Eur. Phys. J. D **34**, 307–310 (2005)
DOI: 10.1140/epjd/e2005-00165-x

THE EUROPEAN
PHYSICAL JOURNAL D

Morphology evolution of Si nanowires synthesized by gas condensation of SiO without any catalyst

J.F. Zhou[1,a], F.Q. Song[2], Z.T. Shi[2], Y.F. Chen[1], and M. Han[1]

[1] National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, P.R. China
[2] National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing 210093, P.R. China

Received 6 September 2004

Abstract. A series of Si nanowires are synthesized at constant temperature of 970 °C on Si substrate by gas condensation of pure SiO vapor without any metal catalysts, by controlling the coverage of SiO_x deposits. The morphologies are characterized by scan electron microscopy (SEM) and their evolution during the growth process is observed: from isolated clusters in earlier stage to linked cluster assemblies, and developing to smooth nanowires in the later stage. The growth mechanism is discussed based on the newly proposed clustering-aggregation-sintering model.

PACS. 68.65.-k Low-dimensional, mesoscopic, and nanoscale systems: structure and nonelectronic properties

1 Introduction

One-dimensional materials, such as carbon nanotubes [1,2], silicon nanowires [3,4] have been synthesized by a variety of methods. Several mechanisms, such as screw-dislocation [5], vapor-liquid-solid (VLS), vapor-solid (VS) and oxide-assisted growth (OAG) [6], have been forwarded to explain the formation of these structures. Among them the VLS technique, in which metal or metal compounds acts as the catalysts, has been frequently exploited for 1D structure synthesis. For oxide nanowire synthesis, OAG mechanism is introduced which suggests oxides, instead of metal catalysts, play an important role in the one-dimensional growth. Recently we proposed a new mechanism for the Si-riched oxide nanowire synthesis from vapor deposition under relatively low temperature [7]. It is suggested that under such condition, Si-riched oxide nanowires be formed from sintering of individual Si_mO_n cluster aggregates rather than through continuous growth by absorption of small units at the tip from the gaseous ambiance. The one-dimensional sintering of these aggregates generates smooth nanowires, on the other hand the surface and bulk diffusion of Si along the wire results in periodic particle chains at last.

In this paper, a series of samples are synthesized by decomposition of SiO vapor, with different percentage of coverage. The morphology evolution of the nanowires as a function of coverage is systematically investigated and more distinct proofs can be identified. The results provide further evidences to clarify the sintering mechanism for the nanowire formation we suggested based upon our previous experiments.

2 Experimental

Detailed synthesis process can be referred to reference [7]. SiO powder (purity > 99.99%) was evaporated from a boron nitride (BN) crucible by means of thermal evaporation in a condensation chamber. The evaporation temperature was maintained at 970 °C which can be controlled by adjusting the electric current of the graphite heater. The background pressure of the condensation chamber was 10^{-4} Pa, evacuated with a turbo molecular pump. Argon (Ar) gas at a pressure of 300 Pa was introduced into the condensation chamber as a carrier gas. A flow of the carrier gas was maintained with a nozzle and a differential pumping system. Silicon wafers used as substrates were set inside the effusion hole of the cylinder BN insulating layer that surrounds the graphite heater. And the evaporation rate was monitored by a quartz crystal oscillator, which worked under room temperature.

To investigate the morphology evolution of Si nanowires as a function of coverage under a certain condition, a stable and constant growth condition should be built up and vanishes rapidly. By monitoring the deposition rate, we found that a steep rise of the deposition

---

[a] e-mail: `zhoujf@nju.edu.cn`

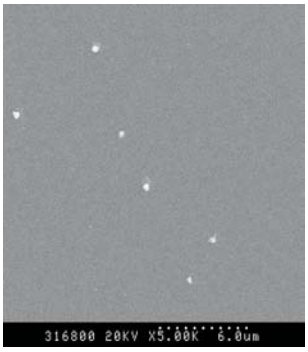


Fig. 1. Isolated clusters are observed in sample S1 with a coverage of 0.1 cluster monolayer.

rate occurs around 970 °C evaporation temperature when the carrier gas pressure is kept at 300 Pa. The deposition rate increased from 0.15 Å/s at 950 °C to about 30 Å/s at 970 °C in a few seconds. Therefore, the inference from the deposition under the evaporation temperature lower than 970 °C is neglectable, if only the structure evolution at a temperature of 970 °C is concerned. Four specimens were deposited at 970 °C with different coverage and named S1, S2, S3, and S4 with the coverage from low to high. After deposition, the electric current of the graphite heater was turned off immediately and the oven temperature dropped to 950 °C within 10 seconds. The morphology of each specimen is observed by scanning electron microscopy (Leo-1530).

3 Result and discussion

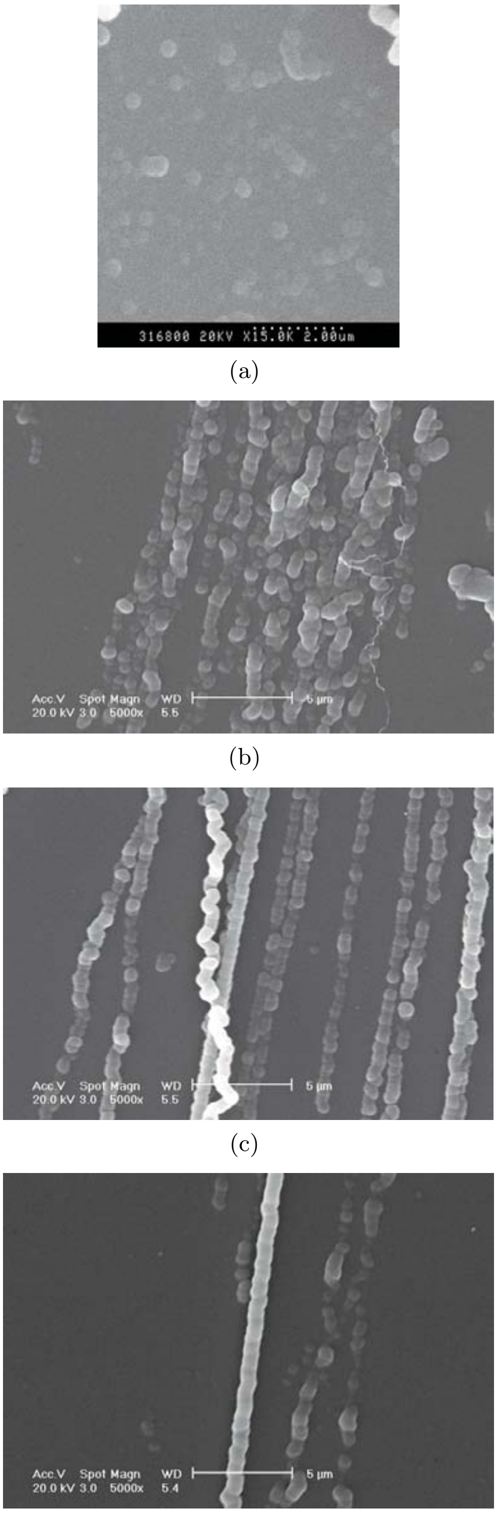
On the common process of gas condensation of SiO vapor, $\mathrm{Si}_m\mathrm{O}_n$ clusters (zero-dimensional) are formed by free nucleation in the vapor at the first step shortly after the evaporation of the SiO [8]. At the early stage of deposition, the cluster number density is low both in the gas phase as well as on the substrate surface. Figure 1 is a SEM micrograph of sample S1 with a coverage of less than 0.1 cluster monolayer deposited within this stage. Only individual clusters with the diameter about hundreds of nanometers are randomly distributed without any aggregating evidence. It should be noted that the lack of smaller clusters on the specimen surface at such a low coverage may reveal that the clusters are highly mobile on the substrate, considering the substrate is close to the oven and the deposition temperature is about 900 °C. Coalescence takes place between smaller clusters on their diffusion path. The clusters may also be pinned at some sites on the substrate, such as the surface defect, where smaller clusters on diffusion can be absorbed and the growth process conduce to the formation of larger clusters. As a result, if the density of the pinning sites is not so high, only some big clusters can be remained individually on the substrate at low coverage. These big clusters can either serve as seeds for one-dimensional growth or be building blocks of the one-dimensional structure under high temperature [7] for further growth.

When the coverage is increased more big clusters will be formed during the deposition. Some of them may still diffuse on the surface and aggregate with others. But for large clusters, it is rather difficult to be absorbed by another one and completely coalesce to a larger cluster. Instead, they can eliminate the interface by neck formation between them and form some short one-dimensional cluster assemblies under the high-temperature ambiance. What's more they can grow further into long wire by neck-link with other clusters or cluster assemblies. Such morphologies can be observed from specimen S2 with coverage of about half cluster monolayer. The structure evolution process can be deduced by a serial of SEM images taken from it locally, namely Figures 2a–2d.

Isolated large clusters are still remained in Figure 2a. They are randomly distributed and piled up and keep the spherical appearance. As a contrast clusters in Figure 2b are no more distributed in random. Instead, they form short one-dimensional assemblies, within which adjacent clusters are connected with each other by neck formation. Figure 2c shows similar structure, but the length of the cluster assemblies is much longer with less breakpoints. The morphologies of these one-dimensional cluster assemblies are obviously undulated, owing to the size mismatch between the sintering necks and the clusters. A relatively smooth nanowire is shown in Figure 2d. The appearance of the smooth morphology may be explained by considering the sintering mechanism. Atomic diffusion across the neck during the sintering reduces the size difference between the necks and the clusters. If the sintering time is long enough, the necks are eliminated and the whole nanowire develops into a smooth one in the end.

The series of SEM micrographs of Figures 2a−2d illustrate the transitional stage when the cluster assemblies are formed by cluster aggregation. At high coverage, large clusters are formed from the growth of smaller clusters. Under the high temperature ambiance clusters are high mobile and can rearrange on the substrate surface by themselves [10]. For large clusters, coarseness is energy-unfavorable. Instead, necks are formed due to the atomic diffusion on the interfaces while these clusters contact and connect them to a one-dimensional structure. Given enough annealing time, nanowire can be synthesized by cluster sintering. An interesting phenomenon here is the ordered arrangement of cluster assemblies. Since sintering itself can not result in ordered growth of nanowires, this phenomenon is discussed based on the steering of carrier gas that lead to the preferred arrangement under the direction of gas flow. The detail will be published elsewhere [9].

According to our suggested mechanism, more and more smooth nanowires should be synthesized if the coverage is further increased and annealing time is further prolonged. Figures 3 and 4 show the micrographs of sample S3 with a growth time of 5 minutes and S4 with a growth time of 10 minutes respectively. Smooth nanowires that can be identified in Figure 3 are much more than those in Figure 2. In fact, smooth nanowires are the main portion of specimen S3. The emergence of smooth nanowire is the



(a)

(b)

(c)

(d)

Fig. 2. Several morphologies corresponding to the different evolution stages are observed from specimen S2, with an average coverage of about half cluster monolayer: (a) isolated clusters can still be observed, (b) short cluster assemblies with ordered alignment, (c) long cluster assemblies with less breakpoints, (d) a relatively smooth nanowire with undulation on the surface.

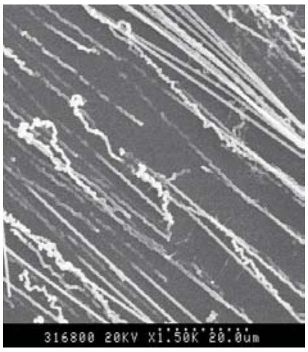


Fig. 3. More smooth nanowires appear in specimen S3 with growth time of 5 minutes.

Fig. 4. Layers of nanowires in specimen S4 with growth time of 10 minutes: flexual nanowires are found on top of smooth nanowires layers.

result of long time annealing in the high-temperature ambiance, which allows atoms to diffuse sufficiently. In Figure 4, the surface is covered by several layers of nanowires. Flexural nanowires can be seen on top of the smooth nanowire layers. Following the deposition process, the nanowires in lower layers are generally synthesized earlier than those in upper layers, that is, they have longer annealing time. So accordingly the nanowires in the lower layers become much smoother while flexural nanowires are principally remained on the top, which gives strong support to our suggestion that smooth nanowires are derived from flexural cluster assemblies by atomic diffusion across the neck.

Thin Si nanowires and thick Si whiskers have both been fabricated by vapor-liquid-solid (VLS) mechanism at temperature higher than 970 °C [11,12]. Alloy droplets should be formed in advance of nanowires/whiskers. However, at a relatively lower temperature without any metal catalyst, sintering mechanism plays a key role in the growth process of nanowires. Since at this temperature large clusters cannot melt into droplets so as to benefit the growth, they can only be sintered to one-dimensional structure, for such process can take place at a temperature much lower than the melting point of the desired material.

In summary, the morphologies evolution of Si nanowires synthesized by gas condensation of SiO is investigated by controlling the coverage of SiO_x deposits. It is found that the growth of Si nanowires undergo several stages, i.e., isolated clusters, one-dimensional cluster assemblies with different length, nanowires with flexural morphologies, as well as smooth nanowires. The mechanism is discussed based on the clustering-aggregation-sintering growth mode [7].

This work is financially supported by the National Nature Science Foundation of China (Grant Nos. 10274031, 90206033, 10021001, 10474030, 60478012), and the Foundation for University Key Teacher by the Ministry of Education of China (Grant No. GG-430-10284-1043). Supports from the Analysis and Measurement Foundation of Nanjing University should also be acknowledged.

References

1. Z.F. Ren, Z.P. Huang, J.W. Xu, J.H. Wang, P. Bush, M.P. Siegal, P.N. Provencio, Science **282**, 1105 (1998)
2. M. Terrones et al., Nature **388**, 52 (1997)
3. A.M. Morales, C.M. Lieber, Science **279**, 208 (1998)
4. Wen-Sheng Shi, Hong-Ying Peng, Yu-Feng Zheng, Ning Wang, Nai-Gui Shang, Zhen-Wei Pan, Chun-Sing Lee, Shuit-Tong Lee, Adv. Mat. **12**, 1343 (2000)
5. F.C. Frank, Disc. Faraday Soc. **5**, 48 (1949)
6. R.Q. Zhang, Y. Lifshitz, S.T. Lee, Adv. Mat. **15**, 635 (2003)
7. J.F. Zhou, M. Han, M.D. Liu, F.Q. Song, J.G. Wan, Y.F. Chen, G.H. Wang, J. Crys. Growth **207**, 269 (2004)
8. M. Han, J.F. Zhou, F.Q. Song, C.R. Yin, M.D. Liu, J.G. Wan, G.H. Wang, Eur. Phys. J. D **24**, 269 (2003)
9. J.F. Zhou, Z.L. Li, Y.F. Chen, M. Han, G.H. Wang, Sol. State Comm. **133**, 271 (2005)
10. S. Saito, T. Konno, A. Sawaoka, Jap. J. Appl. Phys. **11**, 629 (1972)
11. N. Wang, Y.H. Tang, Y.F. Zhang, C.S. Lee, S.T. Lee, Phys. Rev. B **58**, R16024 (1998)
12. E.I. Givargizov, J. Cryst. Growth **31**, 20 (1975)