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One Dimensional Silicon Nanostructures Synthesized via Thermal Evaporation on Nickel Coated Silicon Wafer: Effect of Substrate Position

A. Ahmad and S.D. Hutagalung
School of Materials and Mineral Resources Engineering,
Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

Abstract: One-dimensional silicon nanostructures were synthesized via thermal evaporation technique using nickel catalyst. Effects of nickel catalyst and silicon substrate position on the formation of silicon nanostructure were studied extensively. Silicon powder that used as silicon source was evaporated at 900-1000°C for 1 h using tube furnace under controlled environment. The uncoated and nickel-coated silicon substrates were positioned at 3-12 cm from the silicon powder at downstream nitrogen gas flow. It was found that on the substrate without nickel catalyst have no traces of silicon nanostructures. However, on the nickel-coated silicon substrate obtained nanowires and needle-like nanostructures with various diameter and length. These results prove that nickel catalyst is playing an important role on the growth of silicon nanostructures on silicon substrate. Most of the grown one-dimensional silicon nanostructures are not in vertical alignment but bends to the certain direction. This bent-shaped formation might be due to the applied force of carrier gas flow during thermal evaporation. The nickel catalyst at the tip of silicon nanowires could be confirmed the growth mechanism of one-dimensional silicon nanostructures is similar to vapor-liquid-solid mechanism.

Key words: Silicon nanowires, thermal evaporation, nickel catalyst, substrate position, electron microscopy

INTRODUCTION

Semiconductor nanowires have been studied intensively over the past year due to their potential applications for nanoscale device fabrication (Takahashi *et al*., 1998; Lee *et al*., 2000; Huang and Lieber, 2004; Wu *et al*., 2007; Riyadi *et al*., 2010). Typically, these nanostructures can be single crystal, polycrystalline, amorphous or organic chains with diameter of 10 to 100 nm and length of several microns. The ability to predictably control their properties makes nanowires particularly promising to be used as a building block for the next generation of nanoscale devices. As one of the semiconductor nanowire types, the one-dimensional (1-D) silicon nanostructures such as silicon nanowires (SiNWs) have attracted much attention in recent years for their valuable electrical and optical properties, as well as their potential applications in mesoscopic research and nanodevices (Nagase *et al*., 2003). Silicon whisker is the first silicon nanowire type prepared by Wanger and Ellis (1964) with diameters from one hundred nanometers to hundreds of microns.

Many techniques and growth mechanism have been proposed in the formation of 1-D nanostructures (nanowires, nanorods, nanotubes, etc.). Most of the successful semiconducting nanowire growth is based on the vapour-liquid-solid (VLS) mechanism (Carter, 1973; Wokulski, 1987; Hiruma *et al*., 1991; Motojima *et al*., 1995; Yumoto *et al*., 1999; Feng *et al*., 2000). The VLS growth is commonly referred to as either impurity or catalyst, which purposely introduced to direct and confine the crystal growth on to a specific orientation and within a confined area. A catalyst forms a liquid droplet by itself or by alloying with grown material during the growth, which acts as a trap of growth species. Enriched growth species in the catalyst droplets subsequently precipitates at the grown surface resulting in the one dimensional growth (Cao, 2004). Nanowires obtained by such a crystal growth mechanism are catalyzed by a metal eutectic nanodroplet. The metal nanoparticle has a major role in a VLS assisted nanowire growth.

There are many methods have been developed to synthesize 1-D silicon (Si) nanostructures that ranging from chemical or electrochemical to physical deposition approach (Gotza *et al*., 1995; Holmes *et al*., 2000; Hwang *et al*., 2000; Yu *et al*., 2001; Hu *et al*., 2002; Peng and Zhu, 2003; Prokes and Arnold, 2005; Hutagalung *et al*., 2007; Sulieman *et al*., 2010). By

Corresponding Author: S.D. Hutagalung, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

choosing one of these techniques, a large variety of 1-D Si nanostructures such as nanowires, nanowhiskers, nanorods, nanofibres, nanoneedles could be successfully obtained. Producing silicon nanowire with desired chemical composition and morphology requires precise control of the parameters during the growth process. In the fabrication of silicon nanowire via thermal evaporation technique, there are few parameters have to be controlled properly including growth temperature, soaking time, heating rate, gas flow rate, catalyst and substrate. The controllable synthesis process is very important for silicon nanowire production (Xing *et al*., 2003).

The use of nickel (Ni) as a catalyst for the silicon nanowire growth seems very promising. Thermodynamically, nickel is compatible with the VLS assisted silicon nanowire growth where the Ni-Si alloy has a eutectic reaction at 964, 966, 1143 and 1215°C (Massalski *et al*., 1986). For silicon nanowire synthesized via thermal Chemical Vapor Deposition (CVD) on electroless Ni-coated Si substrate found that the growth density of nanowires increases as the thickness of the coating layer increase (Hsu and Huang, 2006). The diameters, lengths and growth densities of silicon nanowire could be controlled by the Ni content of the electroless plating layer on the Si substrate.

The thermal evaporation method is widely used for silicon nanowire fabrication due to its simple process setup and use simple precursor or raw materials. However, the key parameters to synthesize silicon nanowire are needed in order to form high quality of nanowires. Therefore, the effect of growth temperature and substrate position on the growth of 1-D Si nanostructures via thermal evaporation was studied extensively in this work.

MATERIALS AND METHODS

In this study, silicon nanowires were synthesized by thermal evaporation using nickel catalyst. Silicon (Si) wafer p-type (111) (Siltronix), Si powder (Aldrich) and 5 mM nickel nitrate ($Ni(NO_3)_2.6H_2O$) (Merck) were used as the starting materials to grow silicon nanowires (SiNWs) using high purity nitrogen (N_2) gas as the carrier gas. The growth system consisted of a horizontal furnace tube, quartz tube, gas supply, and gas flow meter. The furnace is Nabertherm R40 horizontal furnace with an alumina tube mounted in the furnace. A quartz tube inserted into the alumina tube which houses the substrate and quartz boat containing the source materials. At one end of the tube, the carrier gas enters through a flow meter.

Si powder of source material was put into a quartz boat located in the centre of furnace. A quartz holder with Ni-coated Si substrates was positioned at 3, 6, 9 and 12 cm from the source material at downstream gas flow as shown in Fig. 1. Before heating, the quartz tube was flushed with a purified N_2 gas for 20 min to produce inert atmosphere in the system. During the entire process, a constant N_2 gas flow of 100 mL min^{-1} was introduced. Furnace was rump-up from room temperature to 900 or 1000°C at heating rate of 20°C min^{-1} for an hour soaking time. After heating process, the furnace is cooling down to room temperature by nature cooling under N_2 environment.

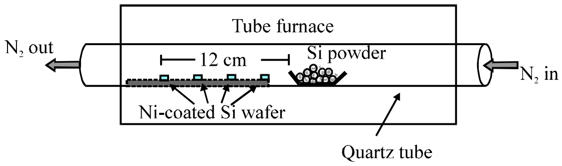

Fig. 1: Schematic diagram of experimental setup

The morphology and topography of Si nanostructures were characterized by field-emission scanning electron microscopy (FESEM) (Leo Gemini) and Transmission Electron Microscopy (TEM) (Phillips CM12) equipped with Docu Version 3.2 image analysis system. The chemical composition of the Si nanostructures was determined by Energy Dispersive X-ray (EDX) spectroscopy which attached to FESEM machine.

RESULTS AND DISCUSSION

Nickel (Ni) catalyst was prepared from 5 mM nickel nitrate solution deposited on Si substrate by spin coating process. Figure 2 shows the FESEM micrograph of Ni-coated Si substrate surface. The small dots are Ni nanoclusters that distributed homogenously on Si substrate. These Ni nanoclusters were used as metal catalyst on the formation of Si nanowires (SiNWs).

In order to investigate effect of metal catalyst on the growth of nanostructures, a preliminary study had been done. Two pieces Si substrates were prepared for SiNWs synthesis. One of the substrates is blank (uncoated) wafer and the other was coated with a very thin Ni layer. The substrates were placed together in the chamber with horizontally position at 6 cm downstream from the source (Si powder). The substrates were thermally evaporated at 900°C for 1 h. The evaluation of Si substrate surface after growth process was confirmed by FESEM analysis.

Figure 3a shows the result which indicates there are no Si nanostructures grown on the substrate without Ni catalyst. Meanwhile, on the Ni coated substrate obtained 1-D nanostructures (nanowires and needle-like nanostructures) with various diameter and length (Fig. 3b). Nanowires obtained by such a crystal growth

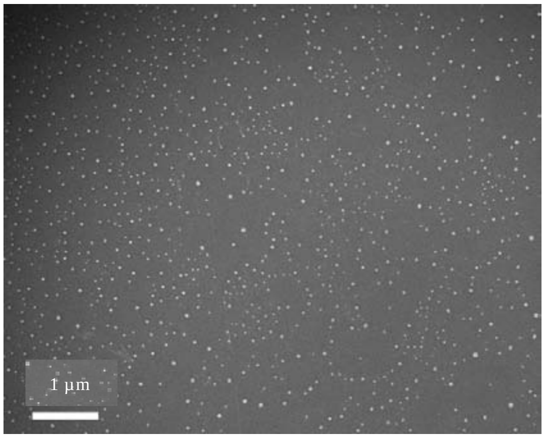

Fig. 2: FESEM image of spin coated 5 mM nickel nitrate on Si substrate

mechanism are catalyzed by a metal eutectic nanodroplet. The results in this work were in disagreement with those reported by Pan *et al.* (2005). They claimed that a metal catalyst is not essential on the growth of SiNWs by thermal evaporation at high temperature. However, in this work, we found that Ni catalyst is playing a very important role in the formation of SiNWs via thermal evaporation. Moreover, the SiNWs were grown in preferred orientation by using Ni catalyst. On the other hand, the growth of SiNWs at high temperature without catalyst could be assisted by oxide (Hutagalung *et al.*, 2007).

In a VLS mechanism, the growth species is evaporated first and then diffuses and dissolves into liquid droplets. The surface of the liquid has a large accommodation coefficient and is therefore a preferred site for deposition. Saturated growth species in the liquid droplet will diffuse to and precipitate at the interface between the crystal growths. Continued precipitation or growth will separated the substrate and the liquid droplet, resulting in the growth nanowires (Cao, 2004). At the end of the process, it can be obtained a high purity of silicon nanowires except at the tip which contains the solidified metallic catalyst. The metal nanoparticle has a major role in vapor-liquid-solid assisted nanowire growth. Moreover, the metal particle catalyst determines the diameter of the grown nanostructures. Consequently, the choice of the metal catalyst based on its physical and chemical properties, effects of many of the nanowire properties. To be processed via the VLS growth mechanism, the metal catalyst has to be physically active, but chemically stable. To find an eligible metal catalyst, the phase diagram is first consulted to choose a suitable material that forms a liquid alloy with the nanowire material of interest.

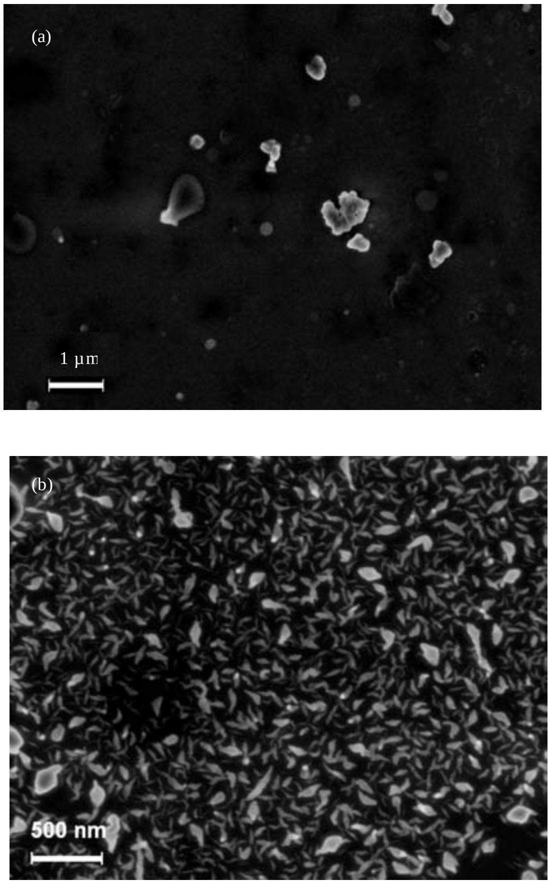

Fig. 3: FESEM images of thermal evaporated Si substrates at 900°C for 1 h: (a) without catalyst and (b) with Ni catalyst

Since the thermally evaporated sample at 900°C is not very good in formation of 1-D nanostructures, the growth temperature was increased to 1000°C. On the other hand, the substrate without catalyst gave no nanostructures formation. Therefore, we decide to continue experimental work by using Ni catalyst. Thermodynamically, nickel is compatible with the VLS assisted silicon nanowire growth. It was suggested that growth temperature of 1000°C would gave better formation of SiNWs based on the phase diagram of the Ni-Si alloy which has the lowest eutectic reaction at 964°C (Massalski *et al.*, 1986). Furthermore, we believed the substrate location has direct relation with a distance in which the source silicon particles transported by gas flow. The different substrate location inside tube furnace could give different substrate temperature during thermal evaporation process. Therefore, the determination of optimum substrate

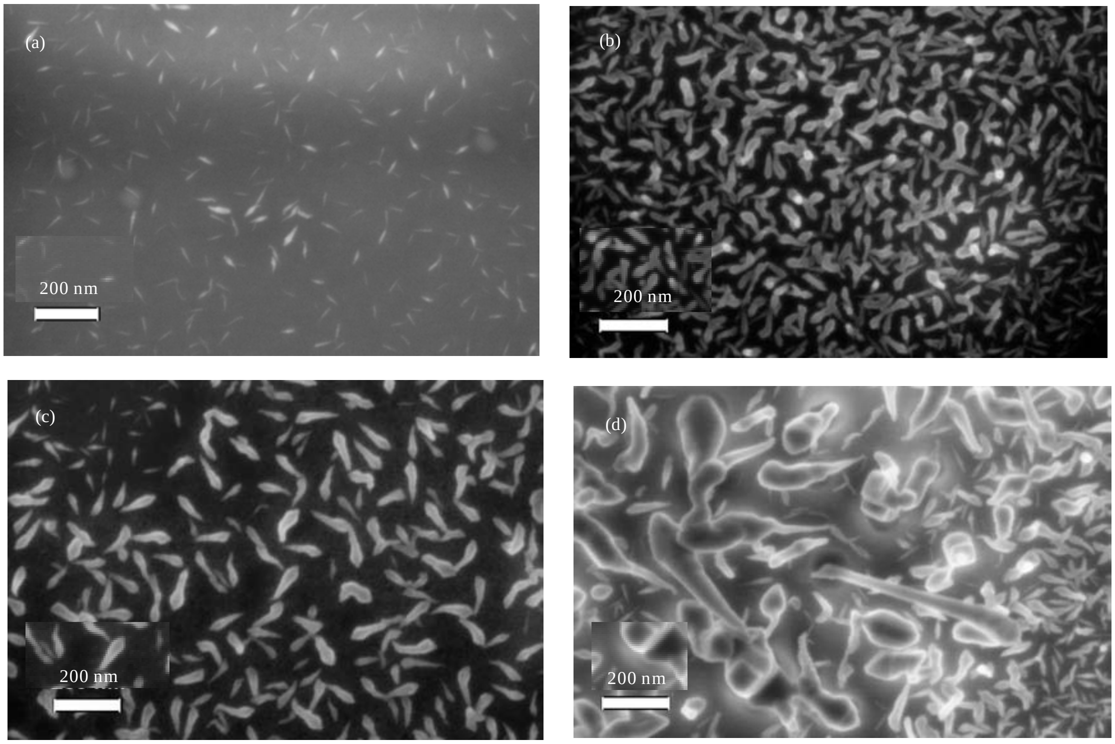

Fig. 4: SEM images of evaporated samples at 1000°C for 1 h. Substrates position from Si source are: (a) 3 cm, (b) 6 cm, (c) 9 cm and (d) 12 cm

location is important on the growth of 1-D Si nanostructures. For this study, the substrates were placed horizontally position at four different locations which are 3, 6, 9 and 12 cm from the source material. All of four Ni-coated Si substrates were thermally evaporated at 1000°C for 1h.

Figure 4 shows the FESEM images on the sample prepared at 1000°C for various substrate distance (3, 6, 9 and 12 cm) from the source material. All of samples produced one-dimensional Si nanostructures (nanowires and nanoneedles) with various diameter and length. At the distance of 3 cm, it can be seen a very little number of grown nanostructures (Fig. 4a). It might be due to less supply of Si vapour or inhomogenity of Si vapour supply at this area. In addition, the grown nanostructures were seems embedded underneath oxide thin layer. The formation of oxide layer is more easily at the 3 cm position sample since it closer to the centre of heating zone. Thus, substrate experience relatively higher temperature compared to others substrates. At the 6 cm position found better formation 1-D nanostructures compared to the 3 cm sample but still not homogeneous rather than low growth density (Fig. 4b). Sample positioned at 9 cm away from source gave the highest density and uniform in size of grown 1-D nanostructures (Fig. 4c), whereas, sample at 12 cm produced bigger and longer needle-like structures (Fig. 4d). Results suggested that substrate position also play an important parameter on the growth of 1-D nanostructures via thermal evaporation. To prepare high density and uniform 1-D Si nanostructures, the substrates should be positioned not too far way or too close to the source material.

Careful observation to the grown 1-D Si nanostructures (nanowires and nanoneedles) found that they are not in vertical alignment but bends to the certain direction as shown in Fig. 5. This bent-shaped formation might be due to the applied force of N_2 gas flow during thermal evaporation. Based on this observation, a schematic diagram for the formation of bent down shaped nanowires and nanoneedles was proposed as shown in Fig. 6. In the first stage, the nanowire was initially grown in vertical direction on Si substrate with a liquidous spherical of Ni on the top of wire.

As growth process continue, the grown nanowire become taller as suggested by VLS mechanism. The bent-shaped nanowire was formed when the unstable grown nanowire pushed by a slow speed flowing gas. In the mean time, some nanowire could be transformed from

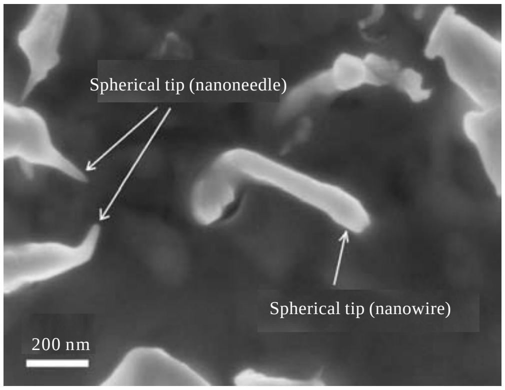

Fig. 5: A various types of 1-D nanostructures grown on Si substrate

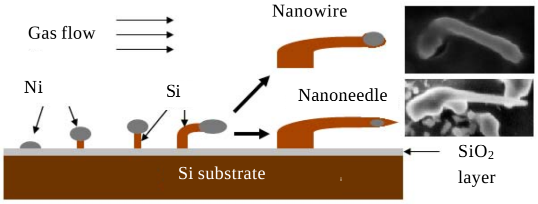

Fig. 6: Schematic diagram formation of bent shaped 1-D Si nanostructures

nanowire to needle-like structure if hit by a strong force of higher speed gas flow. Therefore, almost all of the samples gave mixed products of nanowires and needle-like nanostructures.

The EDX analysis was performed to a selected nanowire in order to understand the growth mechanism and its elemental composition. Figure 7 shows the EDX analysis results recorded at the spherical tip and body of nanowire. It was found that only Si element (100% at Si) detected at the wire body (Fig. 7b), however, there are 89.05 Si, 7.18 O and 3.78% at Ni at the spherical tip of wire (Fig. 7a). Based on the existence of Ni catalyst at the tip, it is confirmed that the growth mechanism of nanowire and nanoneedle similar to a vapour-liquid-solid (VLS) mechanism. Kim *et al*. (2003) was reported that solidified spherical catalyst at the tip or in the middle of nanostructures is commonly considered as evidence of the VLS growth mechanism. For Si nanowires growth via the VLS mechanism, the morphological and dimensional evolution of the Si nanowires are considerably related to mass transport through the Ni-Si liquid droplets and surface and interface energies at the interface of liquid-solid (Kwak *et al*., 2007).

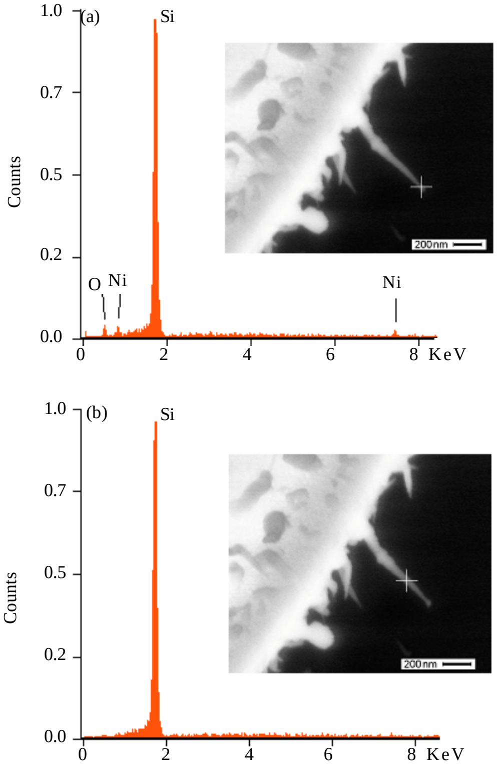

Fig. 7: EDX spectrums recorded at the: (a) spherical tip of wire (89.05 Si; 7.18 O; 3.78% at Ni) and (b) wire body (100% at Si)

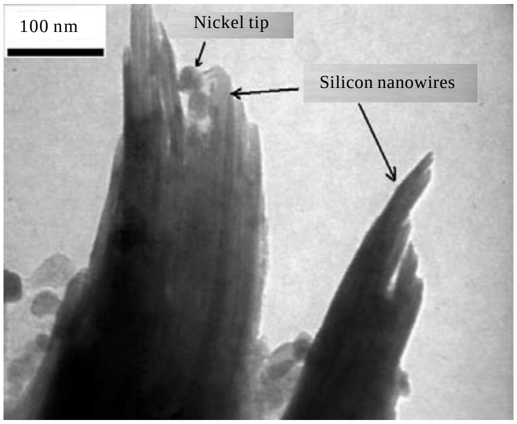

Fig. 8: TEM image shows 1-D Si nanostructures with spherical Ni catalyst at the tip

A sample at the distance of 9 cm synthesized at 1000°C for 1 h has been chosen for TEM observation due to its better uniformity and higher growth density of nanostructures. The micrograph obtained from TEM analysis (Fig. 8) shows has similarity with image captured by FESEM (Fig. 4) which some of Si nanostructures crooked and mostly bent in certain direction. From TEM image in Figure 8 is clear to see the formation of nanowire and nanoneedle structures with spherical tip. The diameter of the structures is around 19 to 30 nm. From EDX analysis was confirmed that spherical tip is containing Ni catalyst (Fig. 7a). Liu *et al.* (2001) reported that crooked nanostructures formed due to the weight of the catalyst on their tip.

CONCLUSION

The one-dimensional Si nanostructures had been grown on the Ni catalyst coated Si substrate by thermal evaporation technique. The growth temperature, duration and substrate position were found as the very important parameters on the formation of 1D Si nanostructures. Results show that grown nanowires or nanoneedles are not in vertical alignment but some of them are bending to the certain direction. The bent shape nanostructure formation might be due to the flow direction of applied carrier gas during thermal evaporation. The Ni catalyst was found at the tip of nanowires as similar to a vapour-liquid-solid (VLS) mechanism.

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