SCHOOL OF MATERIALS AND MINERAL RESOURCES ENGINEERING

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SYNTHESIS OF SILICON NANOWIRES BY CARBOTHERMAL EVAPORATION METHOD USING METAL CATALYST

By

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DECLARATION

I hereby declare that I have conducted, completed the research work and written the dissertation entitled "**Synthesis of Silicon Nanowires by Carbothermal Evaporation Method Using Metal Catalyst**". I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or university.

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Finally, I would like to dedicate this thesis to my parents, Kamal Bahrin bin Abd Majid and Wan Rohaya binti Wan Adnan. Their sacrifice, love and support meant so much to me which in the end gave me the motivation to complete my studies and research in Universiti Sains Malaysia.

Muhamad Dzulnawarin bin Kamal Bahrin

2017

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LIST OF ABBREVIATION

AFM	Atomic Force Microscopy
Au	Gold
AuNPs	Gold nanoparticles
CVD	Chemical Vapour Deposition
EDX	Energy-dispersive X-ray spectroscopy
FESEM	Field Emission Scanning Electron Microscope
MBE	Molecular Beam Epitaxy
MWNTs	Multi-walled nanotubes
Ni	Nickel
Si	Silicon
SiNWs	Silicon nanowires
SWNTs	Single-walled nanotubes
RCA	Radio Corporation of America
TEM	Transmission Electron Microscopy
VLS	Vapour-liquid-solid

SINTESIS WAYARNANO SILIKON MELALUI TEKNIK PENYEJATAN KARBOTERMA MENGGUNAKAN PEMANGKIN LOGAM

ABSTRAK

Wayarnano silikon telah berjaya dihasilkan melalui teknik penyejatan karboterma dengan bantuan pemangkin. Wayarnano silikon berdimensi di antara 45 nm hingga 65 nm dan di antara 35 nm hingga 65 nm telah dihasilkan dengan menggunakan pemangkin partikel nano emas dan nikel. Teknik penyejatan karboterma telah digunakan kerana penyediaan yang mudah dan tidak menggunakan kos yang tinggi. Campuran serbuk silikon dan serbuk karbon aktif dalam nisbah 1:1 telah digunakan sebagai bahan mula. Bahan mula tersebut dipanaskan di dalam relau yang mempunyai persekitaran gas lengai. Relau telah dipanaskan pada kadar 20 ^{o}C/min untuk mencapai suhu 1100 ^{o}C. Serbuk silikon yang tersejat dibawa oleh aliran gas nitrogen dan dimendap ke atas pemukaan wafer silikon yang berorientasi (111). Dengan mengawal parameter fizikal seperti kadar pemanas, masa dan suhu pertumbuhan serta posisi dan kedudukan wafer silikon morfologi dan komposisi kimia produk yang termendap telah dinilai dengan pelbagai teknik pencirian. Wayarnano silikon telah dihasilkan pada suhu 1100 ^{o}C selepas 1 jam dan 5 jam dengan menggunakan pemangkin nikel dan partikel nano emas. Wafer silikon telah diletakkan 12 cm secara menegak dari bahan mula. Berdasarkan uji kaji ini, boleh dikatakan bahawa wayarnano silikon telah dihasilkan melalui mekanisme gas-cecair-pepejal.

SYNTHESIS OF SILICON NANOWIRES BY CARBOTHERMAL EVAPORATION METHOD USING METAL CATALYST

ABSTRACT

Silicon nanowires (SiNWs) have successfully been synthesised by carbothermal evaporation method with the use of catalyst. SiNWs with the diameter range of with 45 nm to 65 nm and from 35 nm to 65 nm were grown by using gold nanoparticles (AuNPs) and nickel (Ni) catalyst respectively. Carbothermal evaporation method was utilised since the procedure is simple and inexpensive. The precursor used was the 1:1 mixture of silicon powder with activated carbon powder. The precursor was heated in an inert furnace atmosphere. The furnace was ramped up at 20 ^{o}C/min to reach the temperature of 1100 ^{o}C. The evaporated silicon powder was carried by flowing nitrogen gas and was deposited on the surface of (111) silicon substrate. By controlling the physical parameters such as heating rate, growth temperature and time, substrate position and location the morphology and chemical composition of deposited products were evaluated by various characterization techniques. SiNWs were grown at 1100 ^{o}C after 1 hour and 5 hours with the use of Ni and AuNPs catalyst respectively. The silicon substrate was placed 12 cm away from the precursor vertically. Based on the experimental results, it can be said the SiNWs were synthesised using the vapour-liquid-solid (VLS) growth mechanism.

CHAPTER 1

INTRODUCTION

1.1 Nanotechnology

Nanotechnology can be defined as the science and engineering that is involved in the design, synthesis, characterization, and application of materials which is at least one dimensional and on the nanometer scale (Silva et al., 2004). Nanotechnology encompasses the forming and use of materials, structures, systems and devices that have unique properties due to their small size. Not only that, nanotechnology also includes the technologies that make the control of materials at nanoscale possible.

The origin of the term ‘nanotechnology’ can be traced back to a speech given by Richard Feynman at California Institute of Technology in December 1959 called “There’s Plenty of Room at the Bottom” (Allhoff et al., 2009). He talked about the principles of miniaturization and atomic-level precision and how the concepts do not violate the law of physics. The word “nanotechnology” was introduced by N. Taniguchi in 1974 at the international conference on industrial production in Tokyo. He used the word to describe the superthin processing of materials with nanometer accuracy and creation of nano-sized mechanisms. In the late 1980s to early 1990s more research on nanotechnology was done and the revolution in nanotechnology begins with the discovery of one-dimensional (1D) nanostructure in the form of cabon nanotubes by Iijima. The unique properties offered by materials in nanoscale together with many possible applications have encouraged more research and development in the field of nanotechnology.

1.2 Nanomaterials

A nanomaterial is a material where some relevant dimension which is controllable is in the scale of 100nm or less (Ramesh, 2009). Nanomaterials are newly developed materials whereby the controlled structure has a dominant effect on the desired behaviour of the material or device. Nanomaterials can be divided into three classes which are discrete nanomaterials, nanoscale device materials, and bulk nanomaterials. Discrete nanomaterials are materials that are self-supporting with the scale in the range of 1-10nm and in at least one dimension. Discrete nanomaterials exist in the form of particles (zero-dimensional (0D) nanostructures) or fibers (one-dimensional (1D) nanostructures). Nanoscale device materials are nanoscale material elements that are contained within devices. Usually nanoscale device materials are in the form of thin film (two-dimensional (2D) nanostructures). Bulk nanomaterials on the other hand are materials that are available in bulk quantities but yet the structure is controlled at nanoscale. Bulk nanomaterials may be built up of discrete nanomaterials or nanoscale device materials which when grouped together will form three-dimensional (3D) nanostructures.

1.3 One-dimensional (1D) nanostructures

Compared to 0D nanostructures and 2D nanostructures, 1D nanostructures had a slow start in advancement in the beginning. However, 1D nanostructures such as nanowires, nanorods and nanotubes have received a lot of attentions lately.

Generally, nanomaterials can be synthesised by top-down and bottom-up approach. Top down approach refer to the process of producing nanomaterials from a bulk sample. Bottom-up approach on the other hand refers to the process of producing nanomaterials from smaller building block or through chemical synthesis of nanomaterials. Throughout the last decade, many synthesis methods involving top-down and bottom-up approaches for 1D nanostructure have been developed. Some of the popular processes are electric arc discharge, chemical vapour deposition and laser ablation.

A lot of researches on 1D nanostructures have been done due to their unique characteristics and behaviour. Based on researches done, it is expected that 1D nanostructures to play an important role as interconnects and functional units in electronic devices in nanoscales (Xia et al., 2003). Furthermore, it is widely accepted that 1D nanostructures give a good system to study on the reliance of thermal and electrical transport or mechanical properties on dimensionality and size reduction.

1.4 Problem statement

There are many methods that can be used to synthesis SiNWs. A cheap and simple alternative method is needed in order to reduce the cost to synthesis SiNWs. Among the available methods to synthesis SiNWs, carbothermal evaporation method is the best method that can be utilised. This is because carbothermal evaporation method is a simple method and the cost to synthesis SiNWs with this method is low. During the synthesis of SiNWs, oxide layers will form at high temperature. Moreover, the temperature to grow SiNWs is high since the melting temperature of Si is around 1400 ^{o}C. Therefore, the presence of activated carbon in the precursor mixture can help to reduce or eliminate the problem related to oxide layer since carbon is a reducing agent. Also, the activated carbon can as well reduce the growth temperature of SiNWs. However, from this method suitable parameters are required in order to successfully grow SiNWs. The parameters that can affect the outcome are such as the growth temperature, heating rate, growth time and also the location and position of the substrate. Thus, it is important to study the suitable parameters to grow SiNWs. Carbothermal evaporation method can still grow SiNWs without using metal catalyst. Despite that, metal catalysts are used in this experiment to facilitate the SiNWs growth. Therefore the effect of using different metal catalysts is observed in this experiment.

1.5 Research objectives

This thesis focus on the fabrication of SiNWs by carbothermal evaporation method which is controlled by a few parameters such as the presence and type of catalyst, gas flow rate, growth time and heating rate. Therefore, the objectives of this study are:

i) To synthesis SiNWs by using carbothermal method.

ii) To study the effect of different catalysts used to grow SiNWs.

iii) To study the effect of growth time and temperatureto grow SiNWs.

1.6 Scope of project

The scope of this study is to synthesis SiNWs by carbothermal evaporation method. This process is a modification of conventional thermal evaporation method and was carried out with predetermined growth temperature and time. Activated carbon is used as the reducing agent as well as lowering the growth temperature in this experiment. The source materials were mixed accordingly and nitrogen gas was used as the carrier gas for the source material to deposit on the silicon wafer. Catalyst was used in order to facilitate the growth of SiNWs. Observation and analysis on the produced SiNWs was carried out. Such observation and study is important in determining the best parameters to grow SiNWs by carbothermal evaporation method.

CHAPTER 2

LITERATURE REVIEW

2.1 Nanotechnology, nanomaterials and nanostructures

Nanotechnology is a technology that involves small small-sized structures or materials (Cao, 2004). Generally, nanotechnology can be described as the technology of design, fabrication and application of nanostructures and nanomaterials. These nanostructures can be divided into: 0D nanostructures, 1D nanostructures, 2D nanostructures and 3D nanostructures. As for the term nanomaterials, according to according to Khot and co-workersare materials with particle size less than 100 nm in at least one dimension (Khot et al., 2012). Typically, the dimension of nanomaterials ranges from subnanometer to several hundred nanometers. These types of materials have different properties compared to conventional materials whereby their thermal, mechanical, electronic, and biological properties differ and not found in conventional materials. As for an example, the melting point of crystals in nanometer scale has a low melting point and reduced lattice constant due to the number of ions or atoms. The total number of ions or atoms and the energy of surface play an important role in thermal stability. Energy of surface can be defined as the sum of intermolecular forces on a material’s surface. These sorts of properties enable advancement in different kinds of applications across chemistry, biology, engineering and physics.

2.1.1 Zero-dimensional (0D) nanostructures

0D nanostructures are materials whose sizes are confined to the nanoscale in all three dimensions (Li & Wu, 2013). There are several terms which are used for 0D nanostructures such as nanoparticles, nanospheres and nanocrystals for nanoparticles which are single crystals. Recently, 0D nanostructures such as quantum dots (Landry et al., 2014), core–shell quantum dots (György et al., 2012) and hollow spheres (Abdollahi et al., 2013) have been synthesized by several research groups. Figure 2.1 shows an example of 0D nanostructures in the form of quantum dots under scanning electron microscope (SEM).

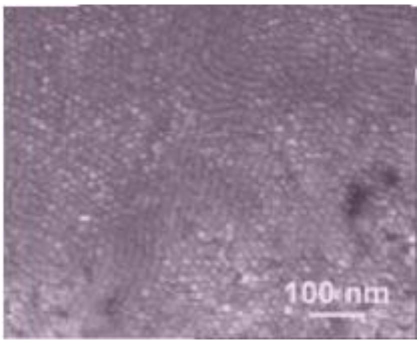

Figure 2.1: 0D nanostructures in the form of quantum dots under SEM(Tiwari et al., 2012).

2.1.2 One-dimensional (1D) nanostructures

Nanowires, nanotubes and nanorods are among the terms used for 1D nanostructures. These 1D nanostructures have demonstrated many novel properties due to their high aspect ratios, large specific surface areas and structural confinement on the circumference. It is also known as quantum wire it can conduct electricity whereby the quantum effects manipulate the transport properties. Since the discovery of carbon nanotubes by Iijima the 1D nanostructures has achieve significant attention. Carbon nanostubes is an example of 1D nanostructures that exists in the form of single-wall nanotubes or multi-wall nanotubes. Since its discovery, 1D nanostructures have made profound interest in the field of nanoelectronic and devices as well as nanocomposites. Figure 2.2 shows an example of nanowires under SEM.

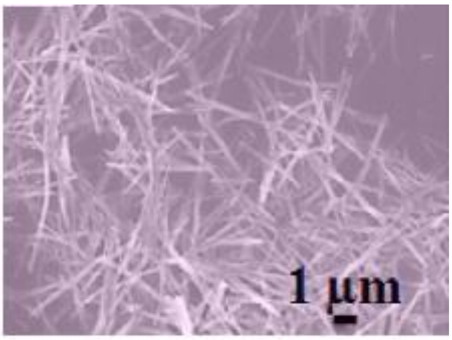

Figure 2.2: Image of nanowires under SEM(Tiwari et al., 2012)

2.1.3 Two-dimensional (2D) nanostructures

Terms used for 2D nanostructures are nanofilm, nanosheets and nanolayers. 2D nanostructures are also known as quantum well. The term “well” refers to a semiconductor region that is grown to possess a lower energy. It acts as a trap for electrons and holes and due to small thickness and therefore only specific energies and band gaps are allowed. Because of quantum well structures are very thin, they are easy to be modified and the properties can be altered. Figure 2.3 shows 2D nanostructures in the form of nanosheets under transmission electron microscope (TEM).

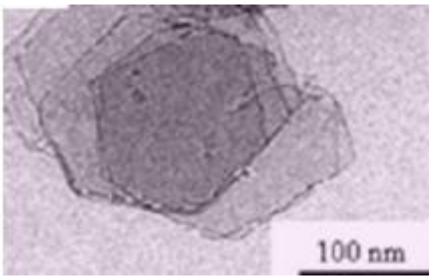

Figure 2.3: 2D nanostructures in the form of nanosheets under TEM (Tiwari et al., 2012)

2.1.4 Three-dimensional (3D) nanostructures

3D nanostructures are other types of nanostructures which are attached to a bulk material. The nanostructures attached to the bulk material usually are the form of nanoparticles or nanospheres which are 0D nanostructures. 3D nanomaterials can also contain dispersions of nanoparticles, bundles of nanowires, and nanotubes as well as multinanolayers. Box-shaped graphene (BSG) nanostructure is an example of 3Dnanomaterial (Lapshin, 2016). This nanostructure is a multilayer system of parallel hollow channels which the quadrangular cross-section extending along the surface. Figure 2.4 shows an example of nanocones, 3D nanostructures under TEM.

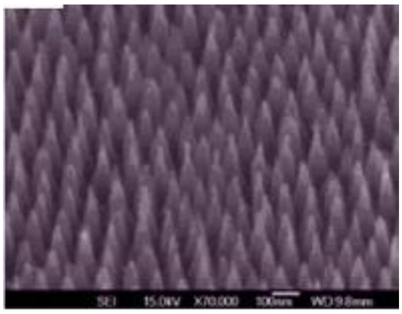

Figure 2.4: Nanocones, a 3D nanostructures under TEM (Tiwari et al., 2012).

2.2 Semiconductor nanowires

Semiconductors are materials either crystalline or amorphous solids with distinct electrical characteristics. Typically semiconductors have higher conductivity than insulators but lower than conductors. The conductivity of semiconductor is somehow can be altered by doping process. Doping is the process of intentionally introducing impurities into an intrinsic semiconductor. Lightly doped semiconductors are known as extrinsic semiconductors and heavily doped semiconductors are known as degenerated semiconductors.

For semiconductors or insulators, there exist a gap between the filled and empty electronic states (Rockett, 2008). The charge in the material can be carried by electrons moving in the empty states of conduction band or by the absence of electron which creates a 'hole' moving towards the normally filled states of the valence band. For conduction to happen, electrons from the valence band must be excited into the conduction band and in order for the electrons in the valence band to excite into the conduction band, the electrons must overcome certain energy level associated with the band gap before being excite. Figure 2.5 shows the band gap of a conductor, semiconductor and insulator.

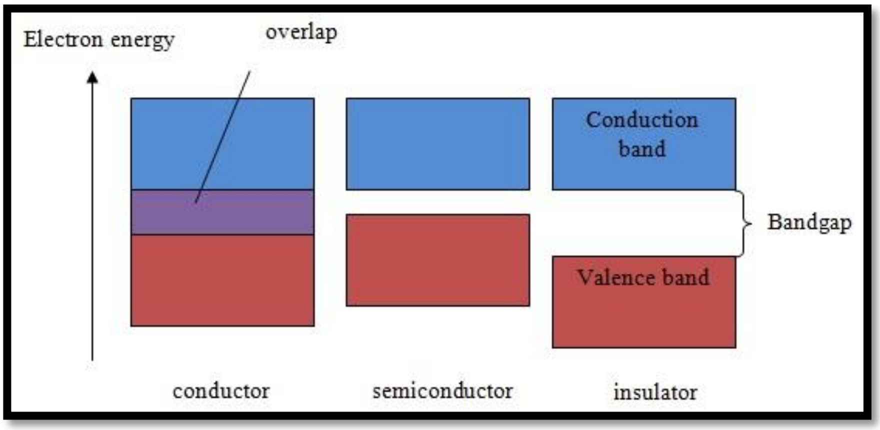

Figure 2.5: Band gap of a conductor (metal), semiconductor and insulator

Among the semiconductor materials available the most well known are silicon (Si) and germanium (Ge). These semiconductors are normally used in electrical devices and as the device size shrinks, the device characteristics become increasingly sensitive to dimensional variations. Due to the small sizes of devices these days, semiconductors in the form of nanowires are being extensively studied and will be used a lot more in future devices. Moreover, the use of 1D nanostructures offers unique opportunities to control the density of states of semiconductors as well as their electronic and optical properties. Density of states is the number of allowed electron (or hole) states per volume at a given energy. The density of states as a function of electrons conduction energy is different in 0D nanostructures, 1D nanostructures, 2D nanostructures and 3D nanostructures. This is due to the different confinement and delocalisation of electrons in all different types of nanostructures.

2.3 Silicon nanowires (SiNWs)

SiNWs are 1D structures with a diameter of less than 100 nm (Mikolajick & Weber, 2015). SiNWs have large surface to volume ratio due to diameter.

In the process of fabrication, SiNWs can be produced by either top-down or bottom-up approach. For SiNWs, vapour liquid solid (VLS) mechanism is the most prominent approach (Mikolajick & Weber, 2015). In this approach normally a metal catalyst is utilised in order to promote the growth of SiNWs. Metal catalysts, such as aluminium, nickel, titanium, zinc, tin, and indium have been used in the growth of SiNWs but Au has been the most widely utilised. An important note on the VLS mechanism is that the size of the Au cluster determines the diameter of the nanowires which means the bigger the size of Au cluster, the bigger the diameter of the nanowires.

In one-dimensional shape, Si exhibits unique properties and the 1D behaviour of SiNWs with very small dimensions can be utilized in devices in many different ways. Due to its unique properties, SiNWs can be used in Li ion batteries (Prosini et al., 2015), solar cells (Ko et al., 2015) and drug delivery (Peng et al., 2013) for biological applications.

2.3.1 Possible applications of silicon nanowires

SiNWs have a lot of possible applications by taking the advantage of their surface-dependent physical and chemical properties. The SiNWs may be developed for various applications in biological applications, batteries and solar cells.

2.3.1.1 Biological applications

Recently, nanotechnology has received increased attention in biological research. Among the nanomaterials, SiNWs have emerged as promising materials for biological application such as tissue engineering, biosensors and drug delivery. The nanoscale diameter and high aspect ratio of SiNWs make them easy to get to the interiors of living cell and making it possible to be used in biological applications. In drug delivery, one of the disadvantages of conventional drug tablets is the lack of proper control of drug release rate and target delivery area. Nanoscale drug delivery systems can be created to adjust the release kinetics and bioavailability over time, regulate biodistribution as well as minimize the toxic side effects, thus enhancing the remedial index of a given drug (Shao et al., 2010).

2.3.1.2 Li Ion batteries

SiNWs can also be used in lithium ion batteries. As for an example, Prosini and co-workers have synthesised a lithium-ion battery based on $LiFePO_4$ and SiNWs (Prosini et al., 2015). Si is a particularly attractive material due to high theoretical storage capacity of about 4000 mAh/g, which is more than 10 times that of graphite (Ball,2015). Other than being low-cost, large-area and easy to prepare,the SiNWs have good conductivity, nanometer-scale rough surfaces, larger charge capacity, andlonger cycling stability and these features aid the transport of charge and the ions of Li. Moreover the use of SiNWs can improve the storage capacity for the Li ion battery anode, since storage of four Li ions can be stored in one Si atom but a normal Li ion generally needs six C atoms. This happens due to the ability for Li ions to intercalate into Si structures. This shows that by using SiNWs as the electrode, higher storage of lithium ion batteries can be achieve rather than using carbon as the electrode.

2.3.1.3 Solar Cells

Photovoltaic devices using SiNWs with a radial p-n junction have received much attention due to their excellent optical and electrical characteristics recently. From the material and device structure point of view, high-aspect-ratio nanowires are possible candidates to convert photons to charges capably (Shao et al., 2010). The antireflection properties of Si improve light absorption and the orthogonal direction between the charge-carrier collection path and incident light. These features enables the use of low-quality Si in the production of solar cells (Ko et al., 2015). In solar cells, the key steps involved are photon absorption, exciton transport, exciton dissociation and charge collection. Not only that, a solar cell based on SiNWs can achieve efficient absorption of sunlight. Figure 2.6 shows a schematic of a SiNWs based solar cell with a radial p-n junction.

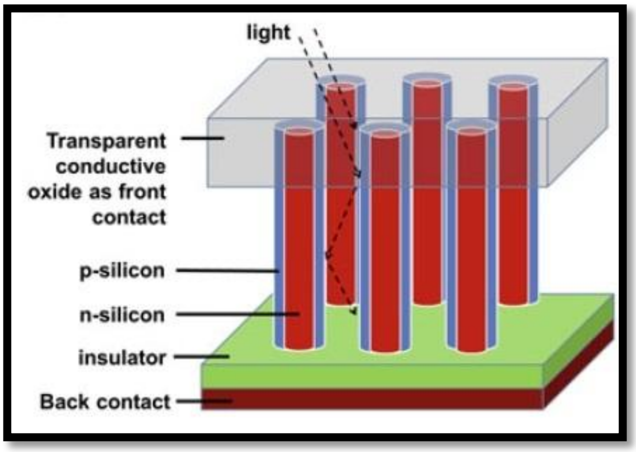

Figure 2.6: Schematic view of a SiNWs based solar cell with a radial p-n junction (Mikolajick & Weber, 2015).

2.4 Vapour-liquid-solid (VLS) growth mechanism

VLS growth mechanism is a growth mechanism that is assisted by a metal catalyst for 1D nanostructures. For this mechanism, the metal catalyst will form liquid alloy droplets at a high temperature by adsorbing vapour components (Choi, 2012). When the alloy is supersaturated, it becomes a solution on which the actual concentration of the components is higher than the equilibrium concentration. Then the solution drives the precipitation of the component at the liquid-solid interface to achieve minimum energy of the alloy system. As long as the vapour concentration is supplied, the nanostructures will begin and continue to grow. Since vapour which carries solid components, liquid which is the catalyst alloy and solid which is the precipitated one-dimensional structures phasesare involved, it is known as the VLS mechanism(Choi, 2012). In VLS, the position and size of the 1D nanostructures depends on the position and size of the catalyst as the liquid phase is confined to the area of the precipitated solid phase. In order for the metal catalyst to form liquid alloy, the process needs to be done at high temperature. Examples of processes that involve VLS growth mechanism are laser ablation, chemical vapour deposition (CVD), molecular beam epitaxy (MBE) and carbothermal reduction.

Figure 2.7 shows a schematic of the growth mechanism via VLS. In the beginning a thin Au film is deposited onto a Si wafer either by sputtering or thermal evaporation. Then the wafer will be annealed to temperature higher than the Au-Si eutectic temperature. This will later create Au-Si alloy droplets on the surface of the wafer. The function of Au-Si droplets is to lower the activation energy of the normal vapour-solid growth. SiNWs will be grown as Si atoms precipitate out of the super saturated liquid-alloy at the liquid-alloy/solid-Si interface.

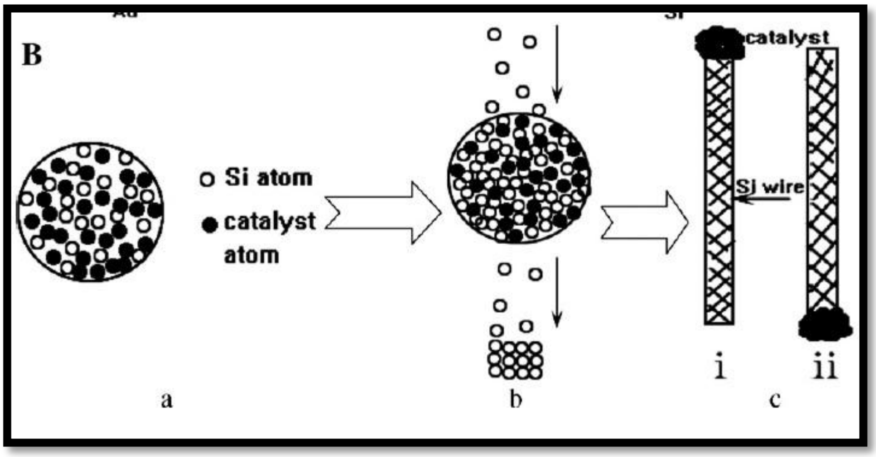

Figure 2.7: Schematic of the growth mechanism via VLS (Niu & Wang 2008).

2.4.1 Role of catalyst in VLS growth

Metal catalysts are necessary in VLS growth despite not all metals can work as catalyst in the growth mechanism. For a metal to be used as a catalyst it must fulfil certain requirements which are i) it must form a liquid solution with the component of a solid phase; ii) the catalyst must have higher solubility in the liquid phase than that in the solid phase; iii) the metal must be inert to the reaction product; iv) it must not form intermediate solid; v) the vapour pressure of the catalyst component over the liquid alloy should be small to avoid the catalyst from evaporating during the growth process (Choi, 2012). Examples of metals that can be used as catalyst are Au and Ni as both metals work well for the growth of group IV materials and III-V semiconductors.

2.4.2 Gold nanoparticles (AuNPs) as catalyst

Au is a common metal used in the growth of SiNWs and other group IV materials. Au is a good choice of catalyst for VLS growth since it greatly reduces the growth temperature. Based on the Au-Si phase diagram (Figure 2.8), it can be seen that the eutectic point is 363 ^{o}C. Therefore the energy required for the growth is less since the temperature is lower. Above the eutectic point the Au-Si composition will follow the liquidus line that indicates equilibrium between the solid and liquid. For instance, at 1100 ^{o}C liquid alloy can be found on the liquidus line. However, due to temperature or vapour pressure fluctuation over the liquid alloy dissolves more Si than the equilibrium composition and thus causing supersaturation. This supersaturation state is thermodynamically unstable. This unstable condition causes solid phase precipitated from the supersaturated liquid alloy until an equilibrium state is reached (Choi, 2012). Despite this, it should be acknowledged that the current available phase diagram is based on bulk material. Since nanomaterials have unique thermodynamic properties the phase diagram can be different compared to the system of bulk materials.

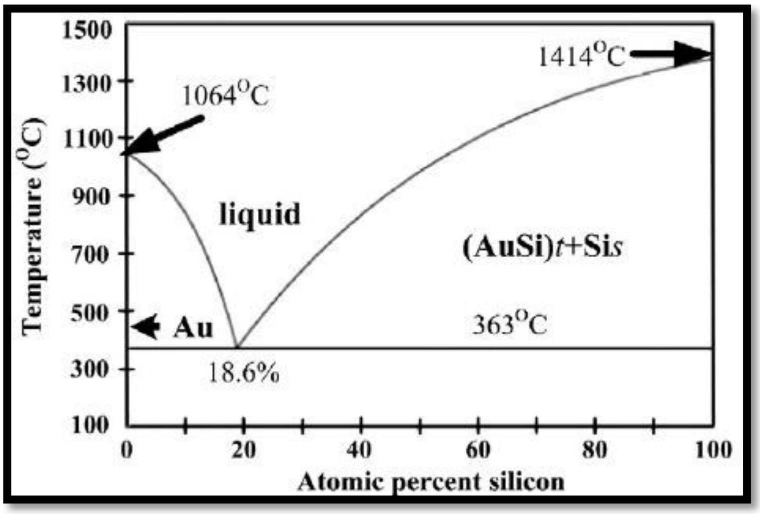

Figure 2.8: Au-Si binary phase diagram (Kuo & Gau, 2011)

2.4.3 Nickel (Ni) as catalyst

The Au-Si eutectic temperature is easily reachable, however Au forms deep carrier traps in Si and therefore need to be avoided for electronic applications (Tuan et al., 2005). Other than that, Au is an expensive material and a cheaper metal catalyst alternative that can be used in SiNWs growth is Ni. The use of Ni as a catalyst seems to be very promising since Ni is thermodynamically compatible with VLS assisted SiNWs growth. Despite being a cheaper material than Au, the synthesis of SiNWs is done at higher temperatures. Based on the Ni-Si phase diagram (Figure 2.9) it can be seen that eutectic reactions happen at four different temperatures which are
964 °C, 966 °C, 1143 °C and 1215 °C.

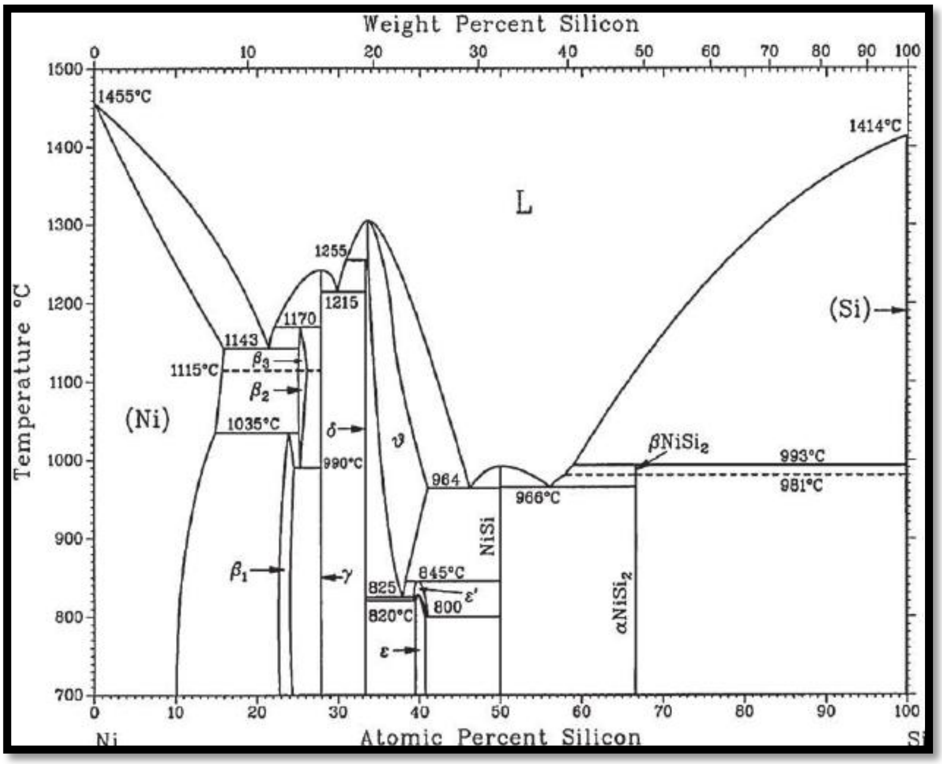

Figure 2.9: Ni-Si binary phase diagram (Connetable & Thomas, 2011)

2.5 Techniques of growing silicon nanowires

SiNWs can be grown in many different kinds of methods with each method has their own advantages and disadvantages. In a broad sense, SiNWs can be grown by top-down approaches whereby a bulk material is processed to make a nanomaterial and bottom-up approaches, in which the nanomaterial is built up from finer scales (Ramesh, 2009).

Bottom-up approaches of nanomaterials synthesis are mostly chemical methods such as sol-gel, chemical precipitation, vapour deposition, sonochemical, electrochemical, microemulsion, combustion and so on (Singh et al., 2012). The ability to control the growth parameters at the synthesis stage with pre-defined properties is the advantage of bottom-up approach. Top-down approach on the other hand is the process involves evaporating, melting or breaking bulk materials into atoms or smaller particles thermally or by focusing electron, laser, ion or molecular beams (Singh et al., 2012).

Other examples of top-down approach are by using electron beam lithography, focused ion beam lithography and atomic force microscopy lithography. For electron beam lithography technique, it utilises an accelerated electron beam focusing on an electron-sensitive resist to make an exposure. Subsequently, this electron-beam spot with a nanometer diameter is scanned on the surface of resist in a dot-by-dot fashion to generate patterns in sequence (Pimpin & Srituravanich, 2012). For focused ion beam, it utilises and accelerated ion beam instead of electron beam that directly punches a metallic film on the substrate. This is made possible because ions are heavier than electrons (Pimpin & Srituravanich, 2012). As for atomic force lithography, interaction between the probe and substrate separation in close contact condition ~1 nm is the principle of how it works (Hutagalung et al., 2014). As suitable external field or forces are exerted, the probe will induce various physical and chemical processes on the surface of the substrate. Therefore, localised nanostructures are generated due to physical and chemical processes on the surface of the substrate.

2.5.1 Laser ablation

Laser ablation technique is one of the earliest methods used to synthesise SiNWs. In this process, the target is heated in a furnace to about 1200 °C and then ablated by a laser beam (Shao et al., 2010). Inert gas is used as the carrier gas that transports and cools down the ablated products when they are deposited as nanowires. The advantage ofthis method is that SiNWs can be synthesized in high purity, high yield, and in large quantity (Shao et al. 2010). However, this technique requires low wavelength, high energy and focused pulsed laser which prevents the method from having a wider application.

2.5.2 Chemical vapour deposition (CVD)

Chemical vapour deposition is the process of depositing thin film on substrate a usually silicon substrate. In this process, the deposited product is formed by exposing the substrate to volatile precursors such as SiH_4 or $SiCl_4$ that will react and decompose on the substrate. Not only that, in this process the inert gas flow vital to remove the volatile byproducts produced from the reaction. In the synthesis of nanowires, the substrate can be modified by coating with metal and in the synthesis of SiNWs, Au is usually used to coat the substrate and act as the catalyst for the growth. Figure 2.10 shows a schematic of CVD set-up.

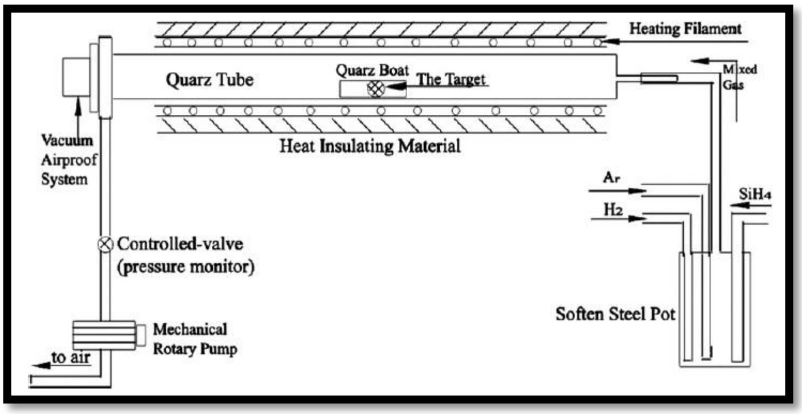

Figure 2.10: Schematic of CVD set-up (Niu & Wang, 2008)

2.5.3 Molecular beam epitaxy (MBE)

Molecular beam epitaxy (MBE) technique have been in use since 2000 to synthesis Si, II-VI and III-V compound semiconductor nanowires based on the nanocluster-catalysed VLS growth mechanism. According to (Shao et al., 2010) synthesis of silicon by the MBE technique usually needs a high-purity solid Si source heated and crystallized under ultrahigh vacuum with gold as seed and for example, SiNWs were produced by MBE on Si substrates. The growth behaviour differs from CVD and the difference lies in the role of the metal seed, the wire morphology and the aspect ratio. In this process, elemental Si is used as the source material instead of chemical compound of Si such as SiH_4. MBE growth strongly relies on Si surface diffusion and therefore the growth temperatures are typically higher than 500 °C to facilitate this diffusion process. Figure 2.11 shows the schematic of MBE set-up.

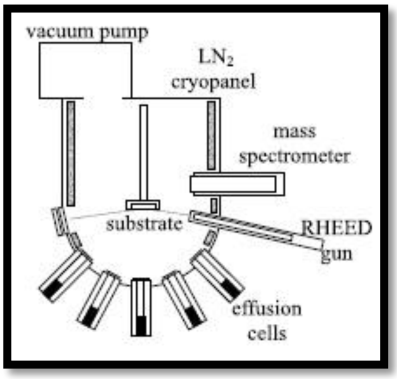

Figure 2.11: Schematic of MBE set-up (Rinaldi, 2002)

2.5.4 Thermal Evaporation Oxide-Assisted Growth (OAG)

This process is one of the promising methods to synthesis SiNWs due to its simplicity and low costs. The growth of SiNWs through this process involves thermal evaporation of either mixed powders of SiO_2 and Si to produce SiOvapour or a pure SiO powder. In this approach the SiNWs growth is proposed to be ‘semi-liquid’ SiO_x, while the solid SiO_2 can avoid lateral growth. It was stated by Shao and co-workers that the yield and growth rate of SiNWs by this method is higher in a closed deposition system without circulation of inert carrier gas, but decreases with increasing ambient gas pressure (Shao et al., 2010). Not only that, at low pressure a smooth surface of SiNWs can be produced. Also the size, shape and structure of the SiNWs can be controlled by their composition as well as temperature and other parameters of the process such as the heating rate.

2.5.5 Carbothermal evaporation

The name carbothermal is adapted from essential existence of carbon to promote high purity nanowires that is synthesized at high temperature (Hutagalung et al., 2007). The carbothermal reactions make use of activated carbon as the reducing agent which is mixed with oxide as well as reducing the growth temperature of SiNWs. The oxide is allowed to react with gaseous reactant to produce desired nanowires.

Carbothermal evaporation technique involves the heating of SiO_2 and with the addition of C in appropriate atmosphere, usually inert atmosphere. During the heating process, the presence of carbon will assist in the formation of oxidic species in the vapour phase which then will be transformed into final crystalline SiNWs. In this process, it is crucial to control the amount of C because too much C will produce carbides. Figure 2.12 shows the Si-C phase diagram. From the phase diagram it can be seen that the presence of C lowers the growth temperature as the eutectic point is at 1400 ^{o}C.

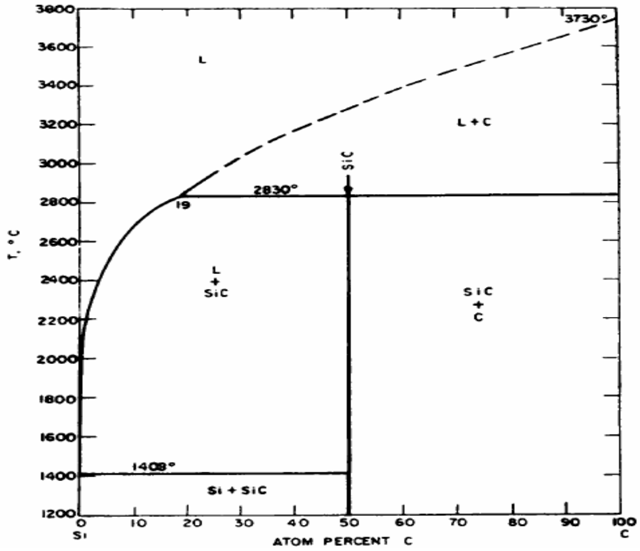

Figure 2.12: Si-C phase diagram (Sadler & Shamsuzzoha, 1997)

According to (Gundiah et al., 2003) the formation of SiNWs in the presence of carbon can be explained as follows. Generally, the Si is covered by oxide layer. The mechanism proposed by them contributed a great understanding the growth of SiNWs by carbothermal evaporation method. Si is generally covered by an oxide layer. The oxide layer gets reduced by carbon into SiO by the following reactions.

Si_xO_2 (s) + C (s) → Si_xO (g) + CO (g) ($x>1$) (2.1)

Si_xO (g) → Si_{x-1} (g) + SiO (g) (2.2)

2SiO (g) → Si (s) + SiO_2 (s) (2.3)

This process can be modified in certain ways in order to produce SiNWs. Apart from controlling the growth temperature and time, heating rate, substrate location and position, the substrate can also be coated with metal to facilitate the growth of the SiNWs. The metal coating will act as catalyst but can also affect the purity of the nanowires formed.

2.5.5.1 Carbon

C can be found almost everywhere in the world. In the periodic table, carbon can be found in the same group as silicon which is group IV with the atomic number of six. C is a very reactive element and it can form a hug number of compounds with many other elements. Other than joining with other elements, C atoms can also form strong bonds with up to four other C atoms. Although C is normally bond to other elements, it also can exist on its own and the most common form of carbon is the amorphous carbon. Figure 2.13 shows and image of amorphous carbon under SEM.

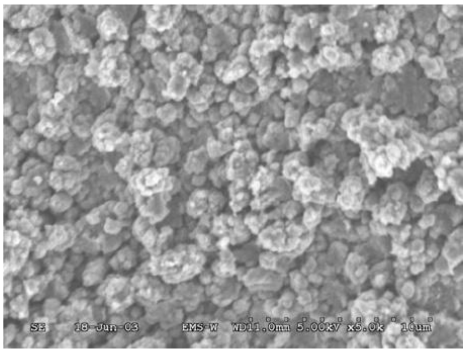

Figure 2.13: Image of amorphous carbon under SEM (Sen & Puri, 2004).

The next allotrope of C is the strongest material on earth which is diamond. In diamond the bonding between the C atoms in a tetrahedron gives the high hardness of the material. Recently, a new allotrope of C is found which is fullerene. Fullerene is a large molecule of C atoms linked in hexagons and pentagons. The most famous is buckminsterfullerene which has 60 C atoms. Graphite is also another allotrope of C. It is a crystalline and a semimetal. Graphite has a layered, planar structure and each individual layers is call graphene. In each of the layers, the C atoms are arranged in a honeycomb lattice and the atoms are covalently bonded with only three bonding satisfied.

In the 1990s, Sumio Iijima discovered another allotrope of carbon called carbon nanotubes with a cylindrical nanostructure. Carbon nanotube is a tube made of a single graphite layer rolled up into a hollow cylinder is called a single-walled nanotubes (SWNTs) and if the tube comprising several, concentrically arranged cylinders is referred to as multiwall tubes (MWNTs). The properties are different and unusual compared to bulk C due to the fact that the structure is in nanoscale (Reich et al., 2004). The discovery by Iijima has led to the advancement in today's research and technology.

2.5.5.2 Activated carbon

Family of carbons ranging from carbon blacks to nuclear graphites, from carbon fibres and composites to electrode graphites and activated carbon is one of the member of the family (Marsh & Rodríguez-Reinoso, 2006). Activated carbon is an adsorbent materials that can be used in water treatment, gas and chemical purification, and medical poisoning treatment to gas storage (Romanos et al., 2011).

Activated carbon does not occur naturally, it has to be synthesised. In the synthesis of activated carbon, further porosity and widening of existing porosity as well as modification on the surfaces of porosities and carbonization process are done. The process involves the use of either carbon dioxide or steam or mixture of both gases. As a result of high numbers of pores, the micropores provide superb conditions for adsorption to happen. Adsorption is the process whereby liquid or gaseous molecules are contracted on a solid surface.

Physically, activated carbon binds materials by London dispersion force or by van der Waals force. London dispersion force is an attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary dipoles. However, activated carbon does not bind well to chemicals such as alcohol,