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Novel Silicon Nanotubes

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Abstract: Novel silicon nanotubes with inner-diameter of 60-80 nm was prepared using hydrogen-added dechlorination of $SiCl_4$ followed by chemical vapor deposition (CVD) on a Ni_xMg_yO catalyst. The TEM observation showed that the suitable reaction temperature is 973 K for the formation of silicon nanotubes. Most of silicon nanotubes have one open end and some have two closed ends. The shape of nanoscale silicon, however, is a micro-crystal type at 873 K, a rod or needle type at 993 K and an onion-type at 1023 K, respectively.

Keywords: Silicon nanotubes, chemical vapor deposition, chemical etching.

The preparation of silicon nanotubes is a subject of great importance for both the theoretical and experimental work in the nanotube research field since it could lead to a wealth of new physics and chemistry because of the unique properties of silicon as compared with its carbon analogue. Some structures of nanoscale silicon and silicon composites, such as silicon nanowire[1], silicon nano-clusters[2] and SiC nanorods[3] have been discovered and investigated. The silicon nanotubes, however, have not been prepared and observed up to now although silicon nanotubes[4] were predicted in theoretical models and *ab initio* calculations more recently. Recently, the silicon nanotubes have been prepared and observed successfully in our laboratory.

The silicon nanotubes were prepared using hydrogen-added dechlorination of $SiCl_4$ followed by chemical vapor deposition (CVD) on a Ni_xMg_yO catalyst. The catalyst was prepared as follows. $Ni(NO_3)_2$ and $Mg(NO_3)_2$ were mixed with citric acid, then distilled water was added and stired to solve them. The solution was vaporized in vacuum for 3 hr at 333 K and 1 hr at 353 K and then dried at 383 K overnight. The precursor was calcined for 5 hr in the air at 973 K, and in a continuous fixed-bed reactor, was reduced and activated with H_2 flow at 873 K for 1 hr, then the temperature was controlled rapidly to the designed reaction temperature. The $SiCl_4$ was heated at 330 K in water bath. The vapor of $SiCl_4$ with the H_2 flow were introduced to the above mentioned reactor for 20 minutes and then, in the H_2 flow, rapidly cool down to room temperature. The product was washed with 6 mol/L HCl and treated with hydrofluoric acid to remove possible remaining SiO_2 species, filtered and dried at 383 K. The grey-white final

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product was obtained.

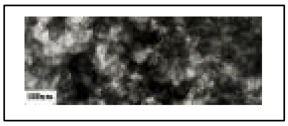
The nanoscale micro-structure was observed with TEM, JEM-100CXII, at 100 kV. The TEM observation showed that the suitable reaction temperature is 973 K for the formation of silicon nanotubes (**Figure 1**). Most of silicon nanotubes have one open end and some have two closed ends. The inside diameter of the silicon nanotubes is about 60-80 nm and the outside diameter is about 100-140 nm. The shape of nanoscale silicon, however, is a micro-crystal type at 873 K (**Figure 2A**), a rod or needle type at 993 K (**Figure 2B**) and an onion-type at 1023 K (**Figure 2C**).

A part of reduced silicon atoms may be deposited on the catalyst surfaces and then self-packed up and grown to form the nanotube structure. The species of chlorine may be favorable to both the formation and the bending of the big π structure of silicon. This situation may be similar to the formation of the carbon nanotubes. Gaseous $SiCl_4$ may react with the ring-type silicon atoms to form chloro-silicone hydrides and chloro-silicon composites. They may be dechlorinated and dehydrogenated at high temperature and under H_2 flow to perform big silicon system. The silicon atoms on the surfaces and terminals may be passivated by hydrogen and the formed silicon nanotubes can be stabilized.

Figure 1 Silicon nanotubes (reaction temperature, T = 973 K)

Figure 2 Other shapes of nanoscale silicon crystals

A



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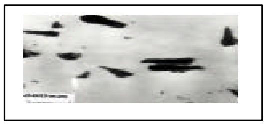

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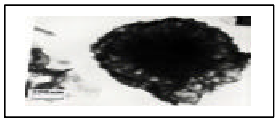

(A. microcrystal type, T=873 K; B. rod or needle type, T=993 K; C. onion type, T=1023 K)

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References

1. J. T. Hu, O. Y. Min, P. D. Yang, C. M. Lieber, *Nature*, **1999**, *399*, 48.
2. X. T. Zhou, H. L. Lai, H. Y. Peng, F. C. K. Au, L. S. Liao, N. Wang, I. Bello, C. S. Lee, S. T. Lee, *Chem. Phys. Lett.*, **2000**, *318*, 58.
3. M. F. Jarrold, *Science*, **1991**, *252*, 1085.
4. S. B. Fagan, R. J. Baierle, R. Mota, A. J. R. da Silva, A. Fazzio, *Phys. Rev.*, B, **2000**, *61*, 9994.

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