GROWTH OF NICKEL SILICIDE NANOWIRES BY USING THERMAL CHEMICAL VAPOR DEPOSITION

FATEMA ABDELLAH AL SALMANI

SUBMITTED TO THE FACULITY OF SCIENCE UNIVERSITY OF MALAYA, IN PARTIAL FULFILMENT OF THE REQUIRMENT FOR THE DEGREE OF MASTER OF SCIENCE (APPLIYED PHYSICS)

2015

UNIVERSITI MALAYA PERAKUAN KEASLIAN PENULISAN

Nama: FATEMA ABDELLAH AL SALMANI (No. K.P/Pasport: 02896153) No. Pendaftaran/Matrik: SGB1300190 Nama Ijazah: SARJANA SAINS (FIZIK GUNAAN) Tajuk Kertas Projek/Laporan Penyelidikan/Disertasi/Tesis ("Hasil Kerja ini"): PERTUMBUHAN NIKEL SILISIDA NANO-DAWAI MENGGUNAKAN HABA WAB_KIMIA_PEMENDAPAN

Bidang Penyelidikan: NANOTEKNOLOGI DAN NANOBAHAN

Saya dengan sesungguhnya dan sebenarnya mengaku bahawa:

(1) Saya adalah satu-satunya pengarang/penulis Hasil Kerja ini;

(2) Hasil Kerja ini adalah asli;

(3) Apa-apa penggunaan mana-mana hasil kerja yang mengandungi hakcipta telah dilakukan secara urusan yang wajar dan bagi maksud yang dibenarkan dan apa-apa petikan, ekstrak, rujukan atau pengeluaran semula daripada atau kepada mana-mana hasil kerja yang mengandungi hakcipta telah dinyatakan dengan sejelasnya dan secukupnya dan satu pengiktirafan tajuk hasil kerja tersebut dan pengarang/penulisnya telah dilakukan di dalam Hasil Kerja ini;

(4) Saya tidak mempunyai apa-apa pengetahuan sebenar atau patut semunasabahnya tahu bahawa penghasilan Hasil Kerja ini melanggar suatu hakcipta hasil kerja yang lain;

(5) Saya dengan ini menyerahkan kesemua dan tiap-tiap hak yang terkandung di dalam hakcipta Hasil Kerja ini kepada Universiti Malaya ("UM") yang seterusnya mula dari sekarang adalah tuan punya kepada hakcipta di dalam Hasil Kerja ini dan apa-apa pengeluaran semula atau penggunaan dalam apa jua bentuk atau dengan apa juga cara sekalipun adalah dilarang tanpa terlebih dahulu mendapat kebenaran bertulis dari UM;

(6) Saya sedar sepenuhnya sekiranya dalam masa penghasilan Hasil Kerja ini saya telah melanggar suatu hakcipta hasil kerja yang lain sama ada dengan niat atau sebaliknya, saya boleh dikenakan tindakan undang-undang atau apa-apa tindakan lain sebagaimana yang diputuskan oleh UM.

Tandatangan Calon

Diperbuat dan sesungguhnya diakui di hadapan,

Tandatangan Saksi

Nama: Jawatan: Tarikh

Tarikh

UNIVERSITI MALAYA ORIGINAL LITERARY WORK DECLARATION

Name of Candidate: FATEMA ABDELLAH ALSALMANI

I.C/Passport No: 02896153

Registration/Matric No: SGB130010

Name of Degree: MASTER OF SCIENCE (APPLYIED PHYSICS)

Title of Project Paper/Research Report/Dissertation/Thesis ("this Work"):

"GROWTH OF NICKEL SILICIDE NANOWIRES BY USING THERMAL CHEMICAL VAPOR DEPOSITION"

Field of Study: NANOTECHNOLOGY AND NANOMATERIAL

I do solemnly and sincerely declare that:

(1) I am the sole author/writer of this Work;

(2) This Work is original;

(3) Any use of any work in which copyright exists was done by way of fair dealing and for permitted purposes and any excerpt or extract from, or reference to or reproduction of any copyright work has been disclosed expressly and sufficiently and the title of the Work and its authorship have been acknowledged in this Work;

(4) I do not have any actual knowledge nor ought I reasonably to know that the making of this work constitutes an infringement of any copyright work;

(5) I hereby assign all and every rights in the copyright to this Work to the University of Malaya ("UM"), who henceforth shall be owner of the copyright in this Work and that any reproduction or use in any form or by any means whatsoever is prohibited without the written consent of UM having been first had and obtained;

(6) I am fully aware that if in the course of making this Work I have infringed any copyright whether intentionally or otherwise, I may be subject to legal action or any other action as may be determined by UM.

Candidate's Signature	Date
Subscribed and solemnly declared before,	
Witness's Signature	Date
Name:	
Designation:	

Abstract

Formation of nickel-silicide nanowires (NiSiNWs) using nickel foil as a catalyst were studied in this research. The deposition of NiSiNWs was carried out by using homebuilt thermal chemical vapor deposition system (CVD). A tungsten filament with purity of 99.95% was employed as hot-wire for evaporation of Ni catalyst. A silane gas was used as precursor for the formation of NiSiNWs. The deposition temperature were varied between 300°C to 577°C and the surface morphology structure, elemental analysis and crystallinity of NiSiNWs were analyzed on the effect of temperature. The characterization study was done by using Field emission scanning electron microscope (FESEM), high resolution transmission electron microscopy (HRTEM), electron diffraction x-ray (EDX) and X-Ray diffraction (XRD). Moreover, the sample was measured on the electrical properties by using cyclic voltammetry system. At low temperatures 300°C, 350°C and 393°C, Ni particles only appears on the surface of sample. As temperature increased at 437°C, a little amount of NiSiNWs started to appear on the sample. The appearance of Ni₃Si₂ was observed at higher temperatures starting from 477°C. The high density of the nanowires was demonstrated at high temperatures of 437° C to 577° C.

Keywords: nickel silicide, thermal chemical vapor deposition, nanowires, FESEM, XRD.

Abstrak

Pembentukan nikel silicide (NiSiNWs) nanodawai menggunakan kerajang nikel sebagai pemangkin telah dikaji dalam penyelidikan ini. Pemendapan NiSiNWs telah dijalankan dengan menggunakan kimia haba wap pemendapan (CVD) system yang telah dibina sendiri. Satu filamen tungsten dengan ketulenan 99.95% telah digunakan sebagai wayar pemanas untuk penyejatan Ni pemangkin. Silana gas telah digunakan sebagai pelopor untuk pembentukan NiSiNWs. Suhu pemendapan telah diubah di antara 300 ° C hingga 577 ° C dan struktur permukaan morfologi, analisis unsur dan penghabluran NiSiNWs telah dianalisis berdasarkan kesan suhu. Kajian pencirian dilakukan dengan menggunakan pelepasan bidang mikroskop elektron imbasan (FESEM), resolusi tinggi penghantaran elektron mikroskop (HRTEM), elektron pembelauan x-ray (EDX) dan pembelauan X-Ray (XRD). Selain itu, ciri-ciri elektrik sampel telah diukur dengan menggunakan sistem kitaran voltammetri. Pada suhu rendah 300 ° C, 350 ° C dan 393 ° C, Ni partikel hanya muncul pada permukaan sampel. Apabila suhu meningkat kepada 437 ° C, sedikit NiSiNWs mulai muncul diatas sampel. Kemunculan Ni₃Si₂ telah dikesan pada suhu yang lebih tinggi mulai dari 477 ° C. Ketumpatan tinggi nanodawai telah ditunjukkan pada suhu tinggi 437° C hingga 577 C.°

Kata kunci: nikel silicide, menggunakan kimia haba wap pemendapan (CVD), wayarnano, FESEM dan XRD.

Acknowledgement

I wish to express my great appreciation to Dr. Zarina Binti Aspanut my supervisor for her supervision and guidance throughout this work. I would also like to express my thanks to my senior, Mohammad Mukhlis Bin Ramly for his assistance and guidance through the lab work and analyzing process. And also not forget to thank all LDMRC teams and students for their cooperation.

I wish to express my deep appreciation to my husband and my children for their supporting and understanding during the period of my studying.

I would like to thanks my parents and all my family members for their praying and supporting.

Table of Contents

Abstractiii
Abstrakiv
Acknowledgementv
Chapter 1 1
INTRODUCTION
1.1Importance of Nickel Silicide Nanowires and Applications1
1.2Effect of temperature on material growth techniques2
1.3Motivation of this work
1.4Objectives
1.5Outline of thesis
Chapter 2
LITERATURE REVIEW
2.1 Introduction
2.2 Nickel Silicide Nanostructures
2.3 Deposition techniques of NiSi Nanostructres
2.4 Studies on Surface Morphology and Elemental analysis of NiSi Nanostructures 9
2.4.1 FESEM
2.4.2 HRTEM
2.4.3 EDX
2.5 Studies on Structural properties
2.5.1 X-ray diffraction14
2.6 Electrical Measurements
Chapter 3

METHODOLOGY/ EXPERIMENTAL DETALS	17
3.1 Introduction	17
3.2 Thermal Chemical Vapor Deposition System	17
3.3 Sample Fabrication	21
3.3.1 Substrate Cleaning	21
3.3.2 Pre-heating of Filament	21
3.3.3 Ni Evaporation	22
3.3.4 Deposition Process	23
3.4 Characterization Techniques and Electrochemical Measurment	24
Chapter 4	26
RESULTS AND DISCUSSIONS	26
4.1 Introduction	26
4.2 Surface and Morphology of NiSi nanostructures	26
4.2.1 FESEM Analysis	26
4.2.2XRD Analysis	31
4.2.3 HRTEM Analysis	33
4.3 Electrical Analysis	33
4.3.1 CV Measurements	33
Chapter 5	38
CONCLUSION AND SUGGESTION FOR FUTURE WORK	38
5.1 Conclusion	38
REFERENCES	39

List of Figures

Figure 1 a) Schematic diagram of the main component of FESEM, b						
	schematic of signal generated when electron beam strike the					
	sample (Goldstein et al. 1981), and c) a photograph of FESEM.					
Figure 2	Schematic representation of an energy-dispersive X-ray	14				
	spectrometer (Goldstein et al. 1981).					
Figure 3	a) Schematic diagram of the X-ray diffractometer, and b) a	16				
	photograph of X-ray diffractometer (model of SIEMENS D5000					
	XRD with thin film attachment operating with CuK α radiation).					
Figure 4	(a) Schematic diagram of Home-built Thermal CVD system. (b) A	21				
	photograph of Home-built Thermal CVD system.					
Figure 5	A photograph of cleaned Ni substrate.	22				
Figure 6	(a) Photograph of the setup of the filament, hold by the filament	23				
	holder and (b) the pre-heated tungsten coil.					
Figure 7	Ni evaporation process.	24				
Figure 8	Substrate after deposition process.					
Figure 9	FESEM images of NiSi nanowires prepared by thermal CVD at	29				
	different substrate temperatures of (a) 300, (b) 393, (c) 437, (d)					
	477, (e) 510 and (f) 577°C.					
Figure 10	FESEM image of NiSi nanowires with respective EDX spectra	31				
0	prepared by Thermal CVD at different substrate temperatures of					
	prepared by Therman C v D at unreferit substrate temperatures of					

(a) 393°C, (b) 477°C

- Figure 11 (a) Dark-field STEM image of NiSi nanowire prepared by Thermal 32 CVD at substrate temperature of 437°C, (b–e) EDS element maps of the nanowire.
- Figure 12 XRD patterns of NiSi nanowires prepared by Thermal CVD at 33 different substrate temperature
- Figure 13HRTEM image of NiSi nanowires at 437°C34
- Figure 14 Cyclic voltammetry (CV) curves of NiSiNWs at different scan 36 rates within a potential window of -0.4 to 0.7 V for different substrate temperatures.
- Figure15 Cyclic voltammetry (CV) curves of NiSiNWs at scan rates 5mV/s 37 within a potential window of -0.4 to 0.7 V for different substrate temperatures.
- Figure16 Capacitance and specific capacitance of NiSiNWs at different step 38 size

List of Tables

	Page
29	Table 1

List of Symbols and Abbreviations

CVD	chemical vapor deposition
EDX	energy-dispersion X-ray spectroscopy
FESEM	field emission scanning electron microscope
HRTEM	high resolution transmission electron microscopy
Ni	nickel
NiSi	nickel silicide
NiSiNWs	nickel silicide nanowires
sccm	standard cubic centimeters per minute
Si	silicon
SiH ₄	silane
SiNWs	silicon nanowires
T_{f}	filament temperature
Ts	substrate temperature
XRD	X-Ray diffraction

Chapter 1

INTRODUCTION

1.1 Importance of Nickel Silicide Nanowires and Applications

Nanotechnology is known as the fabrication, design and applications of nanostructures and nanomaterial. The interest in nanomaterial is mainly due to their exhibit structural, optical and electrical properties, which are distinctively different from bulk or even micron-scaled of materials.

Si nanowires (SiNWs) have been widely used in prototype devices such as integrated electronics, chemical and biological sensors, thermoelectric devices and lithium ion batteries. To operate these devices efficiently, low resistance contact with the SiNWs is essential [1]. Metallic silicide nanowires are promising candidates, because their growth can be easily integrated with silicon processing technology [1]. The synthesis of single-crystalline, transition metal silicide nanowires, such as TaSi and CoSi has been recently reported using divers methods. For example, laser ablation [2], chemical vapor deposition (CVD) [3], and plasma enhanced chemical vapor deposition (PECVD) [4]. As devices size decreases, the amount of Si consumed in the course of the Si-metal reaction becomes a major issue, because low Si consumption is crucial to maintain shallow source and drain junction [2]. Therefore metal silicide that have lower Si consumption are more desirable. Among all metal silicides, NiSi is superior and convenient due to its lower Si consumption.

NiSi is an attractive candidate use as a gate contact material due to its low metallike resistivity, large processing window $(350 \degree C - 750 \degree C)$ and high temperature stability [5, 6]. Although the NiSi has many phase formations, the predominant phases are Ni₂Si, NiSi and NiSi₂. The variation of temperature range during the deposition of Si determines the phase formation of nickel silicide [7].

NiSiNWs have a high potential in the nanoscale electronics due to the tiny scale and excellent electrical conductivity [8]. NiSiNWs are considered as potential candidates to solve the general concerns in terms of electrical resistance and device speed. NiSiNWs has been intensively researched for use as a contact material of gate and source/drain in complementary metal oxide-semiconductor (CMOS) devices [9]. NiSiNWs interconnect has proven a potential to deliver high level current. It also confirmed that each NiSiNWs delivered current uniformly. Moreover, NiSiNWs has a high advantage to be a field emitting entity [10].

1.2 Effect of temperature on material growth techniques

The recent studies on NiSiNWs showed that the temperature of substrate for growing NiSiNWs played a dominant role in controlling the diameter of nanowires and the formation of various kinds of silicon nanowire-related morphologies [7, 11, 12]. For example, using HWCVD technique at 400, 450 and 527°C they obtained the diameters of about 157,165 and 178nm respectively [13]. Moreover, using simple CVD process a diameters of 40-60, 100-200 and 100-200nm at 450, 500 and 600°C were obtained respectively [14]. The diameters of NiSiNWs increased with increasing substrates temperatures. The lengths of NiSiNWs varied from tens micrometers to a few hundreds micrometers as the temperature increased from 450°C to 500°C respectively [14].

According to Fan.X.et.al., the morphology and the phase of NiSi can be tuned by modulating the reaction temperature [14]. Liu, H., et al reported that the amount of Ni source and the reaction temperature are crucial parameters for the formation of the NiSi [15].

Different phases of NiSiNWs can be formed at different temperatures. For example, the Ni₂Si phase is formed approximately at low temperature range of 250–300° C, whereas NiSi₂ is formed at temperatures exceeding 800°C [7].

It has been reported in previous works how the substrate temperatures affect the growth of NiSiNWs [13, 16]. During the deposition process, a low substrate temperatures from 300 to 393 ° C are not sufficient to activate the reaction between Si and Ni to form NiSiNWs [13, 16], while this formation can be achieved at high temperatures.

In this research the effects of substrate temperatures on the growth of NiSiNWs will be studied. While fixing other parameters such as the silane flow rate and the deposition pressure during the experiment.

1.3 Motivation of this work

Considering that the amorphous Si technologies took more than 60 years to mature and emerge in a variety of electronic applications, however, SiNw technology is still in its early stage for current technological applications. One of the main reasons is the high cost of large-scale industrial production. Low temperature and a large area synthesis of well-aligned SiNWs are the main requirements to satisfy current industrial, scientific and technological applications of SiNWs. NiSiNWs are expected to further enhance the properties of the nanowires in their mechanical, chemical resistivity, thermal stability and in a wide range of optical properties.

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

Recent studies on the growth of NiSiNWs by thermal CVD demonstrated that it is a promising technique for the growth of 1-D Si-based nanostructure, owing to the lower production coasty and the capability for large-scale production making this method more attractive for industrial applications. This technique also have been proven to enhance the growth rate of NiSiNWs besides have advantages of low-temperature growth processes. In addition, thermal CVD provides an ion-free deposition by catalytical decomposition of the source gas using a catalyzer usually tungsten is comparatively a better technique for the growth of NiSiNWs. Due to the demand from industrial application, the fundamental study on the effect of substrate temperature by using thermal CVD will be explored in this research. Moreover, the relation of morphology surface of the sample will be investigating with the electrical measurement study.

1.4 Objectives

The objectives of this work are as follows:

- To growth nickel silicide nanowires by using thermal chemical vapor device method with nickel as a catalyst.
- To investigate the role of substrate temperature on the structural and morphology of nickel silicide nanowires.

1.5 Outline of thesis

The report is written in five chapters; Introduction on importance of NiSiNWs and the effect of temperature on material growth technique (Chapter 1), literature review on NiSi nanostructures, deposition methods and analyses technique (Chapter 2), preparation of NiSiNWs (Chapter 3), results of each characterization on the NiSiNWs accompanied by discussion (Chapters 4), and end up with conclusion and suggestions for future works (Chapter 5). In chapter 1, importance and applications of NiSiNWs are provided. Some of the synthesis methods are introduced. Moreover, the effects of temperature on material growth techniques are discussed. The objectives and motivation of this work are introduced.

In chapter 2, in this chapter literature review of previous works are illustrated. Some informations about nickel silicide nanostructures are provide and different deposition techniques of NiSiNWs are discussed. Moreover, studies on surface morphology and elemental analysis of NiSiNWs are presented.

Chapter 3 will clarify the methodology/experimental details of this research. It contributes description of home built thermal CVD system used in this work to grow the nanowires. Moreover, it presents explanations of sample fabrication including the substrate cleaning process, filament pre-heating, nickel evaporation, deposition process and characterization techniques.

Chapter 4, in this chapter the effect of substrate temperature on the morphology and electrical properties of NiSiNWs are explained. The morphology structure of samples can be view from FESEM and HRTEM images, XRD spectra for crystallinity and phases, EDX spectra for elemental analysis and cyclic voltammetry curves are illustrated with related explanations.

Finally, conclusion and suggestions for future work are presented in Chapter 5. The results and discussion in Chapters 4 aid to build up the conclusive ideas on the formation of NiSis by employing Ni foil as catalyst and thermal CVD as deposition technique.

5

Chapter 2

LITERATURE REVIEW

2.1 Introduction

In this chapter a review on nickel silicide nanostructures is presented. Some deposition techniques are illustrated as well as some characterization techniques.

2.2 Nickel Silicide Nanostructures

Silicide is a compound of Si with an electropositive component [17]. 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.

Nickel silicides are transition metal silicides with low suitable work functions and resistivity. They have been applied in several fields [18]. For example, Ni-rich silicides, such as Ni₂Si nanowires, are attractive nanoscale building blocks for interconnects and fully silicided gate applications in nanoelectronics [19]. Silicon-rich nickel silicide, NiSi₂, has been explored for use in low-power memory devices, and for using an optical absorber in optical communications applications [20].

Nickel monosilicide (NiSi) is a candidate for deep sub-micron devices due to its low resistivity, low formation temperature and minimal Si consumption. Nickel disilicide (NiSi₂) is used as a metal base transistor and also finds novel applications as buried epitaxial silicides because of its epitaxial relationship with respect to Si substrate. The formation of metal silicide film on Si substrate involves diffusion of either the metal or the silicon species across the interface [21].

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 [5].

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 [22].

Several NiSiNWs growths have been reported. A unique nanowire growth mechanism that the NiSi nanowire follows is the metal-induced growth (MIG) method [17].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.

2.3 Deposition techniques of NiSi Nanostructres

Chemical vapor deposition (CVD) is the oldest techniques in the synthesis of NiSiNWs. CVD is also known as thermal CVD as it thermally decomposes source gas by heating. High, moderate and low temperatures CVD are three categories of thermal CVD according to the deposition temperature.

For high temperature CVD, the reactor is usually constructed by a quartz tube. Heating element is built outside, surrounding the quartz tube. One end of the tube supplies Si-containing vapor, the other end is connected to evacuation tools.

Moderate temperature CVD typically works at a temperature range from 400 to700°C. It is constructed by a stainless steel or quartz-made reactor, with heating element built inside the reactor. Different from high temperature CVD, only substrate rather than the reactor is heated up.

In moderate and low temperature CVD, SiH₄ is frequently used as precursor while in high temperature SiCl₄ is used.

The decomposition process can be presented by the following equation:

 $SiH_4(g) \longrightarrow SiH_2(g) + H_2(g)$

However, a higher temperature (~ 600 °C) is required for decomposition of SiH₄ gas. Thus, the better quality, less kinking and defects SiNWs are mostly synthesized at temperatures beyond 500 °C.

The most important advantages of thermal CVD are the broader choice of catalyst and allowing epitaxial growth of SiNWs. The wide range of operating temperature permits a large variety of metals to be involved in growth. For example Au, Al, Ag, Cu and Ni.

Thermal chemical vapor deposition (CVD) considered as low temperature CVD technique. It utilizes a metallic catalyzer to decompose SiH₄ precursor. Thermal CVD is

constructed by tungsten filament coil served as a catalyzer. It is connected to a high voltage power source which supplies power to heat up the filament for deposition.

2.4 Studies on Surface Morphology and Elemental analysis of NiSi Nanostructures

2.4.1 FESEM

The characterization on NiSi nanostructure is highly dependent on surface morphological imaging technique. An optical microscope is no longer applicable in order to view submicron to nanosize of structures due to the resolution limit. For better resolution and depth of focus electron microscope is needed, due to the natural behavior of electron compared to photon [23].

FESEM is commonly used to study the surface morphology of the nanostructure materials. In this device the electron source is produced by field emission gun. It can achieve up to three orders of magnitude greater electron density and higher brightness. The main components of FESEM, the signal generated when electron beam strike the sample and a photograph of FESEM instrument are shown in Figure1 (a), (b) and (c) respectively. Electrons are liberated from a field emission source and accelerated in a high electrical field gradient. Within the high vacuum column these so-called primary electrons are focused and deflected by electronic lenses to produce a narrow scan beam that bombards the object. As a result the "electron hail" secondary electrons are dislocated from each spot on the object. The smaller the angle of incidence of the electron beam is with respect to the sample surface and the higher a certain point is in the sample, the more secondary electrons are able to reach the detector and the lighter this dot will appear in the final image following electronic signal amplification and digitalization.



Figure 1: a) schematic diagrame of main componant of FESEM, b) schematic of signal generated when electron beam strike the sample (Goldstein et al. 1981), and c) a photograph of FESEM

2.4.2 HRTEM

Transmission electron microscopy (TEM) plays an important role for the characterization of the structural properties and crystallinity of the SiNWs. Atomic structure of a SiNWs can be directly investigated by employing high resolution transmission electron microscopy (HRTEM). A high resolution of ~1 Å is theoretically obtained in a HRTEM due to the shortening in de Broglie wavelength of the high energetic electron beam [23]. This is useful in determination of the crystalline or amorphous structures and structure defects such as twinning and lattice dislocation within NWs. It can also be used to identify the atomic lattice spacing, crystalline plane, preferred orientation and growth direction of the NWs.

TEM is constructed with an electron gun, usually field emission gun for high resolution. The voltage applied to accelerate the electron is in a range of 200 to 300 kV to allow the transmission of electron beam through the specimen. The electron beam is focused by two condenser lenses into a coherent beam, and further restricted from deviation by a condenser aperture. The focused electron beams then strike the specimen and are transmitted through the specimen. The transmitted electrons are focused by the objective lens into an image which is then passed through the intermediate and projector lenses, and then projected on the fluorescent screen. The objective and selected area apertures are used for TEM image and diffraction pattern projections, respectively. For the TEM image projection mode, the objective aperture acts to block the high angle diffracted electrons, while, for the diffraction pattern projection mode, the selected area aperture acts to assist the examination of the diffraction of electrons. The transmitted electrons can be classified into three types, namely unscattered, elastically scattered and inelastically scattered electrons. The electrons transmitted through the specimen without any interaction with the specimen atoms are called unscattered electrons. These unscattered electrons mainly contribute to the TEM images.

The darker area in a TEM image can be due to the thicker or heavier element in that area, thus fewer electrons are transmitted through that area. Elastically scattered electrons are generated when the incident electrons are scattered by the specimen atoms with no loss of energy. The elastically scattered electrons follow Bragg's diffraction law, where the incident electrons are scattered by the atoms with the same atomic spacing and possess same scattering angle. The same angle of scattered electrons forms a pattern of diffraction spots. This diffraction pattern is utilized to generate selected area electron diffraction (SAED) pattern, which gives information on the structures (amorphous or crystalline), orientation and atomic arrangement of the sample. Conversely, the electrons generated when the incident electrons interact with the specimen atoms with loss in energy are inelastically scattered electrons. The inelastic loss of energy by the incident electrons is unique to each of the elements interacted with. Thus, it provides the information of the compositional and chemical bonding of the sample.

In order to obtain higher resolution (up to atomic level), the sample should be thin enough (< 100 nm) to enable the transmission of the electron beam. A TEM grid, usually copper grid with carbon supporting film, is used to hold the sample. The samples on the substrate were immersed in an ethanol solution and sonicated for about 15 minutes to extract the SiNWs from the substrate. The diluted SiNWs in an ethanol solution was then transferred onto a copper grid through a cleaned pipette. The copper grid was dried in a dry cabinet for a few hours before carrying out TEM measurement.

2.4.3 EDX

Energy dispersion X-ray spectroscopy EDX provides a qualitative and quantitative analysis of the chemical composition of the NiSiNWs sample. The detector can be attached in a FESEM or HRTEM to effectively collect the X-ray radiation from the sample. The radiated X-ray at all energies is collected at the same time while a complete spectrum covering the whole energy range can be acquired for analysis using EDX.

A schematic diagram of an EDX is illustrated in Figure 2 [24].Generally, an EDX consists of a detector, an amplifier and a multichannel analyzer. The detector is constructed by a small piece of semiconductor plate, usually Si or germanium (Ge), with a p-i-n junction in reverse biased. The Si is doped with Li and cooled down to ~77 K with liquid N₂ to increase the resistivity of the Si plate, thus limits the current leaking through when voltage is applied through the Si plate. Both sides of the Si plate are covered by thin layers of Au electrodes (~20 nm) so that bias voltage can be applied through the p-i-n junction of Si. A thin beryllium window is placed in the outer surface of the detector to

prevent contaminants coating the detector. As a result, EDX is not able to detect all elements lighter than sodium (Na) because the X-rays radiated by those light elements are not able to transmit through the beryllium window of the detector. However, utilization of Polymer-based thin windows allows for detection of light elements.



Figure 2: schematic representation of an energy-dispersive X-ray spectrometer (Goldstein et al. 1981).

2.5 Studies on Structural properties

2.5.1 X-ray diffraction

X-ray diffraction (XRD) is commonly used in characterization of the crystal structure of a material. Crystallinity of an element can be identify by determining the peak position in XRD spectra, while the orientation plane correspond to the peak can be assigned.

The XRD spectrum provides a qualitative determination of the crystallinity of a material by analyzing the intensity of the diffraction peak. Crystallite size of the material can be quantitatively calculated from the width of the diffraction peak using several methods.

As XRD detector is only sensitive to crystalline structures, it can be applied for both homogeneous and inhomogeneous samples, which is suitable for the structural characterization of nanomaterials.

A schematic diagram and a photograph of X-ray diffractometer are illustrated in Figure 3 (a) and (b) respectively. The diffractometer is designed according to the Bragg-Brentano geometry. It consists of a monochromatic X-ray radiator and a detector, which are placed on the circumference of a circle centered on the sample. X-rays are generated in a cathode ray tube by accelerating electron towards a Cu anode plate. CuK α is commonly used as X-ray source. The produced X-ray beam is then filtered by monochromator to a wavelength of 0.7 to 2 A and collimated towards sample. The X-ray beam diverges from the source and diffracted by the sample to form a convergent diffracted beam. The convergent diffracted beam is filtered by a monochromator and focused at a slit, then enters the detector. Intensity of the diffracted X-ray beam is measured as the number of current pulses per unit time by an electronic X-ray detector. During the measurement, the X-ray detector is mechanically rotated in an angle of 20 accompanied by a rotation of sample holder in an angle of θ , while the angle of incident beam to sample holder always keeps at θ . Thus, the angle of incident beam is always equal to the angle of diffracted beam.

The detector measures data of each angular increment in a minimum order of 0.01°, while the length of time per count and step size of the angular increment are controlled by the computerized program.

When Bragg's law is satisfied in measuring a crystalline sample, the X-rays scattered by all the atoms in all of the planes are completely in phase, thereby forming constructive interference and the X-rays are diffracted at maximum intensity. This results in the diffraction peak in XRD pattern. The intensity of the diffraction peak is proportional to the degree of crystallinity of the sample. In the rest of angles, the scattered rays cancel out each other (destructive interference).





Figure 3: a) schematic diagram of the X-ray diffractometer, and b) a photograph of X-ray diffractometer (model of SIEMENS D5000 XRD with thin film attachment operating with CuK_{α} radiation)

2.6 Electrical Measurements

The electrochemical measurements were carried using a three-electrode configuration in 0.5M Na₂SO₄ electrolyte. NiSiNWs used directly as a working electrode with Pt and SCE as the counter and references electrode respectively. CV operation was conducted to evaluate the electrochemical performance of the samples. The specific capacitance was calculated from the CV curve using equation 1:

$$C = \frac{1}{m \, v \, \Delta V} \int i \, V \, dV \tag{1}$$

Where C is the specific capacitance, m is the mass of the active materials in the electrode, v is the potential scan rate, ΔV is the potential window in the CV and $\int i V dV$ is the integrated area of the CV curve.

Chapter 3

METHODOLOGY/ EXPERIMENTAL DETALS

3.1 Introduction

In this chapter, setup for the home-built thermal CVD is presented. Sample fabrication is explained by illustrating the substrate cleaning, filament pre-heating, and nickel evaporation and deposition process respectively. Information about characterization techniques are included at the end of this chapter.

3.2 Thermal Chemical Vapor Deposition System

A schematic diagram and a photograph of the home-built thermal CVD system is illustrated in Figure 4 (a) and (b) respectively. The system consists of six parts; the CVD reactor, plasma generator, hot-wire power supply, vacuum system, gas line management and heating elements.

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 $2.5 \times 2.5 \text{ cm}$. 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.

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.

For the purpose of materials fabrication in CVD, a high vacuum level is important to provide a clean deposition environment and minimize contaminations in the sample. A vacuum pump is a device that removes gas molecules from a sealed volume in order to leave behind partial vacuum. A 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 centers of these two circles are offset, causing eccentricity. The 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. The rotary vacuum pumps can attain pressures as low as 10^{-3} mbar.

A highly purified SiH₄ (99.9995%) is used as the precursor gas and H_2 gas with purity of 99.999% is used to dilute the SiH₄ gas in deposition, it's also serves as a precursor in pre-heating of coiled tungsten filament process.

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 a 316L 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. A 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 and H₂ gas flow rate are controlled by a MFC in a flow rate range of 0 - 10 sccm and 0-200 sccm respectively.





(b)

Figure 4: (a) Schematic diagram of Home-built thermal CVD system. (b) A photograph of Home-built thermal CVD system.

3.3 Sample Fabrication

3.3.1 Substrate Cleaning

Prior to the substrate cleaning, the tools such as tweezers, petri disc and beakers were cleaned using acetone and dried under N_2 purging. A Ni substrates were cleaned using deionized water and acetone. First, Ni foil substrate were immersed in a beaker containing deionized water. Then, Ni foil substrates were immersed in a beaker containing acetone. This step was repeated for two times to remove organic impurities. The Ni foil cleaning process was ended with purging N_2 gas on the sample. A cleaned Ni foil substrate is shown in Figure 5.



Figure 5: A photograph of cleaned Ni Foil substrate.

3.3.2 Pre-heating of Filament

The tungsten filament was pre-heated to remove surface contaminations such as carbon and other metallic elements before deposition. Pre-heat treatment was 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. The setup of the filament,

hold by the filament holder and the pre-heated tungsten coil are shown in Figure 6 (a) and (b) respectively.







(b)

Figure 6: (a) photograph of the setup of the filament, hold by the filament holder and (b) the pre-heated tungsten coil.

3.3.3 Ni Evaporation

Figure 7 illustrates a photograph of CVD system during Ni evaporation process. Samples were prepared by Ni evaporation using heated tungsten filament. Ni foil with 1mm width and 12mm length (1 mm x 12 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 hot wire voltage supply used for Ni evaporation was 150 V. The evaporation time was fixed at 5 minutes.



Figure 7: Ni evaporation process

3.3.4 Deposition Process

Deposition process is accomplished by the decomposition of silane gas on Ni surfaces to make different composition (NiSi, Ni₂Si, and Ni₃Si₂) of nanowires[9].

Deposition process was carried out by varying the substrate temperature from 300° C to 577° C. The SiH₄ and H₂ gas flow rate were fixed at 7sccm, 100sccm respectively. The chamber pressure was fixed at 0.5 mbar. The filament to substrate distance was fixed at 2.5 cm. The deposition time was fixed 5 minutes. A photograph of substrates after deposition process is shown in Figure 8.



Figure 8: substrate after deposition process

3.4 Characterization Techniques and Electrochemical Measurment

The morphological study for the FESEM images of the nanowires were obtained using a (JEOL- JSM 7600-F) at low electron accelerating voltage of 2 kV. While the elemental analysis for the EDX spectrum was collected by (JEOL- JSM 7600-F). The working distances for the imaging and EDX were fixed at 8 mm and 15 mm respectively. Nanostructure analysis for the HRTEM image of the nanowires were obtained byTEM (JEOL JEM-2100F) with an accelerating voltage of 200 kV. The crystalline orientation for the X-ray diffractometry (XRD) spectra were recorded in the 2 range of 20–70° at a fixed grazing incidence angle of 1.5° using a PAN-alytical Empyrean X-ray diffractometer with X-ray wavelength of 1.5406 °A. The step time and step size of the scanning were fixed at 2 s and 0.026°, respectively. The XRD was the most widely used technique in materials characterization, which is based on the diffraction of X-ray radiation within the film structure. The electrochemical measurements were carried using a three-electrode configuration in 1M KOH as electrolyte. NiSiNWs used directly as a working electrode with Pt and Hg/HgO as the counter and references electrode respectively.

Chapter 4

RESULTS AND DISCUSSIONS

4.1 Introduction

This chapter presents the results and discussions involved in this study on the growth of NiSiNWs using nickel as a catalyst by thermal chemical vapor deposition (CVD). The results obtained from Field emission scanning electron microscopy (FESEM), X-ray diffractometr (XRD), high resolution transmission electron microscopy (HRTEM) and electrical analysis are presented in different subsections of this chapter.

4.2 Surface and Morphology of NiSi nanostructures

4.2.1 FESEM Analysis

FESEM images of NiSiNWs prepared by thermal CVD at different substrate temperatures are presented in Figure 9. The sample prepared at 300°C showed a formation of spherical grains of Ni nanoparticles distributed on the substrate surface. At this low substrate temperatures, SiH₄ and Ni catalyzed decomposition are not sufficient to form NiSi particles during the reaction [5]. The reaction of Ni and Si most probably occur on the Ni nanoparticles surface only. Therefore, no nanowires formed at this low temperature due to the insufficiency of Si to Ni ratio for achieving its nucleation [13]. As the temperatures increased to 437 °C short nanowires started to grow on the roots and randomly distributed on the surface of the substrate. This could be due to the low substrate temperature attributed to a low surface mobility for forming NiSi solid particles. Further increasing in the temperatures result in randomly growth and few nanowires grown on

the same root as demonstrated in Figure 9 at 477°C. The moderate mobility of the growth species at this temperature are sufficiently enhances the formation of NiSi phase solid particles and increase the precipitation of the nanowires. At temperatures of 577°C the roots are still observed and higher density, longer nanowires are appeared. The decomposition of SiH₄ and Ni diffusion at this temperature is sufficient as a result the reaction forms different phases of NiSi and the nanowires formed are higher density and longer comparing with those formed at lower temperatures. From the insert image of Figure 9 (d-f), it is observed that more than one nanowire are grown from one root. The average estimated length of the nanowires prepared at 437, 477, 510 and 577°C are about 179.3nm, 436.5nm, 580.8nm and 853.6nm respectively. While the average estimated width of the nanowires roots at these temperatures are 43.4nm, 124.1nm, 345.4nm and 529.8nm respectively. This increase in the nanowires density is similar to several reported works previously [11, 12]. It is believed that this increase in nanowires' lengths and roots' widths is due to the increase in surface mobility of the growth species [13]. It is also depend on the diffusion rate of Ni and Si in the CVD chamber. At high temperatures the diffusion of Si increased and this give rise to the formation of NiSi at different phases.



Figure 9: FESEM images of NiSi nanowires prepared by thermal CVD at different substrate temperatures of (a) 300, (b) 393, (c) 437, (d) 477, (e) 510, and (f) 577°C.

The FESEM images of the samples prepared at substrates temperatures 393°C and 477°C with respective EDX spectra are shown in Figure 10. The elemental composition of the samples at 393°C and 477°C are tabulated in table 1. It is noticed that at 393°C the sample consist of 89.17% Ni, 9.41% Si and 1.42% O. At this temperature Ni is dominant because the diffusion rate of Ni is faster than Si. However, the NiSi is not observed in XRD spectra in Figure 12 at 393°C. This is because the amount of Si is not sufficient enough to form nanowires.

At 477°C the percentage of Ni, Si and O are 80.72%, 18.06% and 1.22% respectively. As the temperature increased the diffusion of Si increased and this give rise to the formation of NiSi at different phases. The Ni to Si ratio at 393°C and 477°C can be calculated from table 1 and they are 9.48 and 4.47 respectively.

Table 1

Element contents of NiSi nanowires at 393 °C and 477 °C

Temperatures	Ni (%)	Si (%)	O(%)	Ni to Si ratio
(°C)	111 (70)	51 (70)	0(70)	
393	89.17	9.41	1.42	9.48
477	80.72	18.06	1.22	4.47



Figure 10: FESEM image of NiSi nanowires with respective EDX spectra prepared by thermal CVD at different substrate temperatures of (a) 393°C, (b) 477°C.

Figure11 illustrated the composition of NiSiNWs investigated by STEM/EDS elemental mapping at 437. As Figure11 (a) shows a typical bright-field STEM image of a single nanowire on a carbon film supported by a TEM copper-grid clearly reveals that the nanowire consisted of a core only without a shell. The Ni, Si, C and O elemental maps of the nanowires are presented in Figure11 (b), (c), (d) and (e) respectively. From the elemental mapping result it is observed that the nanowires consist of Ni and Si only. The appearance of O generally occurs in CVD grown nanowires it might originate from residual air inside the chamber. While the C come from the carbon film supported by TEM copper-grid.



Figure 11: (a) Dark-field STEM image of NiSi nanowire prepared by thermal CVD at substrate temperature of 437°C, (b–e) EDS element maps of the nanowire.

4.2.2XRD Analysis

The XRD pattern of NiSiNWs prepared at different substrate temperatures are shown in Figure 12. At low temperatures 300°C and 393°C, Ni only appears in the surface of the sample. It is located at 44.50° and 76.37° belongs to the (111) and (220) crystalline planes according to the JCPDS card number 00-004-0850. At these low temperatures, the arrival of Si- rich species on the Ni surface is not sufficient to activate the reaction of Ni and Si or the formation of NiSi is very low through the solid diffusion control process described by Peng et al [7, 13, 25]. This observation support the FESEM images in Figure 9 a, b and c in which no NiSiNWs observed.

As the temperature increased at 437°C, a little amount of NiSi located at 47.28° belongs to the (202) crystalline planes according to the JCPDS card number 00-038-0844 started to appears in the sample. The appearance of Ni₃Si₂ is observed at higher temperatures starting from 477°C. And it is located at 46.74° belongs to the (531)

crystalline planes according to the JCPDS card number 00-017-0881. These results support the previous discussed FESEM images where the nanowires can be seen clearly on the surface of the samples prepared at higher substrate temperatures 437, 477, 510 and 577°C. The increase in the temperature leads to transition of Ni-rich silicide to Si-rich silicide. And different silicide phases to appear such as NiSi and Ni₃Si₂.



Figure 12: XRD patterns of NiSi nanowires prepared by thermal CVD at different substrate temperature

4.2.3 HRTEM Analysis

The microstructure of these nanowires was investigated by HRTEM as shown in Figure 13. A single nanowire of the sample prepared at 437°C was selected for this HRTEM measurement. From the image it is clear that the NiSi nanowires consist no shell but only core. The elemental composition contents Si and Ni as discussed previously. The estimated lattice spacing is about 0.19 nm corresponds to NiSi (202) crystallographic plane JCPDS card No. 00-038-0844 which agreed with XRD spectra of 437°C as reported above.



Figure 13: HRTEM image of NiSi nanowires at 437°C

4.3 Electrical Analysis

4.3.1 CV Measurements

Figure 14 shows cyclic voltammograms of the nickel silicides at different scan rates over the main potential region of -0.5 to 0.7 V at different substrate temperatures from 300°C to 577°C. The current density increases with the scan rate. The anodic peaks

shift toward the positive region and the cathodic peaks shift toward the negative region. This resulted in an increase of the peak separation between the anodic and cathodic peaks. When this phenomenon happen, it indicates to irreversible formation of the passive film on the electrode surface [26].

At 393°C the CV profiles of the sample retain a distorted rectangular shape and do not significantly change with the increasing scan rates from 5mvs to 100mvs. From the figure the anodic peaks are located at about 0.54 V over 393°C sample.

The anodic peaks over the samples prepared at 437, 477, 510 and 577°C are located at about 0.5, 0.48, 0.5 and 0.48 respectively. The rectangular shape become less distorted as the temperature increases [27]. The anode peak has been reported at 0.7 V for the Ni oxidation: Ni–OH + Ni–OH = Ni–O + H₂O [18, 28].

To further explain the electronic properties of nickel silicides, CV curves of the samples prepared at different temperatures at scan rates 5 mV s⁻¹ are shown in Figure 15. With the increasing substrate temperature, the electrochemical surface areas of NiSiNWs were increased. The anodic peak potentials shifted in the negative direction and the cathodic peak potentials shifted in the positive direction. The highest current intensity was observed at sample prepared at 477° C. This can be related to the structural and morphology of NiSiNWs at this temperature. As can be observed from FESEM image in Figure 9 (e) the surface area of NiSiNWs at 477°C is high and this will enhance the current intensity.



Figure 14: Cyclic voltammetry (CV) curves of nickel silicides at different scan rates within a potential window of -0.5 to 0.7 V for different substrate temperatures.



Figure 15: Cyclic voltammetry (CV) curves of nickel silicides at scan rates 5mV/s within a potential window of -0.5 to 0.7 V for different substrate temperatures.

Figure 16 shows the capacitance and specific capacitance values of NiSi electrodes calculated at different step size from 0.005 to 0.1 (V/s). The results showed that the sample prepared at 477°C exhibited the highest specific capacitance at all the scan rate. This can be related to the structure morphology of the NiSiNWs prepared at this temperature. As can be observed from FESEM image in Figure 9 (e) the surface area of NiSiNWs at 477°C is higher comparing with sampled prepared at 510°C and 577°C. Such higher surface areas would make the access of ions in the electrolyte in the electrode surface more easy and enhance the capacitance [29].The specific capacitance of NiSi obtained at temperatures higher than 477°C decreased with the heat-treatment temperature due to possible loss of the electrode-electrolyte interface area. The surface area is important because the redox reaction is basically an interfacial phenomenon. Therefore, increasing the reaction sites will help to improve the overall capacitance [30].

The low temperatures 300°C and 393°C, contribute to low capacitance. This result support previous discussed FESEM images where the nanowires are not grown at this low temperatures.



Figure 16: Capacitance and specific capacitance of NiSi at different step size

Chapter 5

CONCLUSION AND SUGGESTION FOR FUTURE WORK

5.1 Conclusion

In this work, the NiSiNWs were synthesized by using thermal CVD with assistant of Ni as catalyst. The effects of substrate temperature on the growth, structural and electrical of NiSiNWs was studied.

Ni nanoparticles was acted as a catalyst templates by forming NiSi solid particles to initially grow the nanowires through a solid diffusion reaction process of Ni and Si at substrate temperature above 393 °C.

At higher substrates temperatures, more intensive nanowires grown due to the sufficient diffusion of Ni and Si.

The crystalline NiSi with core only was successfully observed by HRTEM. The NiSi phase changes from Ni-rich to Si- rich as the temperature increased.

The CV measurements showed that the sample prepared at 477°C exhibited the highest specific capacitance at all the scan rate. However, for temperatures higher than 477°C the capacitance decreased with the heat-treatment temperature due to possible loss of the electrode-electrolyte interface area.

38

REFERENCES

- 1. Peng, B., J.-K. Ha, and K.-K. Cho, Fabrication of silicon oxide nanowires on Ni coated silicon substrate by simple heating process. Materials Technology, 2012. 27(1): p. 30-33.
- Fukata, N., et al., Synthesis of silicon nanowires using laser ablation method and their manipulation by electron beam. Science and Technology of Advanced Materials, 2005. 6(6): p. 628-632.
- 3. Chang-Beom Jin, C.-J.K.a.M.-H.J., Growth of nickel silicide nanowire by chemical vapor deposition.
- 4. Chong, S.K., et al., Structural and photoluminescence investigation on the hot-wire assisted plasma enhanced chemical vapor deposition growth silicon nanowires. Journal of Luminescence, 2012. 132(6): p. 1345-1352.
- 5. Kim, C.J., et al., Spontaneous Chemical Vapor Growth of NiSi Nanowires and Their Metallic Properties. Advanced Materials, 2007. 19(21): p. 3637-3642.
- 6. Yu Huang, K.-N.T., Silicon and silicide nanowires : applications, fabrication, and properties.
- 7. Kim, J., Y. Park, and M.M. Kumar, Influence of temperature, metal layer, and groove angle in the nanowire growth: a prospective study on nickel silicide nanowires. Journal of Nanoparticle Research, 2015. 17(1): p. 1-7.
- 8. Zhang, X., et al., Nickel silicide nanocrystal-containing magnetoceramics from the bulk pyrolysis of polysilazane and nickelocene. Ceramics International, 2014. 40(5): p. 6937-6947.
- 9. Kim, J., Nickel Silicide Nanowire Growth and Applications 2010.
- 10. Tinani, M., et al., In situ real-time studies of nickel silicide phase formation. Journal of Vacuum Science & amp; Technology B, 2001. 19(2): p. 376-383.
- Chen, Y.Q., et al., Temperature dependence of morphology and diameter of silicon nanowires synthesized by laser ablation. Chemical Physics Letters, 2002. 358(5–6): p. 396-400.
- 12. Yang, M.-R., S.-Y. Chu, and R.-C. Chang, Synthesis and study of the SnO2 nanowires growth. Sensors and Actuators B: Chemical, 2007. 122(1): p. 269-273.
- Hamzan, N.B., et al., Effects of substrate temperature on the growth, structural and optical properties of NiSi/SiC core–shell nanowires. Applied Surface Science, 2015. 343(0): p. 70-76.

- 14. Fan, X., et al., Phase-controlled synthesis of nickel silicide nanostructures. Materials Research Bulletin, 2012. 47(11): p. 3797-3803.
- Liu, H., et al., Temperature-dependent structure and phase variation of nickel silicide nanowire arrays prepared by in situ silicidation. Materials Research Bulletin, 2012. 47(12): p. 3991-3994.
- 16. Utlu, G., N. Artunç, and S. Selvi, Temperature and thickness dependence of the grain boundary scattering in the Ni–Si silicide films formed on silicon substrate at 500 °C by RTA. Materials Chemistry and Physics, 2012. 132(2–3): p. 421-430.
- 17. Kim, J.A.W.A., Thin Solid Films, 2005. 483: p. 60-65.
- 18. Chen, X., et al., Structural and electrochemical properties of nanostructured nickel silicides by reduction and silicification of high-surface-area nickel oxide. Materials Research Bulletin, 2012. 47(3): p. 867-877.
- 19. Yipu Song , A.L.S., and Song Jin Ultralong Single-Crystal Metallic Ni2Si Nanowires with Low Resistivity 2007
- 20. Chung-Yang Lee, M.-P.L., Kao-Feng Liao, Wei-Fan Lee, Chi-Te Huang, Sheng-Yu Chen and Lih-Juann Chen Free-Standing Single-Crystal NiSi2 Nanowires with Excellent Electrical Transport and Field Emission Properties 2009.
- Abhaya, S., R. Rajaraman, and G. Amarendra, Experimental and theoretical positron annihilation studies on bulk nickel silicides. Applied Surface Science, 2008. 255(1): p. 142-144.
- 22. Lavoie, C.d.H., F. M, Detavernier, C, & Cabral Jr. C., Microelectronic Engineering, (2003): p. 70,144-157.
- 23. Chong, S.K., formation of silicon nanwires by chemical vapour deposition technique using indium catalyst. 2012.
- 24. Goldstein, J.I., Newbury, D. E., Echlin, P., Joyce, D. C , Fiori, C , and E. and Lifshin, . , Scanning Electron Microscopy and X-ray Microanalysis:New York (Plenum). 1981.
- 25. Peng, Y., et al., Thermodynamic evaluation of the C–Ta–Ti system and extrapolation to the C–Ta–Ti–N system. International Journal of Refractory Metals and Hard Materials, 2013. 40(0): p. 36-42.
- Abd El Aal, E.E., S. Abd El Wanees, and A. Abd El Aal, Anodic behaviour and passivation of a lead electrode in sodium carbonate solutions. Journal of Materials Science, 1993. 28(10): p. 2607-2614.

- 27. Siamak Pilban Jahromi, a.A.P., *a Boon Tong Goh,a Yee Seng Lim,a Wan Jefrey Basirun,b Hong Ngee Limc and Nay Ming Huang, Influence of particle size on performance of a nickel oxide nanoparticle-based supercapacitor. RSC Adv, 2015: p. 14010-14019.
- 28. Grdeń, M. and A. Czerwiński, EQCM studies on Pd–Ni alloy oxidation in basic solution. Journal of Solid State Electrochemistry, 2008. 12(4): p. 375-385.
- 29. Zou, X., et al., Remarkably enhanced capacitance of ordered polyaniline nanowires tailored by stepwise electrochemical deposition. Journal of Solid State Electrochemistry, 2007. 11(2): p. 317-322.
- 30. Kumta*, D.C.a.P.N., Chemically Synthesized Nanostructured VN for Pseudocapacitor Application. Electrochemical and Solid-State Letters, 2005: p. 8 (8) A418-A422