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Effects of ambient pressure on silicon nanowire growth

X.H. Fan, L. Xu, C.P. Li, Y.F. Zheng, C.S. Lee, S.T. Lee *

Center of Super-Diamond and Advanced Films (COSDAF), and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, People's Republic of China

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Abstract

Growth of silicon nanowires (SiNWs) by thermal evaporation of SiO in a closed system was studied. The yield of SiNWs obtained in the present closed system was much higher than that from the previous open systems. As the ambient pressure increased, the yield of SiNWs decreased and the diameter of the SiNWs increased, but the surface of the SiNWs was roughened. Transmission electron microscopic examination showed that the originally smooth surface of SiNWs was roughened by the formation of Si nano-particles. The implication of these results on the growth mechanism of the SiNWs is discussed. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Synthesis of silicon nanowires (SiNWs) by SiO sublimation is a simple and efficient method recently reported for the preparation of quasi-one-dimensional semiconductor wires in bulk quantity [1]. Unlike the vapor–liquid–solid (VLS) process [2–5], this new method does not require any metal catalyst. The growth of SiNWs is instead explained by an oxide-assisted growth model [6–8]. The traditional method for the synthesis of SiNWs is by laser ablation at high temperatures [3–6]. In this process, a target made of (metal + Si) or (SiO_2 + Si) is heated in a furnace to about 1200°C and is ablated by a laser beam. Inert gas is usually used as a carrier gas, which cools and transports the ablated products downstream where they are deposited as nanowires or other products. It was later found that laser ablation was not needed for SiNWs growth when a Si + SiO_2 or SiO powder-pressed target was used [1,9–11]. Instead, the growth can be simply achieved by thermally heating the target to above 1100°C. Similar to the laser ablation approach, an inert carrier gas is generally kept flowing during the thermal evaporation process. In these processes (with or without a laser), the yield of the SiNWs is less than 10% of the consumed source materials [1].

Currently the nucleation and growth mechanisms of SiNWs are still not fully understood. It is thus important to collect more relevant experimental data on which accurate and sophisticated models can be built. In this work, we explore the necessity of a flowing carrier gas for the synthesis of SiNWs. The effect of the working ambient pressure is also studied. The implications of the present experimental results on the growth mechanism of SiNWs are finally discussed.

* Corresponding author. Fax: +852-2784-4696.
E-mail address: apannale@cityu.edu.hk (S.T. Lee).

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2. Experimental

The apparatus used here was the same as that reported before [3–8]. An Al_2O_3 tube (about 38 mm in diameter and 760 mm in length) was placed inside a horizontal tube furnace. A few grams of SiO powder (purity: 99.98%, particle size: ~45 μm, density: 2.1 g/cm^3) was put into a 72 mm long Al_2O_3 boat at the center of the furnace. The Al_2O_3 tube was pre-evacuated to 10^{-2} Torr, and then filled with ambient gas (Ar + 5% H_2) to a different pressure. Then the system was closed by cutting off the inert gas and sealing the vacuum system. The temperature of the furnace was then brought to 1350°C and maintained for 2 h. As a result, loose material with a color of light-brown to yellow deposited at both ends of the tube, about 185 mm from the center of the furnace. The temperature of the deposition locations was measured to be about 950°C. In the experiment, it was found that the loose material grew very quickly, and in about 2 h, it filled up the whole cross-section of the tube. Further examinations with transmission electron microscopy (TEM) confirmed that the loose material was SiNWs.

3. Results and discussion

It was found that the ambient pressure had an important effect on the yield and morphology of the SiNWs. The yield of SiNWs obtained in the present closed system was twice that obtained in the previous open system with a flowing inert gas, reaching a value of about 20% (wt) of the consumed SiO source materials. As the pressure increased, the yield of SiNWs decreased.

The reason for a lower yield of SiNWs at high pressure can be attributed to two factors. First, less SiO vapor was evaporated at the position of the SiO source due to the presence of inert gas [12]. In this case, the surface of the source materials was surrounded by a thin vapor layer through which the atoms or molecules evaporating from the source materials would diffuse. Once the atoms or molecules reached the outer boundary of the layer, they could be carried away or returned to and redeposited on the source materials due to collisions with the inert gas, thus leading to a reduced evaporation rate as compared with that in a vacuum. It can be derived that the rate of material loss from the source varies inversely with the inert gas pressure. Next, diffusion was responsible for transporting SiO vapor from the source to the depositing position. The diffusion coefficient also has an inverse relationship with the ambient pressure P [12]. The above two factors both give rise to a slower rate of supply of SiO vapor for deposition at a higher ambient pressure. This in turn leads to a lower deposition rate of SiNWs. For an open deposition system with flowing inert gas, the effect of ambient pressure on the evaporation rate of SiO source is less significant, because the evaporated atoms or molecules are swept away by the carrier gas from the surface of the source material. As the flowing gas keeps on transporting SiO vapor to the deposition location, the ambient pressure would thus have a lesser effect on the partial pressure of the SiO vapor at both the evaporation and the deposition locations. Furthermore, in an open system, some smaller SiNWs are likely to be swept away from the system by the carrier gas. These factors collectively lead to lower yields of SiNWs in an open system than in our closed system.

The morphologies of SiNWs deposited in the present closed system at different pressures were characterized by TEM. As shown in Fig. 1a, under an ambient pressure of 100 Torr, all SiNWs have a smooth surface and an average diameter of 18 nm. As the ambient pressure was increased to 200 Torr, the wires were of similar diameter to those deposited at 100 Torr. However, a certain amount of nano-particles appeared on the surface of some nanowires (Fig. 1b). When the ambient pressure was increased to 300 Torr, the surface of all nanowires was packed with numerous nano-particles (Fig. 1c), and the wire diameters were coarsened to about 45 nm. Fig. 2 shows a typical Si nano-particle whose crystal lattice is separated from that of the bulk SiNW by an amorphous layer. This suggests that the particle was formed on the surface of the SiNW after the nanowire had formed. This kind of particle has not been observed on SiNWs synthesized with the open system.

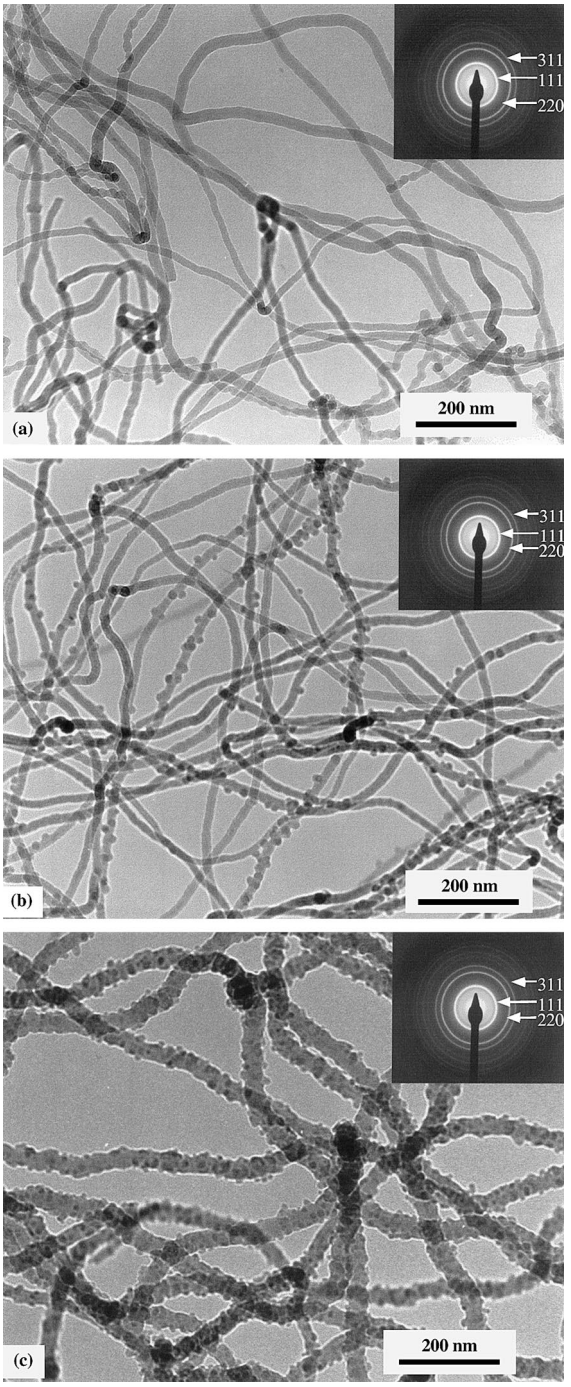

Fig. 1. Morphologies of SiNWs synthesized in a closed system. Inset diffraction patterns show the nanowires are SiNWs. The SiO sublimating temperature is 1350°C and the ambient gas pressure is: (a) 100 Torr; (b) 200 Torr; (c) 300 Torr.

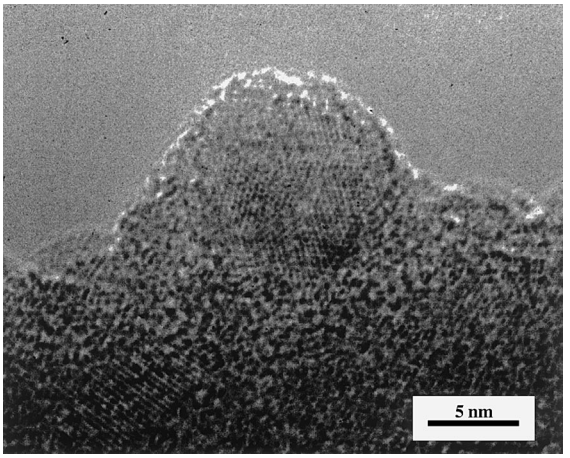

Fig. 2. HRTEM image of a nano-particle attached on the surface of a nanowire.

From the thermodynamics of nucleation, the critical nucleus size is: $r^* = (-2\gamma)/\Delta F_v$; where γ is the specific interfacial free energy of the condensate–vapor interface and ΔF_v is the bulk free energy change per unit volume. ΔF_v can be expressed as: $\Delta F_v = RT \ln(P_p/P_e)/V_m$, where P_p is the virtual partial pressure of the vapor and P_e is the equilibrium vapor pressure at the site of deposition, T is the deposition temperature, R is the gas constant, and V_m is the molar volume of the nuclei [13]. As analyzed above, P_p would be lowered at a higher ambient pressure P because of the lower evaporation rate of SiO at the source and the lower diffusion coefficient in the transportation of vapor from source to deposition site. The parameters P_e and V_m are decided only by the temperature. In our experiments, SiNWs grow at the same temperature under different ambient pressures. Therefore, as P increased, P_p/P_e would decrease, and thus ΔF_v would decrease and r^* becomes larger. This can then explain why the diameter of SiNWs is larger at a higher ambient pressure. The large r^* means that nucleation is more difficult, or it is more difficult for clusters formed in the vapor to become independent nuclei which can grow to form SiNWs, because of insufficient supply of vapor at a higher ambient pressure. On the other hand, the lower SiO vapor pressure at the deposition site also causes a lower growth rate of

SiNWs for the same reason. As a result, only some of the clusters can become independent nuclei and grow one-dimensionally into SiNWs. Other clusters just nucleate and assemble as nano-particles attached on to the surface of the SiNWs, because heterogeneous nucleation on the surface of SiNWs is easier than forming a new independent nucleus. In the case of SiNWs depositing in an open system, there is a continual supply of SiO vapor, and the ambient pressure has less of an effect on the rate of evaporation and nucleation. Thus, the critical size of nuclei is primarily determined by the local temperature at the nucleation site. Nevertheless, the morphology of condensates in different temperature regions is different with different formation mechanisms (these will be discussed elsewhere [14]).

4. Conclusions

In summary, the yield and growth rate of SiNWs by thermal evaporation of SiO powder are higher in a closed deposition system without circulation of inert carrier gas, but decrease with increasing ambient pressure. These are attributed to the change of the evaporating rate of SiO powders with the change of the ambient gas pressure. A lower pressure not only enhances the yield of SiNWs, but also ensures the SiNWs have a smooth surface. At a higher pressure, more Si nano-particles are formed and attached on to the surface of the SiNWs. This can be explained by considering the thermodynamics of nucleation and the supply rate of SiO vapor.

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References

[1] Y.F. Zhang, Y.H. Tang, C. Lam, N. Wang, C.S. Lee, I. Bello, S.T. Lee, J. Cryst. Growth 212 (2000) 115.
[2] J. Westwater, D.P. Gosain, S. Tomiya, S. Usui, J. Vac. Sci. Technol. B 15 (1997) 554.
[3] A.M. Morles, C.M. Lieber, Science 279 (1998) 208.
[4] Y.F. Zhang, Y.H. Tang, N. Wang, C.S. Lee, I. Bello, S.T. Lee, Appl. Phys. Lett. 72 (1998) 1835.
[5] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, I. Bello, S.T. Lee, Chem. Phys. Lett. 283 (1998) 368.
[6] N. Wang, Y.F. Zhang, Y.H. Tang, C.S. Lee, S.T. Lee, Appl. Phys. Lett. 73 (1998) 3902.
[7] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, S.T. Lee, Phys. Rev. B 58 (1998) R16024.
[8] S.T. Lee, N. Wang, Y.F. Zhang, Y.H. Tang, MRS Bull. 24 (1999) 36.
[9] D.P. Yu, Z.G. Bai, Y. Ding, Q.L. Hang, H.Z. Zhang, J.J. Wang, Y.H. Zou, W. Qian, G.C. Xiong, H.T. Zhou, S.Q. Feng, Appl. Phys. Lett. 72 (1998) 3458.
[10] N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, I. Bello, S.T. Lee, Chem. Phys. Lett. 299 (1999) 237.
[11] J.L. Gole, J.D. Stout, W.L. Rauch, Z.L. Wang, Appl. Phys. Lett. 76 (2000) 2348.
[12] J.M. Lafferty, Foundations of Vacuum Science and Technology, Wiley, New York, 1997.
[13] C.F. Powell, J.H. Oxley, J.M. Blocher, Vapor Deposition, The Electrochemical Society, Wiley, New York, 1966, pp. 126–130.
[14] H.Y. Peng, Z.W. Pan, L. Xu, X.H. Fan, N. Wang, C.S. Lee, S.T. Lee, Advanced materials, in press.