

## Si Nanowires Produced by Very High Frequency Plasma Enhanced Chemical Vapor Deposition (PECVD) via VLS Mechanism

(Kajian Dawai Nano Silikon (SiNW) Dihasilkan dengan Pemendapan Wap Kimia Peneguh Plasma (PECVD) dengan Kaedah VLS)

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### ABSTRACT

*Silicon nanowires (SiNWs) with diameter of about a few nanometers and length of 3  $\mu\text{m}$  on silicon wafers were synthesized by very high frequency plasma enhanced chemical vapor deposition. Scanning electron microscopy (SEM) observations showed that the silicon nanowires were grown randomly and energy-dispersive X-ray spectroscopy analysis indicates that the nanowires have the composition of Si, Au and O elements. The SiNWs were characterized by high resolution transmission electron microscopy (HRTEM) and Raman spectroscopy. SEM micrographs displayed SiNWs that are needle-like with a diameter ranged from 30 nm at the top to 100 nm at the bottom of the wire and have length a few of micrometers. In addition, HRTEM showed that SiNWs consist of crystalline silicon core and amorphous silica layer.*

*Keywords: PECVD; silicon nanowire; VLS*

### ABSTRAK

*Nanodawai silikon (SiNW) dengan diameter beberapa nanometer dan panjang 3  $\mu\text{m}$  di atas wafer silikon telah dihasilkan dengan menggunakan pemendapan wap kimia peneguh plasma. Pemerhatian mikroskop elektron imbasan (SEM) menunjukkan nanodawai tumbuh secara rawak dan analisis spektrokopi serakan sinar-X menunjukkan nanodawai mengandungi unsur Si, Au dan O. Nanodawai silikon diukur menggunakan mikroskop transmisi elektron resolusi tinggi (HRTEM) dan spektroskopi Raman. SEM menunjukkan bahawa SiNW adalah seperti jarum dengan diameter berjulat 30 nm di puncak hingga 100 nm di dasar dawai dan mempunyai panjang dalam beberapa mikrometer. Tambahan lagi, HRTEM membuktikan bahawa SiNW mengandungi teras hablur silikon dan lapisan silika amorfus.*

*Kata kunci: Nanodawai silikon; PECVD; VLS*

### INTRODUCTION

In the past few years, nanomaterials, which are of fundamental and technological interest, have attracted increasing attention. Chiefly, one-dimensional nanostructures have attracted extensive interest due to their potential uses in optoelectronic devices and fundamental importance for the study of size-dependent chemical and physical phenomena (Morales & Leiber 1998). Several different methods have been used in the preparation of SiNWs such as laser ablation metal-catalytic method (Zhang et al. 1998), molecular beam epitaxial (MBE) (Wu et al. 2002), chemical-vapor-deposition (CVD) (Rosaz et al. 2011), thermal vapor deposition (Fan et al. 2001), thermal evaporation of Si powder sources mixed with  $\text{SiO}_2$  (Wang et al. 1998), plasma enhanced chemical vapor deposition (PECVD) (Hamidinezhad et al. 2011, Hamidinezhad et al. 2011; Hofman et al. 2003). However, during the last 30 years of booming semiconductor industry which involved a great deal of thin film technology, deposition techniques like CVD (chemical vapor deposition) or sputtering which often offer unquestionable advantages have been developed to perfect. Among chemical techniques PECVD is one of

the most advanced techniques. PECVD is a directional deposition method. In the PECVD process a gas such as silane and the subsequent metal catalyst moderated growth of silicon nanowires. This involves a mechanism that is famous vapour-liquid-solid (VLS) as first proposed by Wagner and Ellis (1964). In the VLS mechanism, a metal catalyst such as Au is deposited onto a substrate as silicon. Upon eutectic temperature the catalyst tends to form islands or droplets. A gas such as  $\text{SiH}_4$  that is containing silicon then introduced into the system and is thermally decomposed. This gas will be absorbed by the liquid metal catalyst. By continuing this process the droplet becomes supersaturated with silicon, crystalline silicon is deposited at the bottom of the catalyst droplet which rides on top of the nanowire.

In this study we investigated a large quantity of SiNWs that were synthesized successfully on silicon wafers by using VHF-PECVD method with VLS mechanism. We investigated the morphology of wires by using scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy.

## EXPERIMENTAL DETAILS

SiNWs were synthesized by very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) according to the vapor–liquid–solid (VLS) growth mechanism on a p-type Si (111) wafer as a substrate. In this research, pure  $\text{SiH}_4$  gas was used as a Si source. In order to clean the substrate surfaces they were immersed in a solution with mixture of HCl, DI water and  $\text{H}_2\text{O}_2$ . The cleaned substrate was then dipped into 0.1% w/v Poly-L Lysine and then rinsed with DI water and dried by nitrogen. The cleaned substrate was deposited with gold colloid particle solution. For this research, 30 nm sized gold colloid particle solution was used. The gold colloid coated silicon substrates was then placed inside a VHF-PECVD reactor that evacuated at the pressure of 77 mtorr. In order to fabricate the silicon nanowires, 10 sccm  $\text{SiH}_4$  (99.9995%) gas was introduced as a silicon source for 30 min at temperature of 440°C. The RF power was set at 15 W.

After the reactor was cooled to room temperature, it was observed that as-grown materials with light-gray color had appeared on the surface of the Si wafer. The morphology, as well as chemical analysis and structure of nanowires were observed by scanning electron microscope (SEM) and high-resolution transmission electron microscopy (HRTEM). The elemental composition of the nanowires and their crystal phase was analyzed through an energy dispersive X-ray spectrometer (EDX). A Raman spectrum was obtained using a spectrum GX (NIR, FT-Raman) system with a Nd crystal laser source.

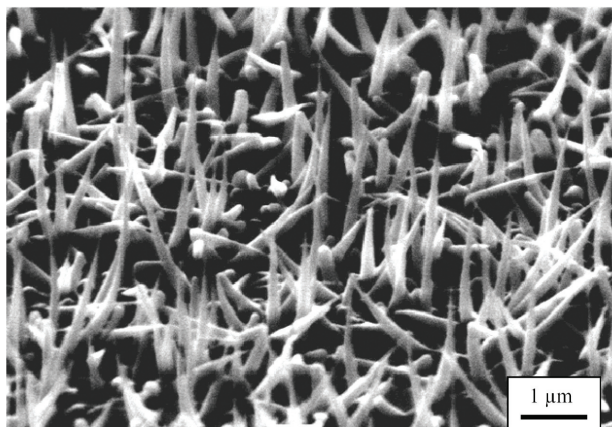


FIGURE 1. SEM image of SiNWs general morphology grown by VHF-PECVD

## RESULTS & DISCUSSION

SEM image (Figure 1) exhibited the general morphology of the SiNWs grown on a large area Si (111) substrate. The image shows clearly the tip of the wires and the nanowires density is dense. The sample consists of needle-like SiNWs with diameter ranged from 30 nm at the top to 100 nm at the bottom of the wire and length a few of micrometers.

Figure 2 displays the TEM image of a section of SiNWs generated on a silicon wafer substrate at temperature

of 440°C and pressure of 77 mtorr, respectively. The transmission electron microscopy (TEM) provides further information regarding the structure of as-grown SiNWs. Low magnified TEM image (Figure 2(a)) shows that the average diameter of nanowires is in the range of 70–80 nm. These wires have smooth surface topology along their length correspond to the SEM image. Low magnification TEM image also indicates that the diameter of the nanowires decreases slowly from bottom to the top with a moderate slope.

Figure 2(b) shows the high-resolution transmission electron microscopy (HRTEM) image of SiNW grown in this experiment. HRTEM image reveals that each nanowire consists of crystalline structure. HRTEM image of SiNWs is taken for further confirmation of structure. According to the HRTEM measurement the inter-planar spacing of crystals is about 0.31 nm which matched with the (111) orientation of silicon. Furthermore, HRTEM evidence that SiNWs consist of crystalline silicon core and amorphous silica sheath. This result is essentially similar to those synthesized by other methods (Jeon & Kamisako 2008; Pei et al. 2006). The figure also displays that the tip of each wire is hemispherical in shape and terminated by a  $\text{SiO}_2$  layer, which is thinner than the core of the nanowires.

Figure 3 shows a quantitative EDX analysis of the Si nanowires grown at RF power of 15 W and temperature of 440°C. The corresponding EDX in the insets indicate that ratio of Si in the SiNWs is more than quantity of oxygen in SiNWs. Silicon came from the decomposition of  $\text{SiH}_4$  gas. In this experiment gold colloid play an important role in the formation of SiNWs, so called vapor-liquid-solid mechanism. The EDX spectrum also shows a little Au that there are on top of the wires. The Au nanoparticle located on top of the SiNWs, implies that the growth mechanism of this SiNWs is according to an Au-assisted VLS mechanism. The O signal was mostly due to the reaction of Si with oxygen in the air. The peaks of Pt and C are generated from the coating process and carbon tape, respectively.

In order to get more information of the SiNWs structural properties, the Raman scattering spectra of the SiNWs were done using Raman spectroscopy. The Raman scattering is the inelastic scattering of a photon. When light is scattered from a molecule or atom, most photons are elastically scattered. These scattered photons have the same energy (frequency) and wavelength as the incident photons. A small fraction of the scattered photons (approximately 1 in 10 million photons) also is scattered by an excitation. The scattered photons usually having a frequency lower than the frequency of the incident photons.

Figure 4 shows the Raman spectrum of the SiNWs synthesized using VHF-PECVD on a silicon wafer in (111) orientation. It reveals that there is a peak at  $517\text{ cm}^{-1}$  for the SiNWs. This result is consistent with the result reported by Niu et al. (2004). This peak is due to the first-order transverse optical phonon mode (TO) (Kanemitsu et al. 1993). There is also other peak at position  $522\text{ cm}^{-1}$

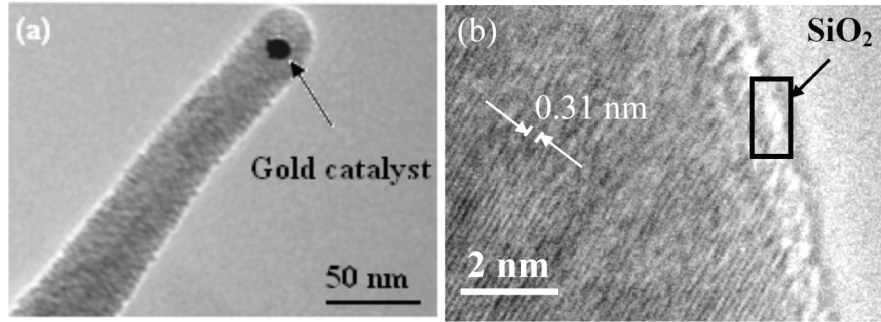


FIGURE 2. TEM image of a section of SiNW produced with pure  $\text{SiH}_4$  gas at temperature of  $440^\circ\text{C}$  and pressure of 77 mtorr by VHF-PECVD on a silicon wafer. a) A typical low magnified TEM image shows the general morphology of SiNWs and b) HRTEM image taken from tip of nanowire showing a crystalline Si core and an amorphous  $\text{SiO}_2$  sheath

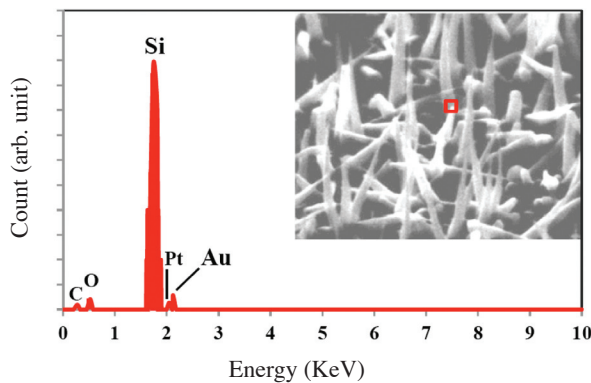


FIGURE 3. The EDX mapped from SiNWs at temperature of  $440^\circ\text{C}$  and RF power of 15 watt. Ratio of Si in the SiNWs is more than quantity of oxygen in SiNWs. C and Pt peaks originated from carbon tape and coating for EDX analysis, respectively. Au peak is due to the gold catalyst

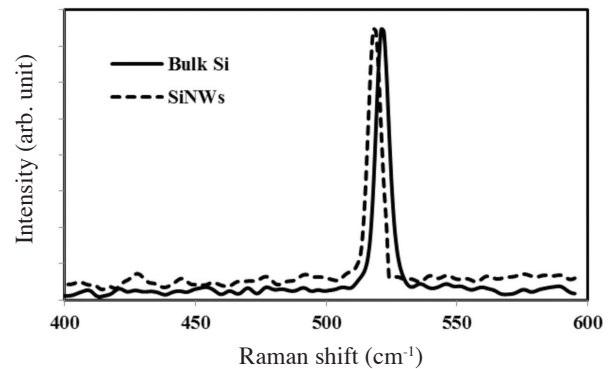
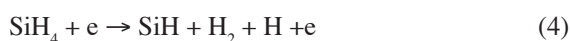
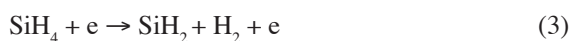
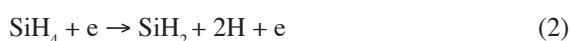


FIGURE 4. Raman spectra of the SiNWs on silicon substrate for bulk Si and SiNWs. There are two peaks at positions  $522\text{ cm}^{-1}$  and  $517\text{ cm}^{-1}$  for bulk Si and SiNWs, respectively

due to silicon substrate, agreeing with other report (Niu et al. 2004). It can be seen from the spectra that the peak is good symmetric and narrow.

In this research, pure  $\text{SiH}_4$  gas was used as a Si source. The above-mentioned observations show that the Si nanowires grown from  $\text{SiH}_4$  vapor are similar to those produced by other researchers (Griffiths et al. 2007; Jeon & Kamisako 2009). When silane gas is introduced to the system, the RF plasma excitation of  $\text{SiH}_4$  produces gas phase  $\text{SiH}_3$ ,  $\text{SiH}_2$ ,  $\text{SiH}$  and Si due to electron impact processes (Hamidinezhad et al. 2011; Jasinski & Gates 1991). The basic inelastic collision reactions which occur in  $\text{SiH}_4$  plasma are as follows:



At high power RF plasma, silane is not dominant Si gas species. When Si atoms precipitate, the atoms will easily centralize to form nuclei on low-energy places of Au-Si alloy. With the increase of Si atoms in Au-Si droplets, the nuclei will grow up to take on needle-like shape nanowires.

## CONCLUSION

In this study, a large-scale crystalline Si nanowire has been synthesized with Au and  $\text{SiH}_4$  as catalyst and source of silicon, respectively, on Si substrate by VHF-PECVD method. The morphology, crystal structures and properties of SiNWs prepared by Au-catalyzed VLS mechanism were presented. The SEM showed that silicon nanowires are needle-like with a diameter ranged from 30 nm at the top to 100 nm at the bottom of the wire and have length a few of micrometers. The TEM images display that SiNWs consist of crystalline silicon core and amorphous silica sheath where the silica sheath is thinner than core of the nanowires. It was found that the SiNWs grew from the tip of the wires, acted as nucleation centers and contain Au-Si alloys. Finally, it was believed that the decomposition



SiH<sub>4</sub> gas by RF power play an important role on the growth of SiNWs.

## REFERENCES

- Fan, X.H., Xu, L., Li, C.P., Zheng, Y.F., Lee, C.S. & Lee, S.T. 2001. Effects of ambient pressure on silicon nanowire growth. *Chem. Phys. Lett.* 334: 229-232.
- Griffiths, H., Xu, C., Barrass, T., Cooke, M., Iacopi, F., Vereecken, P. & Esconjauregui, S. 2007. Plasma assisted growth of nanotubes and nanowires. *Surf. & Coat. Technol.* 201: 9215-9220.
- Hamidinezhad, H., Wahab, Y., Othaman, Z. & Ismail, A.K. 2011. Influence of growth time on morphology and structural properties of silicon nanowires grown by VHF-PECVD. *J. of Cryst. Growth* 332: 7-11.
- Hamidinezhad, H., Wahab, Y. & Othaman, Z. 2011. Ultra-sharp pointed tip Si nanowires produced by very high frequency plasma enhanced chemical vapor deposition via VLS mechanism. *J. Mater. Sci.* 46: 5085-5089.
- Hamidinezhad, H., Wahab, Y., Othaman, Z. & Ismail, A.K. 2011. Au-catalyzed silicon nanoneedles synthesized from pure silane gas at various RF powers on silicon substrate by VHF-PECVD. *Plasmonics* 6: 791-796.
- Hofmann, S., Ducati, C., Neill, R.J., Piscanec, S., Ferrari, A.C., Geng, J., Dunin-Borkowski, R.E. & Robertson, J. 2003. Gold catalyzed growth of silicon nanowires by plasma enhanced chemical vapor deposition. *J. of Appl. Phys.* 94(9): 6005-6012.
- Jasinski, J.M. & Gates, S.M. 1991. Silicon chemical vapor deposition one step at a time: Fundamental studies of silicon hydride chemistry. *Acc. of Chem. Res.* 24(1): 9-15.
- Jeon, M. & Kamisako, K. 2008. Synthesis of silicon nanowires after hydrogen radical treatment. *Mater. Lett.* 62: 3903-3905.
- Jeon, M. & Kamisako, K. 2009. Synthesis of Au-catalyzed silicon nanowires by hydrogen radical-assisted deposition method. *Met. Mater. Int.* 15(1): 83-87.
- Kanemitsu, Y., Uto, H., Masunoto, Y., Matsumoto, T., Futagi, T. & Mimura, H. 1993. Microstructure and optical properties of free-standing porous silicon films: Size dependence of absorption spectra in Si nanometer-sized crystallites. *Phys. Rev. B.* 48(4): 2827-2830.
- Morales, A.M. & Lieber, C.M. 1998. A laser ablation method for the synthesis of crystalline semiconductor nanowires. *Science* 279: 208-211.
- Niu, J., Sha, J. & Yang, D. 2004. Silicon nanowires fabricated by thermal evaporation of silicon monoxide. *Physica E.* 23(1-2): 131-134.
- Pei, L.Z., Tang, Y.H., Chen, Y.W., Guo, C., Zhang, W. & Zhang, Y. 2006. Silicon nanowires grown from silicon monoxide under hydrothermal conditions. *Journal of Crystal Growth* 289: 423-427.
- Rosaz, G., Salem, B., Pauc, N., Gentile, P., Potié, A. & Baron, T. 2011. Electrical characteristics of a vertically integrated field-effect transistor using non-intentionally doped Si nanowires. *Microelectronic Engineering* 88: 3312-3315.
- Wagner, R.S. & Ellis, W.C. 1964. Vapor-liquid-solid mechanism of single crystal growth. *App. Phys. Lett.* 4(5): 89-90.
- Wang, N., Tang, Y.H., Zhang, Y.F., Lee, & Lee, S.T. 1998. Nucleation and growth of Si nanowires from silicon oxide. *Phys. Rev. B.* 58: 16024-16026.
- Wu, Y., Fan, R. & Yang, P. 2002. Block-by-block growth of single-crystalline Si/SiGe superlattice nanowires. *Nano. Lett.* 2(2): 83-86.
- Zhang, Y.F., Tang, Y.H., Wang, N., Yu, D.P., Lee, C.S., Bello, I. & Lee, S.T. 1998. Silicon nanowires prepared by laser ablation at high temperature. *Appl. Phys. Lett.* 72(15): 1835-1837.

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