

VHF-PECVD FABRICATION PARAMETERS DEPENDENT MORPHOLOGY VARIATION OF GOLD CATALYST ASSISTED SILICON THIN FILM GROWTH

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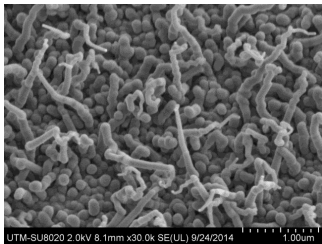
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Graphical abstract



Abstract

Achieving two dimensional quantum structure of silicon with well-defined tunable morphology is an outstanding issue. We present the preliminary results on fabrication parameters dependent silicon thin film production using VHF-PECVD method. Five samples are prepared on Si(100) substrate with gold (Au) catalyst by adjusting different parameters such as deposition time, temperature and the flow of precursor gas. The samples morphology are analyzed using FESEM. The results reveal that the silicon thin film appear to be smooth and more uniform after an enormous amount of hydrogen is inserted together with the precursor gas (silane) during the deposition process. More interestingly, the films exhibit silicon nanowires as the deposition time is increased up to 1 hour. This morphological transformation is attributed to the vapor-liquid-solid (VLS) mechanism related to the deposition process.

Keywords: VHF-PECVD, FESEM, nanowire, VLS

Abstrak

Over recent years, there has been an explosive growth of interest in the development of Mencapai struktur kuantum dua dimensi silikon dengan morfologi boleh laras yang jelas adalah satu isu yang masih belum jelas. Kami membentangkan hasil awal mengenai penggantungan parameter pembuatan saput tipis silikon menggunakan kaedah VHF-PECVD. Lima sampel disediakan di atas substrat Si(100) berpemangkin emas dengan melaraskan parameter yang bertlainan seperti masa pemendapan, suhu serta aliran gas perintis. Morfologi sampel dianalisis menggunakan FESEM. Hasil menunjukkan bahawa saput tipis silikon menjadi lebih licin dan lebih seragam selepas amaun hydrogen yang sangat banyak dimasukkan bersama gas perintis (silane) ketika proses pemendapan. Lebih menarik lagi, saput tersebut menunjukkan wayar nano apabila masa pemendapan dinaikkan sehingga 1 jam. Transformasi morfologi ini adalah merujuk kepada mekanisme wap-cecair-pepejal (VLS) yang berkaitan dengan proses pemendapan ini.

Kata kunci: VHF-PECVD, FESEM, wayar nano, VLS

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1.0 INTRODUCTION

Nowadays, the usage of Plasma Enhanced Chemical Vapor Deposition (PECVD) technique in producing nanostructured materials is relatively common among the material scientists and engineers. Many attempts are made in order to fabricate the desired nanostructured material such as nanowall, nanotube, and nanowire. The growing interest towards these kinds of materials is primarily due to their excellent characteristics compared to their bulk counterparts.

We focused more on the production of silicon (Si) nanowires (NWs) using very high frequency (150 MHz) PECVD. VHF-PECVD is a typical PECVD with higher RF frequency. It is reported that the higher RF frequency would give higher deposition rate and reduce the powder formation during deposition¹. Silicon nanowires became attractive due to their widespread applications in microelectronics while semiconducting nanowires have recently been the subject of great scientific and technological interest for their excellent electrical, optoelectronics, mechanical and chemical features²⁻⁵. For example, Si-NWs is reported to possess unique macroscopic optical properties and yields significantly reduced optical reflection over the full spectrum above the band-gap, as well as reduced transmission for wavelengths greater than ~700 nm for 10 μm long wires⁶.

Fabricating nanowire using VHF-PECVD (150 MHz RF frequency) requires metal catalyst in its procedure. This would allow controlled, selective growth by pre-patterning the catalyst on the substrates⁷. Up until now, various metals such as Au, Fe, Pd, Pt, W, Ti and Ga are used as catalyst⁸⁻¹³. Among all these metals, Ga is the most favorable catalyst for low temperature synthesis since Ga-Si system possesses a very low eutectic temperature. However, we choose Au as

catalyst to avoid the possible contamination arises from Ga¹². Si and Au catalyst combination does not form a silicide and the eutectic temperature of Au/Si is 363 °C which is relatively lower. This makes Au a suitable catalyst because it gives low temperature growth and does not leave a fast diffusing impurity¹³. The morphology of synthesized samples is scrutinized via FESEM measurements.

2.0 EXPERIMENTAL

The experimental process had begun with substrate cutting and cleaning. The silicon (100) wafer as substrate was cut into small squares of 1 cm \times 1 cm dimension before they were cleaned in an ultrasonic bath. The samples were then immersed in HF solution for 10 minute to eliminate any native oxide from the surface.

The deposition of small drops of gold (Au) thin film on the sample was performed using radio frequency magnetron sputtering for 20 s. Au is used as catalyst to assist the growth of Si-NWs on the substrate via VLS mechanism. The Au coated substrate is then placed on a sample holder in the VHF-PECVD's chamber. Then, the chamber was evacuated and pumped down to high vacuum (~20 mTorr). While waiting for the chamber to reach the desired temperature (Table 1), 300 sccm of hydrogen was injected into the chamber. The presence of hydrogen allows in cleaning the substrate surface. After the desired temperature is achieved, 10 sccm of silane is inserted into the chamber together with the hydrogen to reduce the possibility of SiO₂ formation¹⁴. The power was set up at constant value of 24 Watt. The selection of deposition parameters are listed in Table 1.

Table 1 Deposition parameters of sample preparation

Sample Code	Hydrogen (sccm)	Silane (sccm)	Temperature (°C)	Deposition Time (min.)
S1	0	5	300	10
S2	0	5	400	10
S3	300	5	500	10
S4	300	10	500	30
S5	300	10	500	60

In the beginning all parameters were set to their minimum value. No hydrogen was inserted. Only 5 sccm of silane at 300 °C temperature was injected and deposition was performed only for 10 minutes. The as-prepared samples were analysed using Hitachi SU8020 Field Emission Scanning Electron Microscope located at Central laboratory, Universiti Teknologi Malaysia.

3.0 RESULTS AND DISCUSSION

Figure 1(a)-(e) shows the FESEM images of all as-synthesized samples with 50 000 \times magnifications and 2 kV of acceleration voltage.

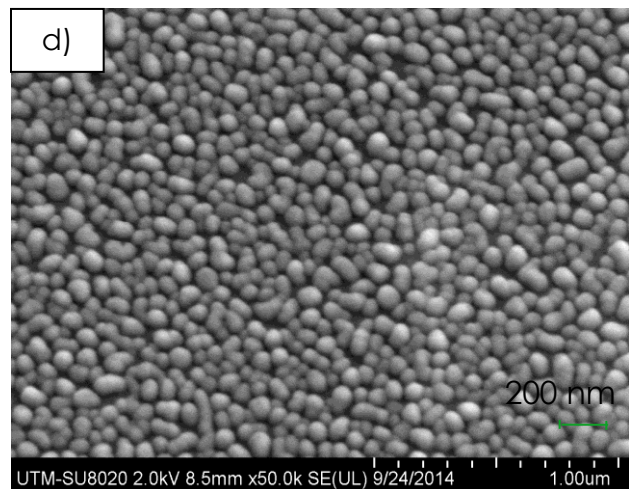
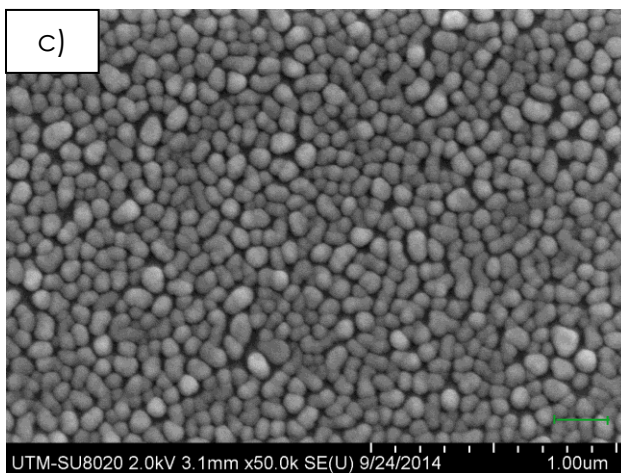
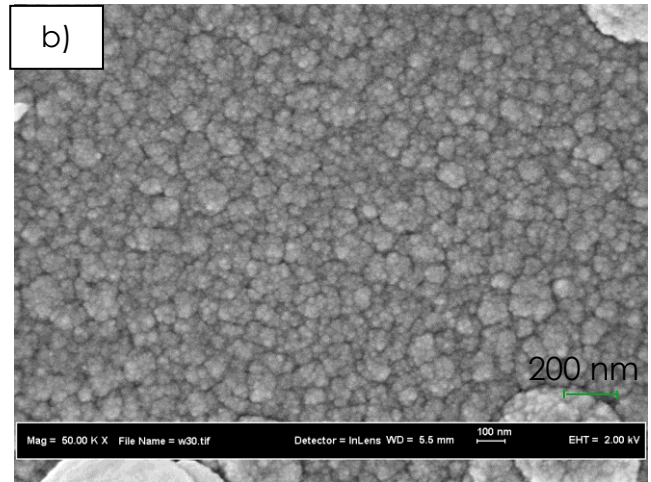
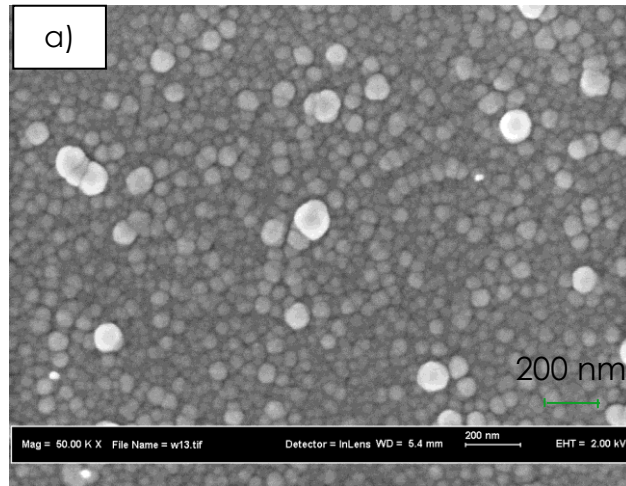
As evident from the first two images (sample S1 and S2), the relatively poor morphology of samples S1 and S2 is solely due to the facile experimental conditions where no hydrogen was used. These two

samples were fabricated with 5 sccm of silane at 10 minute deposition time at 300 °C and 400 °C respectively. Conversely, the other three samples (S1 to S3) show excellent morphology after raising the temperature to 500 °C and inserting hydrogen at 300 sccm into the chamber during deposition. Sample 3 reveals the appearance of individual silicon nanodot (Figure 1 (c)). As the deposition time and temperature were further increased to 30 minute and 500 °C, respectively the silicon thin film with dots transformed to more uniform nanoislands structures (Figure 1 (d)). Furthermore, the increase of the deposition time up to 1 h caused the formation of Si-NWs structures (Figure 1 (e)).

The liquid-vapor-solid (VLS) mechanism is responsible for the NWs growth¹⁴. In this mechanism, Au is firstly gets deposited on the silicon wafer substrate. As the temperature is increased at 363 °C, small liquid of Au-Si alloy droplets is formed on the surface. The molten state of Si-Au liquid droplet would absorb the reactant from¹⁵. This droplet of precursor gas became supersaturated until silicon freezes out at the silicon/droplet interface.

Continuation of this process leads to the growth of nanowires^{10, 16}.

The appearance of highly roughened surface morphology in Figure 1 (a) is ascribed to the effects of low temperature. From the theory of VLS mechanism, the temperature in which the Au-Si alloy is formed should be above 363 °C which explains the smoother thin film surface in Figure 1 (b), (c) and (d). Moreover, introduction of hydrogen during deposition process (Figure 1 (c), (d) and (e)) gives rise to the appearance of individual silicon dot. Previous study reported that introduction of hydrogen during deposition inhibits the formation of Si oxide on the film¹⁴. In plasma environment, hydrogen molecules are dissociated by high energy electrons to form highly reactive species including H_2^* , H_2^+ , H, H^+ and so on^{1, 17}. These species in turn reacting with the hydrogen that exists in the precursor leads to the formation of Si NWs. However, deposition times such as 10 and 30 minutes are not enough for the droplets to become supersaturated. It is noticeable that when the deposition time is increased to 1 h the supersaturation process of silane begins which finally produces Si-NWs on the film.



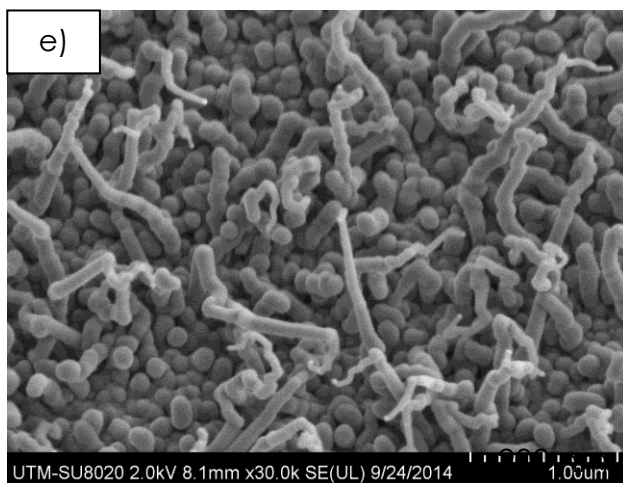


Figure 1 FESEM micrographs of as-prepared samples (a) S1, (b) S2, (c) S3, (d) S4 and (e) S5

4.0 CONCLUSION

The formation of high quality Si-NWs is demonstrated. The VHF-PECVD fabrication parameters dependent silicon thin film production is inspected. Samples are grown on Si(100) substrate with gold (Au) catalyst, silane gas precursor and hydrogen injection. Fabrication parameters such as deposition time, temperature and the rate of flow of the precursor gas are controlled to achieve the optimized growth condition. The FESEM images displayed the formation of Si nanodots and subsequent transformation to NWs with the control of growth parameters. The deposition temperature, time and the amount of hydrogen flow played a significant role in the formation of NWs via VLS mediated growth mechanism. The deposition parameters dependent morphological transformation may constitute a basis for the production of high quality Si-NWs. It is asserted that 10 sccm of silane, 300 sccm of hydrogen, temperature 500 °C, and 1h of deposition time is the optimized parameter for Si NWs fabrication.

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References

- [1] Howling, A. A., Drier, J. L., Hollenstein, Ch., Kroll, U., Finger, F. 1991. Frequency Effects in Silane Plasmas for PECVD. *38th Annual (AVS) Symposium & Topical Conference*. Seattle, Wahington, USA. 11-15 November 1991. 1-16.
- [2] Zheng, G., Lu, W., Jin, S., and Lieber, C. M. 2004. Synthesis and Fabrication of High-Performance n-type Silicon Nanowire transistors. *Journal of Advanced Materials*. 16(21): 1890-1893.
- [3] Qian, F., Li, Y., Gradecak, S., Wang, D., Barrelet, C. J and Lieber, C. M. 2004. Gallium Nitride-Based silicon nanowire Radial Heterostructures for Nanophotonics. *Nano Letters*. 4(10): 1975-1979.
- [4] Nam, C. Y., Jaroenapibal, P., Tham, D., Luzzi, D. E., Evoy, S. and Fischer, J. E. 2006. Diameter-Dependent Electromechanical Properties of GaN Nanowires. *Nano Letters*. 6(2): 153-158.
- [5] Zhang, Y., Kolmakov, A., Chretien, S., Metiu, H., and Moskovits, M. 2004. Control of Catalytic Reactions at the Surface of a Metal Oxide Nanowire by Manipulating electron Density Inside It. *Nano Letters*. 4(3): 403-407.
- [6] Tsakalagos, L., Balch, J., Fronheiser, Shih, J. M. Y., LeBoeuf, S. F., Pietrzykowski, M., Codella, P. J., Korevaar, B. A., Sulima, O., Rand, J., Davuluru, A. and Umakant Rapol. 2007. Strong Broadband optical Absorption in Silicon Nanowire Films. *J. Nanophotonics*. 1(1): 013552 1-10.
- [7] Hofmann, S., Ducati, C., Neill, R. J., Piskanec, S. and Ferrari, A. C. 2003. Gold Catalyst Growth of Silicon Nanowires by Plasma Enhanced Chemical Vapor Deposition. *Journal of Applied Physics*. 94(9): 6005-6012.
- [8] Westwater, J., Gossain, D. P., Tomiya, S., Usui, S. and Ruda, H. 1997. Growth of Silicon Nanowire via Gold/Silane Vapor-liquid-solid Reaction. *Journal of Vacuum Science and Technology B*. 15: 554-557.
- [9] Morales, A. M and Lieber, C. M. 1998. A Laser Ablation Method for the Synthesis of Crystalline Semiconductor nanowires. *Science*. 279: 208-211.
- [10] Wagner, R. S. and Ellis, W. C. 1964. Vapor-Liquid-Solid Mechanism of Single Crystal Growth. *Applied Physics Letters*. 4(5): 89-90.
- [11] Kamins, T. I., Williams, R. S., Chen, Y., Chang, Y. L., and Chang, Y. A. 2000. Chemical Vapor Deposition of Si Nanowires Nucleation by TiSi₂ islands on Si. *Applied Physics Letters*. 76(5): 562-564.
- [12] Barsotti, R. J., Fischer, J. E., Lee, C. H., Mahmood, J., Adu, C. K. W. and Eklund, P. C. 2002. Imaging, Structural, and Chemical Analysis of Silicon Nanowire. *Applied Physics Letters*. 81(15): 2866-2868.
- [13] Sunkara, M. K., Sharma, S., Miranda, R., Lian, G. and Dickey, E. C. 2001. Bulk Synthesis of Silicon Nanowire using a Low Temperature Vapor-Liquid-Solid Method. *Applied Physics Letters*. 79(10): 1548-1548.

- [14] Zardo, I., Yu, L., Conesa-Boj, S., Estrade', S., Pierre Jean Alet, Rossler, J., Frimmer, M., Roca, P., Cabarrocas, I., Peiro', F., J., Arbiol, Morante, J. R., Fontcuberta, A., and Morral, I. 2009. Gallium Assisted Plasma Enhanced Chemical Vapor Deposition of Silicon Nanowires. *Nanotechnology*. 20(15): 155602.
- [15] Zeng, X. B., Xu, Y. Y., Zhang, S. B., Hu, Z. H., Diao, H. W., Wang, Y. Q., Kong, G. L., Liao, X. B. 2003. Silicon Nanowires Grown on Pre-annealed Si Substrate. *Journal of Crystal Growth*. 247(1-2): 13-16.
- [16] Schmidt, V., Wittmann, J. V., Senz, S., Gosele, U. 2009. Silicon nanowires: A Review on Aspects of their Growth and their Electrical Properties. *Advanced Materials*. 21: 2681-2702.
- [18] Hou, W. C. and Hong, F. C. 2009. Controlled Surface diffusion in Plasma-enhanced Chemical Vapor Deposition of GaN Nanowires. *Nanotechnology*. 20(5): 055606.