islands. The substrate temperature, pressure, hydrogen flow-rate and radio-frequency (rf) power were fixed at 450 °C, 0.75 mbar, 100 sccm and 5 W respectively. During the deposition, the filament temperature and substrate temperature were fixed at 1900 and 450 °C respectively. The filament temperature was measured using a pyrometer model Reytek, Raynger 3i. The filament to substrate distance was fixed at 2 cm. The SiH₄, CH₄ and H₂ flow-rates were fixed at 1, 2 and 100 sccm respectively. The deposition pressure was varied from 1 to 3 mbar. The deposition time was fixed 5 minutes.



Figure 3.5 (a) Plasma treatment process to form Ni nano-island (b) Decomposition of gas recursors (SiH₄, CH₄, H₂) during deposition process.

3.6 Characterization Technique

Morphology study for the FESEM images of the nanowires were obtained using a Hitachi SU 8000 SEM at low electron accelerating voltage of 2 kV. Elemental analysis for the EDX spectrum was collected by Oxford Instrument at 15 kV. The working distances for the imaging and EDX were fixed at 8 mm and 15 mm respectively. Microstruture analysis for the TEM and HRTEM images of the nanowires were obtained by means of a TEM (JEOL JEM-2100F) with an accelerating voltage of 200 kV. Elemental analysis and mappings for the EDS elemental mappings of the nanowire were carried out by the STEM/HAADF and Oxford EDS detectors. Crystalline orientation for the XRD spectra were recorded in the 2 range from 20 to 80 ° at a fixed grazing incidence angle of 5 ° using a SIEMENS D5000 Xray diffractometer. The step time and step size of the scanning were fixed to 3 seconds and 0.02° respectively. Phase analysis for Raman spectra of the films were recorded using an InVia Raman microscope with a charge-coupled device detector and a grating of 2400 lines/mm. The argon ion laser with an excitation wavelength and laser power of 514 nm and 10 mW respectively, was used. Optical properties of the same spectrometer for the Raman measurement was used to obtain the PL spectra of the nanowires at room temperature, by selecting the HeCd laser with an excitation wavelength and laser power of 325 nm and 5 mW respectively. Below is the summary of characterization techniques and its details.

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| T 1 : | |
|---------------|--------------------------------------|
| Technique | Details |
| | |
| FESEM | Voltage: 2 kV |
| EDX | Voltage: 15 kV. |
| | Imaging working distances:8 mm |
| | EDX working distance: 15 mm |
| TEM and HRTEM | Voltage: 200 kV |
| EDS | Detectors: STEM/HAADF and Oxford EDS |
| XRD | 2 range: 20 to 80 ° |
| | Grazing incidence angle: 5 ° |
| | Step time: 3 seconds |
| | Step size: 0.02 ° |
| Raman | Detector and grating: 2400 lines/mm |
| | Laser type: Argon ion laser |
| | Excitation wavelength: 514nm |
| | Laser power: 10 mW |
| PL | Laser type: HeCd laser |
| | Excitation wavelength: 325 nm |
| | Laser power: 5 mW |
| | Temperature: Room temperature |

Table 3.4Summary of characterization techniques and its details

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 **FESEM and EDX Elemental Analysis**

Figure 4.1.1 shows the FESEM images of the nanowires prepared by HWCVD at different deposition pressures. The samples prepared at deposition pressure below 2 mbar showed straight nanorods with mostly vertical aligned and randomly distributed on the surface of the sample. The density and diameter of these nanorods increase and decrease respectively for the sample prepared at deposition pressure of 2 mbar. These nanorods showed a better alignment as compared to the samples prepared at deposition pressure below 2 mbar as shown in the insets of each figures. The average length and diameter of these nanorods are about 1.1 ± 0.1 um and 268 ± 2 nm respectively. As the deposition pressure increased to 3 mbar, the sample showed a high density of nanowires randomly distributed on the surface of the sample. The average length and diameter of these nanowires are about 2.6 \pm 0.3 um and 88 \pm 1 nm respectively. The elevation rate for the growth of nanowire with an increase in deposition pressure could be relates to the hydrogen etching effect. Increase in deposition pressure shorten the mean free path of the radicals thus enhances gas phase reactions. As a result, more H radicals are generated and these energetic atomic H could reduce the thickness of the nanowires by the hydrogen etching effect [21, 22]. The EDX elemental analysis of the nanowires prepared at 3 mbar is shown in Figure 4.1.2. The tip of the nanowire contained of 40.2, 24.4, 30.1 and 5.3 % of Si, C, Ni and O respectively, while the stem of the nanowire contained of 40.7, 25.3, 28.2 and 5.8 % of Si, C, Ni and O respectively. There is about 2

% difference of Ni at the tip and stem of the nanowire. The Ni nano-islands act as a template for the formation of NiSi and to catalyze the growth of these core-shell nanowires subsequently.



Figure 4.1.1 FESEM images of NiSi/SiC core-shell nanowires prepared by HWCVD at different deposition pressures. Insets of each figure represent a high magnification of the FESEM images.



Figure 4.1.2 (a) FESEM image of the NiSi/SiC core-shell nanowires prepared by HWCVD at 3 mbar for EDX elemental analysis. (b) EDX spectrum of the nanowires.

4.2 TEM and HRTEM Analysis

The microstructure of these nanowires was investigated by TEM as shown in Figure 4.2. A single nanowire of the sample prepared at pressure of 3 mbar was selected for this TEM measurement. Figure 4.2(a) shows the TEM image of the nanowire that clearly reveals the core-shell nanowire with the diameters of the core and shell of 22 ± 3 and 105 ± 12 nm respectively. The diameters of the core and shell of the nanowire are consistent along the length of the nanowire. Figure 4.2(b) shows a higher magnification of the TEM image of the nanowire at the sidewall of the nanowire. This image clearly illustrates the core-shell structure of the nanowire which consists of single crystalline core and amorphous shell structures. The HRTEM images of this core-shell structure are shown in Figure 4.2(c) and (d). The microstructure of the shell of nanowire reveals a presence of 3C-SiC nano-crystallites embedded within an amorphous matrix. The size of these nano-crystallites is mostly less than 5 nm. The estimated lattice spacing is about

0.25 nm corresponds to 3C-SiC (111) crystallographic plane [23]. The crystalline structure of the nano-crystallites is further verified by a fast Fourier transform (FFT) as shown in the inset of the figure. The HRTEM scans at the near end of the nanowire sidewall reveals clearly a single crystalline structure of the nanowire. The estimated lattice spacing is about 0.16 nm corresponds to Ni₂Si (301) crystallographic plane [JCPDS card No. 00-065-1507]. This indicates that the core of the Si nanowire actually is formed by NiSi nanowire. The NiSi crystalline structure of the core nanowire is further revealed by a FFT as shown in the inset of the figure. An un-tilted selected area electron diffraction (SAED) image agrees with the NiSi crystalline structure as shown in Figure 4.2(e). Appearance of diffraction rings is due to the amorphous shell of the nanowire.



Figure 4.2 TEM (a, b) and HRTEM (c, d) images of NiSi/SiC core-shell nanowire prepared by HWCVD at deposition pressure of 3 mbar. Insets of (c, d) represent the FFT images of it HRTEM images. (e) SAED of the core nanowire as shown in (d).

4.3 STEM/EDS Mapping Analysis

The microstructure and compositions of the nanowire was further investigated by STEM/EDS mappings as shown in Fig. 4.3. The dark-field of the STEM image as shown in Figure 4.3(a) shows a white layer surrounding the nanowire. This could be due to the formation of SiO_x on the surface of the nanowires which is generally occurs during the growth of nanowires by the CVD technique [24]. The average thickness of the SiO_x layer is about 22 \pm 3 nm. Moreover, the thickness of the SiO_x layer deceases along with the length of the nanowire from the root to the stem. This indicates that the formation of SiO_x happened at the initial stage of the nucleation during the growth of nanowires. The compositions of EDS maps of the nanowire are shown in the Figure 4.3(b) to (e). Obviously, the presence of Ni along the center of the nanowire confirms the formation of the core of the NiSi nanowire. The estimated Ni to Si ratio is about 2. Again, the SiO_x layer surrounding the nanowire is verified by the oxygen (O) map. The carbon (C) map is not clearly presented in this case which could be due to the background of C film of the copper grid. Since the formation of NiSi nanowires has been reported widely by metal induced growth (MIG) at growth temperature to be about 350-550 °C [30, 25], it is considered that the growth of the NiSi/SiC core-shell nanowires in this work follows the same growth mechanism. In this case, the hydrogen plasma treatment is used to form the Ni nano-islands at a lower substrate temperature as compared to the previous reports [30]. The shell of SiC could be followed a radial growth mechanism during the nucleation of the growth NiSi nanowires since there is no tapering been observed on the nanowires.



Figure 4.3 (a) Dark-field of STEM image of NiSi/SiC core-shell nanowire prepared by HWCVD at deposition pressure of 3 mbar. The solid line in (a) shows the growth direction of the nanowire from the root to stem. (b to e) represents each EDS element maps of the core-shell nanowire.

4.4 Raman Analysis

Figure 4.4 shows the Raman spectra of the nanowires prepared by HWCVD at different deposition pressures. These Raman spectra have been divided into three region of Raman shift in order to clearly illustrate the Raman excitation bands. Figure 4.4(a) presented typical Raman excitation bands of Si at 150, 300, 380 - 420 and 480 - 520 cm⁻¹ which associated to transverse acoustic (*TA*), longitudinal acoustic (*LA*), longitudinal optical (*LO*) and transverse optical (*TO*) modes respectively [26, 27]. Moreover, the *TO* band of Si can be further divided into two components: *TO*₁ mode at 480 cm⁻¹ and *TO*₂ mode at 510 cm⁻¹ - 520 cm⁻¹ corresponds to amorphous and crystalline Si phases respectively, as shown in Figure 4.4(b). The Si *TO* band shifted to lower wavenumber with increase in pressure above 1.5 mbar. The shift of the Si *TO*

band indicates a phase transition from crystalline Si to amorphous Si with increase in pressure. This also reveals a decrease in crystallite size of the Si nano-crystallites embedded within an amorphous matrix [28]. Appearance of a Raman band near 500 cm⁻ ¹ for the sample prepared at 2 mbar indicates a formation of small Si nano-crystallites or grain boundaries in the matrix. Obviously, the transition from the crystalline to amorphous Si phase happens in the shell of the nanowires. Figure 4.4(c) shows Raman spectra of the nanowires in the region of 550 - 1200 cm⁻¹. Appearance of Raman excitation band at 980 cm⁻¹ associated to second order of Si TO band (2TO). The Si 2TO band shifted to lower wavenumber accompanying with an appearance of a small Raman band at around 800 cm⁻¹, with increase in deposition pressure. Appearance of the Raman excitation bands at 780 and 910 cm⁻¹ revealing a formation of SiC nanocrystallites embedded within its amorphous matrix [29, 58-59]. The red shifts of the Raman peaks and the broadening of the peaks as compared to the bulk 3C-SiC crystal [60], which may be attributed to the quantum confinement effects of the SiC nanocrystallites [61]. Formation of 3C-SiC nano-crystallites embedded with an amorphous in the shell of the nanowires is supported by the HRTEM as shown in Figure 4.4(c).



Figure 4.4 Raman spectra of NiSi/SiC core-shell nanowires prepared by HWCVD at different deposition pressures. (a-c) represents the Raman spectra of the nanowires in different ranges of Raman shift.

4.5 XRD Analysis

Figure 4.5 shows the XRD pattern of the nanowires prepared by HWCVD at different deposition pressures of 1 and 3 mbar. At deposition pressure of 1 mbar, the XRD pattern of the nanowires only showed appearance of crystalline Si diffraction peaks at 28.4, 47.3, 56.1 and 68.7 ° which correspond to c-Si orientations of (111), (220), (311) and (400) planes respectively [62, 63] .For the nanowires prepared at deposition pressure of 3 mbar, the crystalline NiSi and SiC diffraction peaks started to appear as shown in the figure. The crystalline NiSi peaks located at 39.5, 42.6, 45.6, 45.7, 48.9 and 51.9 ° associated to crystalline Ni₂Si orientations of (112), (103), (211), (013), (020) and (004) plane respectively according to the JCPDS card number of 00-

065-1507. The crystalline SiC peak appears at around 35.7 ° corresponds to crystalline 3C-SiC of (111) plane. The phase of the nanowires changes significantly from the Si to SiC for the deposition pressure increases from 1 to 3 mbar. This agrees with the phase change as shown by the Raman spectra. The transition of the Si phase to SiC phase could be due to the change of the gas phase reaction for the deposition pressure above 1.5 mbar. As reported by Wu et al. [64], that increase in deposition pressure enhances the generation of various radicals especially H radicals. The generation of high density of H radicals enhances the decomposition of CH₄ thus induces the nucleation of SiC nano-crystallites [64, 65].



Figure 4.5 XRD pattern of NiSi/SiC core-shell nanowires prepared by HWCVD at different deposition pressures.

4.6 PL Analysis

Figure 4.6(a) shows the PL spectra of the nanowires prepared by HWCVD at different deposition pressures. These nanowires shows broad PL emission spectra over the photon wavelength from 400 to 800 nm which covering the whole visible region. A typical PL spectrum with the Gaussian decomposition components is shown in Figure 4.6(b). As among the decomposed components, there are two major components centered at around 590 and 665 nm which are dominant in the whole spectrum. Apart from that, there are of two small PL emission bands at around 467 and 529 nm. As demonstrated by previous works, the emission band in the range of 650-750 nm is believed to be originated from the quantum confinement effect of the Si nanocrystallites embedded within an amorphous matrix [66, 67]. The emission bands located at around 590 nm is generally referred to the emission due to the oxygen related defects and/or to surface and interface effects [68, 69]. Formation of Si nano-crystallites at the nc-Si/SiO₂ interface creates an intermediate state for electron-hole radiative recombination that leads to the strong PL emission in the visible region. The appearance of two small emission bands at 467 and 529 nm indicate the emission of SiC nanostructures [70, 72]. The peak at 467 nm is comparable to the PL emissions from SiC nanowires [70, 71] or crystalline SiC nanoparticles [72]. However, the emission peak for this core-shell nanowire is obviously shifted to higher wavelength. This phenomenon has been reported due to the quantum size effect of SiC nano-crystallites embedded within an amorphous matrix. The peak at 529 nm could be due to the presence of defect centers within the band gap of SiC shell as previously reported by Gundiah et al. [73]. Various PL emissions from the core-shell nanowires indicate that luminescence characteristics depends strongly on structure and size of the nano-



Figure 4.6 (a) PL spectra of NiSi/SiC core-shell nanowires prepared by HWCVD at different deposition pressures. (b) Decomposition of a typical PL spectrum into 5 PL components by Gaussian plots covering the whole range of the PL spectrum.

4.7 NiSi /SiC Core-Shell Nanowire Growth Mechanisms

A thin layer of Ni was evaporated on glass substrates which act as catalyst to induce the growth of the core-shell nanowires. Prior to deposition, Ni films were treated by hydrogen plasma to form Ni nanoparticles as metal nanotemplates. Decomposition of SiH₄, CH₄ and H₂ as gas precursors by the heated tungsten filament and diffusion of precursors into the metal nanotemplates. Growth of NiSi/SiC core –shell nanowires.

Ni is a dominant moving species to initiate and continue the MIG nanowire growth mechanism. Ni diffuses from the Ni deposited layer to impinging Si from the target to form the NiSi layer and moves inside the nanowires to continue the NiSi mechanism. After reacting with Si, Ni diffusion may continue in the NiSi nanowire growth. Some amount of NiSi contributes to lengthen the NiSi nanowires and some supplies the feedback mechanism to continue the process. The formation of SiC is expected to due to radial growth.



Figure 4.7 NiSi /SiC Core-Shell Nanowire Growth Mechanisms

CHAPTER 5 CONCLUSION

5.1 Conclusion

This growth and structural properties of NiSi/SiC core-shell nanorods and nanowires prepared by HWCVD at different deposition pressures have been studied. These nanorods and nanowires have been grown at deposition pressure below 3 and at 3 mbar respectively. Hydrogen etching effect plays an important role in forming these nanowires at higher deposition pressure. Moreover, these nanowires consisting of single crystalline NiSi and amorphous SiC attributed to core and shell of the nanowires respectively. The shell of the nanowires showed presence of 3C-SiC nano-crystallites embedded within an amorphous matrix. The formation of the NiSi core nanowires followed the metal induced growth at substrate temperature below 500 °C, while the shell of the amorphous SiC could be due to the radial growth. Increase in deposition pressure induced a phase transitions of the shell of the nanowires from crystalline Si to amorphous Si, and accompanied by the transition from Si to SiC phase. Presence of Si and SiC nano-crystallites embedded within an amorphous dutin an amorphous matrix in the shell of the nanowires from crystalline Si to amorphous Si, and accompanied by the transition from Si to SiC phase. Presence of Si and SiC nano-crystallites embedded within an amorphous matrix in the shell of the nanowires companies for the shell of the shell of the nanowires from crystalline Si to amorphous Si, and accompanied by the transition from Si to SiC phase. Presence of Si and SiC nano-crystallites embedded within an amorphous matrix in the shell of the nanowires exhibited broad range of PL emission spectra in the range of 400 – 900 nm.

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