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Fabrication of Silicon Oxide Nanowires Embedded with Au Nanoparticle or Au Nanowire: Its Use as Template to Hollow Silica Nanotube

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Silicon oxide nanowires which contains Au nanoparticles or an Au nanowire were fabricated by thermal evaporation chemical vapor deposition method using Au as catalyst. Silicon oxide wafers were used as the collector. The diameters of silicon oxide nanowires range from 20 to 150 nm. The larger the diameter of Si nanowire is, the larger the diameter of embedded Au nanoparticles. The separation between Au nanoparticles increases with the diameter. Different forms of silicon oxide nanowires were observed at different growth temperature: silicon oxide nanowires embedded with Au-containing nanoparticles at 1250 °C and Au/silicon oxide coaxial nanocable at 1425 °C. Using KCN solution, the nanoparticles or the nanocable inside silicon oxide nanowires were extracted, leaving hollow silicon oxide nanotubes.

Keywords: Nanowire, Silicon Oxide, Heterostructure.

RESEARCH ARTICLE

1. INTRODUCTION

The demand of the fabrication, characterization and control of building blocks in nanoscale devices such nanoparticles, nanowires (NWs) and nanotubes has been the driving force to the recent extensive research activities in NWs and nanotubes, in combination with their potential applications in nanoscale devices in electronics, optics and bio-engineering.[1–3]

One dimensional nanoscale hetero-structures has recently attracted lots of attention because their functionality might be further manipulated by the combination of different materials. The material modulation along the axis of a NW, so called "nano barcode," has been fabricated and characterized.[4] The modulation of materials in the radial direction in a NW has been also realized by vapor-phase, high-temperature methods and solution-based methods. Nanocables of Si core sheathed with silicon oxide,[5] Si-Ge core sheathed with Si_4, SiC core sheathed with BNC (boron nitride and carbon) sheath[6] and SiC core sheathed with SiO_2 (Ref. [7]) have been fabricated. Nanocables of metallic core sheathed with insulator have also been studied.[8,9] They are especially useful as interconnects in nanoelectronic devices.

Several groups report metal nanoparticles embedded nanostructures.[10–13] Hu et al. report the Au nanoparticles embedded Silica NWs fabricated by using microreactor with Si and Au coated substrate.[13] These NWs have lower resistivity when they are exposed to a specific wavelength. This mean that Au nanoparticle-embedded silica NWs can act as a wavelength dependent sensor.

In this paper, we present the fabrication of Au nanoparticles-embedded silicon oxide NWs and Au/silicon oxide coaxial nanocables. All of these nanostructures were grown by thermal evaporation chemical vapor deposition (CVD) method for changing the fabrication conditions. The effect of the growth temperature on the formation of Si/Au nanostructures has been investigated.

Furthermore, Au embedded inside the NWs can be extracted using KCN solution. This method can be applied to the preparation of silicon oxide nanotubes. Silica nanotubes are of special interest because of their hydrophobic nature, easy colloidal suspension formation, surface functionalization accessibility for both inner and outer walls. Hollow inorganic nanotubes are recently attracting a great deal of attention due to their fundamental significance and potential applications in bio-analysis and bio-separation, and bio-catalysis.

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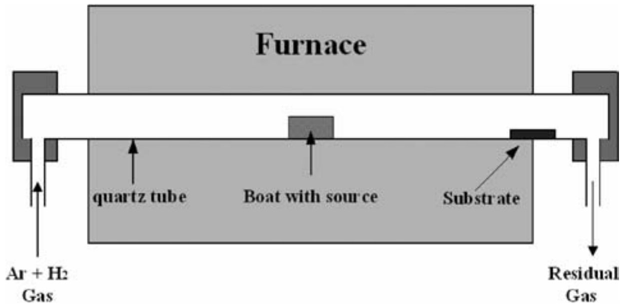

Fig. 1. Schematic diagram of a thermal chemical vapor deposition apparatus.

2. EXPERIMENTAL DETAILS

The technique utilized in this work is thermal evaporation VLS method. As shown in Figure 1, the boat that contains the mixture of Si and Au micro-powders is placed at the center of a furnace. The mixture ratio of Au powder to Si is varied from 0 to 40% in atomic percents to see the effect of the amount of Au catalyst on the growth of Si NWs. The temperature at the center of the furnace is kept during the growth at a temperature in the range of 1010 to 1450 °C. For the promotion of NW growth, Si substrates are coated with an Au nanofilm of 0.6 nm thickness. A substrate is placed about 30 cm downstream from the boat. A mixture of argon and hydrogen gas (5%) flows through the system at a flow rate of 50 sccm and a total pressure of 400 Torr. Si vapor produced from a target condenses on Au/Si molten clusters. The molten clusters become super-saturated in Si. Si is then precipitated from the super-saturated liquid Au/Si clusters in one-dimensional form, leading to the growth of NWs. The growth terminates when the super-saturated clusters passes out of the hot region. The structure and chemical compositions of synthesized silicon oxide NWs have been investigated with a field emission scanning electron microscope (FE-SEM, JSM6330F), a field emission transmission electron microscope (FE-TEM), an energy dispersive X-ray analysis (EDX) and an electron energy loss spectroscopy (EELS).

3. RESULTS AND DISCUSSION

Figure 2 shows the TEM and SEM pictures of nanostructures fabricated in this study. The diffraction patterns of all nanowires shows that the nanowires are single crystalline and the growth direction is (111). Typical Si NWs fabricated without any Au catalyst are shown in Figure 2(a). In this case, it has been known that silicon oxide (SiOx) plays a role of catalyst.[14] The substrate is covered by a dense array of high aspect-ratio straight or curved free-standing Si NWs with a length of several micrometers. Curved NWs are due to growth defects. The diameter of the NWs is in the range of a few ten nanometers. The smallest diameter observed is 13 nm. The crystalline core of a Si NW is wrapped with amorphous silicon oxide sheath as observed in other studies.

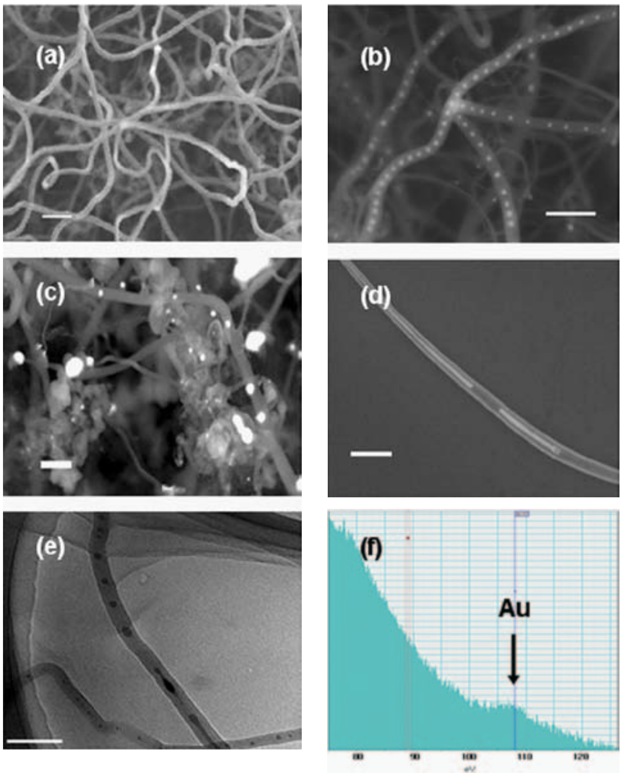

Fig. 2. TEM and SEM pictures of NWs grown at different growth temperatures. (a) 1250 °C, 0% of Au, Scale bar: 200 nm; (b) 1250 °C, 20% of Au; Scale bar: 200 nm (c) 1100 °C, 20% of Au; Scale bar: 200 nm (d) 1425 °C, 20% of Au; Scale bar: 200 nm (e) Au nanoparticles are first embedded, then they merge into a NW structure. Scale bar: 100 nm (f) EELS measurement showing the existence of Au inside the NW.

In the case where Au catalyst is 20%, nanoparticle-embedded NWs as shown in Figure 2(b) are observed. The growth temperature is 1250 °C. Au-nanopaticle-embedded Si NWs with different diameters are also observed. The larger the diameter of Si NW is, the larger the diameter of embedded Au nanoparticles. The NW does not have the crystalline core of Si but is of silicon oxide. The peculiar point to be noted is that as shown in Figure 2(b), the distance between neighboring Au nanoparticles is regular. It is not clear yet but under investigation how their separation becomes regular to a certain degree. It is also observed that the separation between Au nanoparticles increases with the diameter.

When the growth temperature is lowered to 1100 °C, Si NWs with Au nano-particles being attached on their surfaces are observed as shown in Figure 2(c). Some isolated nano-particles (white dots in pictures) are also observed at some local sites on the substrate. The diameters of these particles are ranged from several tens to hundreds of nanometers. The EDX observation shows that nano-particles contain Au (Si and O are also observed.

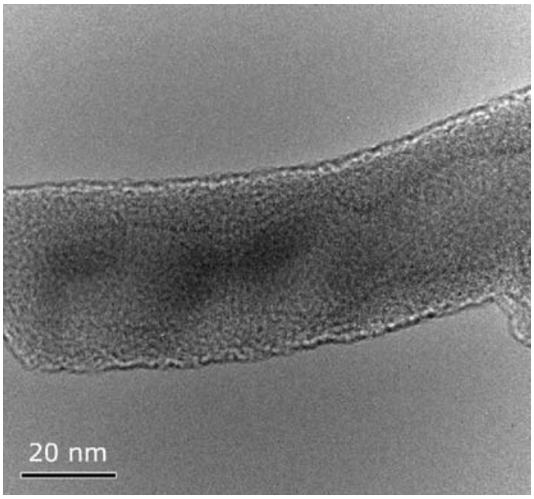

Fig. 3. Hollow silicon oxide nanotube, after Au is removed by KCN solution.

These particles may come from silicon substrate and oxidized silicon nanoparticles). As shown below, the EELS measurement also confirms the containment of Au.

When the growth temperature is raised to 1425 °C, the formation of an Au/silicon oxide coaxial nanocable is observed as shown in Figures 2(d and e), which are the SEM pictures of the NWs dispersed on a silicon wafer after they are diluted in an ethanol solution. The EELS measurement is shown in Figure 2(f). In the EELS measurement, only one single NW was exposed to an electron beam. The EELS measurement confirms that the NW at center contains Au. This is a clear evidence that Au is embedded inside silicon.

Considering these observations, the formation of Au nanoparticles-embedded NW and Au/silicon oxide coaxial nanocable could be explained as follows: the nanoparticles are formed in vapor phase surrounded by ambient Ar gas. Such Au-containing nano-particles from the source material are somehow regularly attached to the surface of a silicon oxide NW, and then "sink," or even completely submerse into the NW. If the growth temperature is sufficiently high, Au nanoparitcles are then in liquid phase and the surface tension between droplet-NW interfaces drives the Au-containing nanoparticles into the silicon oxide NWs[15] as in Figure 2(b); otherwise, the nanoparticles are attached on the surface of a NW. If the growth temperature is even higher like 1425 °C, the embedded-nanoparticles are melted and connected to form a Au or Au-silicide NW inside a silicon oxide NW, as shown in Figure 2(e). This growth mechanism us different from Rayleigh instability-like mechanism proposed by Kolb et al. and capillary force mechanism proposed by Hu et al. Since the growth conditions in these three experiments are different, different growth mechanisms of Au-nanoparticle embedded silicon oxide NW or Au/silicon oxide coaxial nanocable indicate that they grow in various ways.

Since KCN solution has been used widely to dissolve and extract Au from ores, Au-embedded NWs are dispersed in KCN solution for an hour. After this treatment, NWs are observed again with TEM. Figure 3 shows a typical result showing that Au is dissolved out, leaving a hollow silicon oxide NW, or silicon oxide nanotube.

4. CONCLUSION

In summary, it is demonstrated that a simple thermal CVD also allows one to fabricate silicon nanostrucutures such as Au nanoparitcle-embedded NW and Au/silicon oxide coaxial nanocable. Around the growth temperature of 1250 °C, Au nanoparticle-embedded NWs were formed and around 1425 °C, Au/silicon oxide coaxial nanocable formed. Experimental investigation reveals that nanoparticles are formed outside NWs, attach to the surface and merges into a NW, resulting in Au nanopaticle or NW being embedded depending on the growth temperature. It is demonstrated that the KCN treatment of this structure leads to a hollow silicon oxide NW.

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References and Notes

1. A. P. Alivisatos, *Science* 271, 933 (**1996**).
2. X. Duan, Y. Huang, R. Agarwal, and C. M. Lieber, *Nature* 421, 241 (**2003**).
3. M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* 292, 1897 (**2001**).
4. Y. Wu, R. Fan, and P. Yang, *Nano Lett.* 2, 83 (**2002**).
5. A. M. Morales and C. M. Lieber, *Science* 279, 208 (**1998**).
6. Y. Zhang, K. Suenaga, C. Colliex, and S. Iijima, *Science* 281, 973 (**1998**).
7. L. D. Zhang, G. W. Meng, and F. Phillipp, *Mater. Sci. Engg. A* 286, 34 (**2000**).
8. Y. Yin, Y. Lu, Y. Sun, and Y. Xia, *Nano Lett.* 2, 427 (**2002**).
9. S. O. Obare, N. R. Jana, and C. J. Murphy, *Nano Lett.* 1, 601 (**2001**).
10. J. S. Wu, S. Dhara, C. T. Wu, K. H. Chen, Y. F. Chen, and L. C. Chen, *Adv. Mater.* 14, 1847 (**2002**).
11. K. Wang, S. Y. Chung, and D. E. Kim, *Appl. Phys. A* 79, 895 (**2004**).
12. F. M. Kolb, A. Berger, H. Hofmeister, E. Pippel, U. Gösele, and M. Zacharias, *Appl. Phys. Lett.* 89, 173111 (**2006**).
13. M. S. Hu, H. S. Chen, C. H. Shen, L. S. Hong, B. R. Huang, K. H. Chen, and L. C. Chen, *Nat. Mater.* 5, 102 (**2006**).
14. R. Q. Zhang, Y. Lifshitz, and S. T. Lee, *Adv. Mater.* 15, 635 (**2003**).
15. C. P. Li, X. H. Sun, N. B. Wong, C. S. Lee, S. T. Lee, and B. K. Teo, *J. Phys. Chem. B* 106, 6980 (**2002**).

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