

Effect of the Microstructure of Ag Catalysts in the Fabricating Process of Silicon Nanowires

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In this paper, well-aligned silicon nanowire (SiNW) arrays have been directly synthesized on single crystal silicon wafer at room temperature *via* a simple chemical etching method, and the effect of the microstructure of Ag catalysts on the fabricating process of the silicon nanowires has been systematically investigated. The experimental results show that different microstructures of Ag catalysts have been observed with different concentration of AgNO₃/HF solution for different deposition times. The diameters of Ag particles and the mean interstitial sizes among Ag particles are relatively small for a short deposition time, and some large particles are formed when the deposition time increases. A much longer deposition time caused the substrate to be covered with a large amount of Ag dendrite. It can be inferred that 4 min is a good deposition time, because of the proportioned structure of particles and interstitial size, according to our experimental results. Nanostructures of Ag catalyst also vary with a change of concentration of AgNO₃/HF solution. Ag dendrite may be formed at high concentration and affect the fabrication of SiNWs.

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I. INTRODUCTION

Since carbon nanotubes (CNTs) were firstly fabricated by Iijima in 1991 [1], one-dimensional nanostructures, such as nanotubes and nanowires, have been remarkably focused on, due to their novel electrical, optical, magnetic, and mechanical properties resulting from the reduced dimensions and size. Silicon material, as a semiconductor material, plays an important role in the microelectronic-device field. The synthesis, processing, and properties of silicon nanowires (SiNWs) have received significant attention and have been investigated widely, due to their nanostructure effects. Many kinds of methods have been used in the preparation of SiNWs, such as laser ablation [2,3], OAG (oxide-assisted growth) [4, 5], thermal evaporation [6], UHVSTM (ultra-high-vacuum scanning-tunnelling microscopy) [7], technology of RIE and EBL (reactive-ion-beam etching and electron-beam lithography) [8], and electrochemical etching [9–11]. At the same time, varieties of catalysts including Au [12,13], Ag [9–11], Fe [3,14], Ti [15] and Ni [6] were respectively used during the preparation of SiNW. However, in many cases, it is very difficult to control the growth orientation of SiNWs because of different microstructures of catalysts. In order to gain SiNWs ar-

rays with excellent orientation, the growth mechanism of well aligned silicon nanowires and the various processes for the catalyst microstructures should be systematically studied. In this paper, the synthesis process of well self-assembled SiNW arrays and the effect of Ag catalyst microstructure on a well aligned silicon-nanowire array directly synthesized with a chemical etching method have been studied.

II. EXPERIMENTS AND DISCUSSION

A simple electrochemical method was employed to synthesize SiNWs. *N*-type (100) silicon wafers of size $1 \times 1 \text{ cm}^2$ were used as substrates. After ultrasonic cleaning in acetone and ethanol for several minutes respectively to degrease, the silicon slices were immersed into a mixture of HF and H₂O₂ to remove the metallic particles absorbed on the surface and the native oxide layer. Each procedure ended with rinsing the samples under running deionized water and drying naturally at room temperature. The cleaned slices were immersed in AgNO₃/HF solution for 1 to 12 minutes to synthesize Ag catalyst, where the concentration of AgNO₃ is 0.01 to 0.04 mol/L. Then, the samples were quickly transferred into Fe(NO₃)₃/HF or H₂O₂/HF solution for 1 hour to fabricate SiNWs. Scanning-electron microscopy (SEM

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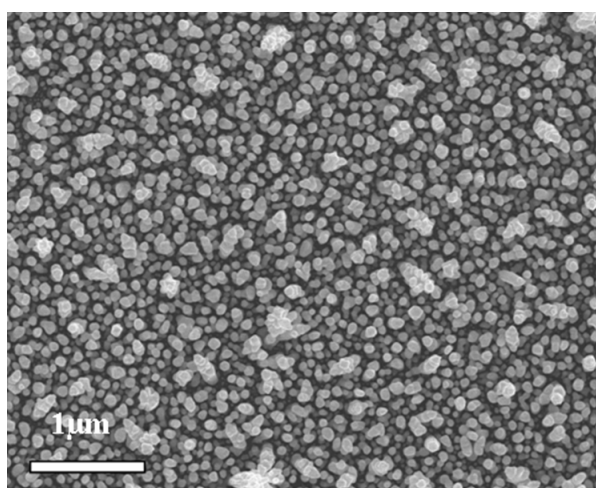


Fig. 1. Morphology of Ag catalyst on silicon substrates etched in AgNO_3 with concentration of 0.01 mol/L for 4 min.

S-4800, Hitachi) was employed to characterize the morphology of catalysts and SiNWs. The mechanism for the fabrication of SiNWs in which Ag catalyst is prepared in AgNO_3/HF solution through a chemical approach has been described by Peng [11]. Redox reactions, in which Ag nanoparticles act as cathodes and silicon substrate can be considered as anode, happen simultaneously at the interface between Ag nanoparticles and silicon. During the process of redox reaction, Si is oxidized to form SiO_2 compound, and then SiO_2 solid is subsequently dissolved by HF solution. At this time, a shallow pit is formed underneath Ag catalysts. The holes are formed gradually in the silicon substrate with increasing chemical-etching time. Therefore, SiNWs are formed in the silicon substrate when the walls between holes are etched out. It can be seen that the morphology and microstructure are very important for the fabrication of SiNWs during the process of chemical etching. For this reason, we systematically investigate the microstructure of Ag catalysts and the effect factor for fabrication of Ag catalysts.

In our investigation, the analysis of morphology for Ag catalysts is clearly dependent on the deposition time. The catalysts deposited for one minute exist in the form of particles with a distribution of well proportioned diameter and high density, and the interstitial size between Ag particles is relatively small. The size of Ag particles gradually increases with increasing deposition time, and they tend to gather as clusters. The mean diameter of Ag particle is about 100 nm during deposition for 4 minutes (as shown in Fig. 1). When deposition time increases to 8 min, a large amount of nanoclusters and Ag dendrite are observed.

In order to understand quantitatively the influence of deposition time on the morphology of Ag catalysts and interstitial sizes between Ag particles, statistical analysis of the distribution of the interstitial size between Ag

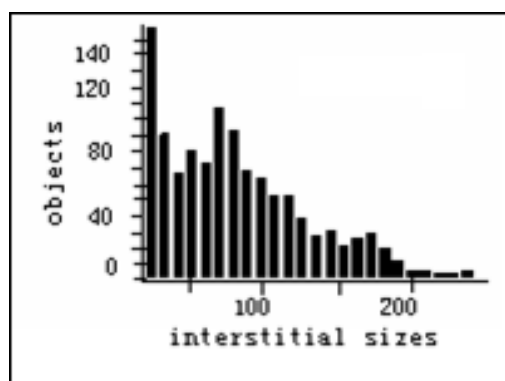


Fig. 2. Statistical diagram of mean interstitial sizes between Ag catalysts fabricated in 0.01 mol/L AgNO_3 solution for 4 min.

particles fabricated for different deposition times is carried out. With increasing deposition time, the average interstitial sizes between Ag catalyst particles vary from 58.99 nm for one minute deposition to 68.43 nm and 90.20 nm, respectively, for 4-min deposition and 8-min deposition. Meanwhile, the density distribution of Ag particles seems relatively proportioned and an interstitial size larger than 150 nm nearly cannot be found at a short deposition time; particles begin to become larger at 4 min (as shown in Fig. 2). A large amount of large particles and clusters can be found at 8-min deposition. The reason is that the structure of Ag catalyst can vary from particle shape to cluster or dendrite structure with increasing deposition time, so the structure uniformity of Ag catalysts gradually declines and the interstitial sizes increase.

Figure 3 shows SEM cross-sectional images of Ag catalysts whose microstructures vary with a change of solution concentration. From Fig. 3, it can be seen that the morphology of Ag catalysts changes dramatically with solution concentration. When the concentration of AgNO_3 is about 0.01 mol/L, Ag catalysts appear in a particle shape with uniform diameter (about 100 nm). However, a few Ag particles with a variety of shapes of rod and antler have been fabricated at a concentration of 0.02 mol/L. At the same time, corrosion pits are also observed on the silicon substrate. When the solution concentration reaches 0.04 mol/L, the silicon substrate is etched deeply and SiNWs with a length of about 1 μm are formed. On the other hand, the higher deposition rate of silver induces quick growth of Ag particles in the solution with higher ion concentration. A large number of silver dendrites are formed quickly at the top of SiNWs and tend to connect to each other to form a network, due to the higher ion concentration in the reacting solution. The thickness of Ag dendrite film is more than 3 μm . The dendrites are useless for the catalytic fabrication of SiNWs in the silicon substrate and must be reduced in the synthesis of Ag catalyst. On comparing our experimental results, lower concentration in

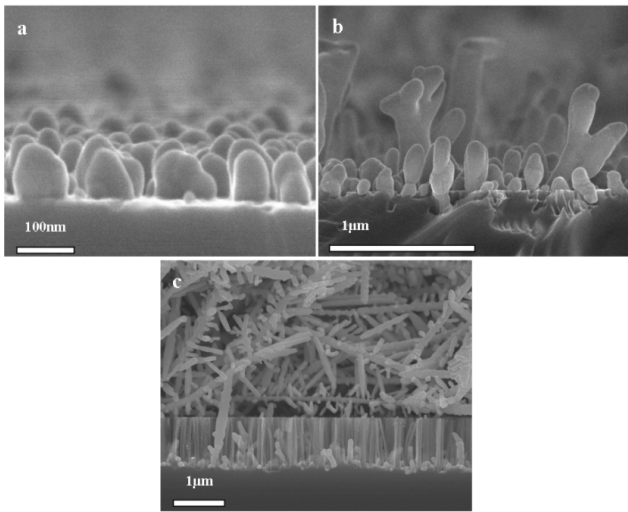


Fig. 3. Cross-sectional views of Ag catalyst on silicon substrates etched in AgNO_3 with concentration of (a) 0.01 mol/L (b) 0.02 mol/L, and (c) 0.04 mol/L.

the reacting solution is propitious to synthesize Ag catalyst film with a uniform microstructure and a suitable interstitial size between Ag particles for the fabrication of SiNWs during chemical etching.

The key problems for the chemical growth of SiNWs are the chemical etching velocity and the reacting activity and microstructure of catalysts. Our results show that the reacting activity and microstructure of catalysts are affected by the deposition time of Ag catalyst and the solution concentration in chemical deposition. In order to understand the influence of solution concentration of AgNO_3/HF solution on the fabrication of SiNWs, further experiments were carried out in which the samples were immersed into $\text{Fe}(\text{NO}_3)_3/\text{HF}$ solution. SEM images of the SiNW array indicate that there are different morphologies of SiNWs synthesized with Ag catalysts fabricated at different AgNO_3/HF solution concentration. With a concentration increase of AgNO_3/HF solution, the microstructure of the SiNW array becomes less compact, and more and more Ag dendrites can be observed on the top of the SiNW array. At the same time, longer SiNWs have been obtained at a higher concentration of AgNO_3/HF solution. This is the same as in the SEM images of Ag catalyst fabricated at a higher concentration of AgNO_3/HF solution.

For the influence of deposition time of Ag catalysts on the fabrication of SiNWs, the Ag catalysts with the shape of dendrites form gradually with increasing deposition time. There is a large amount of Ag dendrites to be formed on the silicon substrate for a longer deposition time, and the existence of these Ag dendrites is adverse to the fabrication of SiNWs. On the other hand, Ag particles with smaller sizes and a dispersed distribution have been formed at a shorter deposition time, which will induce the formation of a large amount of silicon holes, so

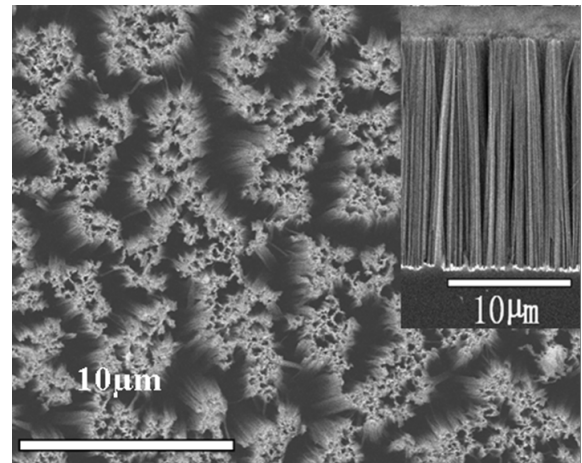


Fig. 4. SEM image of SiNWs fabricated in AgNO_3 solution for 4 min at a concentration of 0.01 mol/L. The insert is the cross-sectional view.

that we cannot observe the fabrication of SiNWs. A well aligned SiNW array is fabricated by using of Ag catalysts deposited in AgNO_3 solution with the concentration of 0.01 mol/L for 4 min (as shown in Fig. 4). From the experimental results, it can be seen that suitable experimental parameters used for the fabrication of SiNWs are important in the chemical-etching process.

III. CONCLUSIONS

According to our experimental investigation, chemical-etching technology is an effective and simple method for the fabrication of SiNWs. One of the key problems for the chemical growth of SiNWs is the synthesis of Ag catalyst film. Different microstructures and morphologies of Ag catalyst film have been obtained by using different deposition times and concentrations of AgNO_3/HF solution. For a longer or shorter deposition time, the morphologies of Ag catalyst are not suitable for the fabrication of SiNWs. Ag catalyst fabricated in 0.01 mol/L AgNO_3/HF solution for 4-min deposition time has good morphology for the fabrication of SiNWs.

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REFERENCES

- [1] S. Iijima, *Nature* **354**, 56 (1991).

- [2] Y. F. Zhang, Y. H. Tang, H. Y. Peng, N. Wang, C. S. Lee, I. Bello and S. T. Lee, *Appl. Phys. Lett.* **75**, 1842 (1999).
- [3] A. M. Morales and C. M. Lieber, *Science* **279**, 208 (1998).
- [4] R. Q. Zhang, Y. Lifshitz and S. T. Lee, *Adv. Mater.* **15**, 635 (2003).
- [5] N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee and S. T. Lee, *Phys. Rev. B* **58**, R16024 (1998).
- [6] H. F. Yan, Y. J. Xing, Q. L. Hang, D. P. Yu, Y. P. Wang, J. Xu, Z. H. Xi and S. Q. Feng, *Chem. Phys. Lett.* **323**, 224 (2000).
- [7] T. Ono, H. Saitoh and M. Esashi, *Appl. Phys. Lett.* **70**, 1852 (1997).
- [8] E. Leobandung, L. J. Guo, Y. Wang and S. Y. Chou, *Appl. Phys. Lett.* **67**, 938 (1995).
- [9] K. Q. Peng, Y. Wu, H. Fang, X. Y. Zhong, Y. Xu and J. Zhu, *Angew. Chem. Int. Ed* **44**, 2737 (2005).
- [10] K. Q. Peng, Y. Wu, Y. Xu, Y. J. Yan, S. T. Lee and J. Zhu, *Small* **11**, 1062 (2005).
- [11] K. Q. Peng, J. J. Hu, Y. J. Yan, Y. Wu, H. Fang, Y. Xu, S. T. Lee and J. Zhu, *Adv. Funct. Mater.* **16**, 387 (2006).
- [12] R. S. Wagner and W. C. Ellis, *Appl. Phys. Lett.* **4**, 89 (1964).
- [13] Y. Cui, L. J. Lauhon, M. S. Gudiksen, J. F. Wang and C. M. Lieber, *Appl. Phys. Lett.* **78**, 2214 (2001).
- [14] J. T. Hu, O. Min, P. D. Yang and C. M. Lieber, *Nature* **399**, 48 (1999).
- [15] T. I. Kamins, R. S. Williams, Y. Chen, Y.-L. Chang and Y. A. Chang, *Appl. Phys. Lett.* **76**, 562 (2000).