J. Am. Chem. Soc. **2001,** *123,* 11095−11096

Free-standing Single Crystal Silicon Nanoribbons

Wensheng Shi, Hongying Peng, Ning Wang,[†] Chi Pui Li,
Lu Xu, Chun Sing Lee, Rafi Kalish,[‡] and Shuit-Tong Lee*

Center Of Super-Diamond and
Advanced Films (COSDAF) and the
Department of Physics and Materials
City University of Hong Kong, Hong Kong SAR, China

Received May 28, 2001

In recent years much scientific and technological excitement was raised by the discovery of different forms of nanostructures in many materials (nanospheres, nanotubes, nanowires, oxide-nanobelts, as well as derivatives of the above).[1,2] Silicon is one of the most important electronic materials. Its nanoscale forms, such as nanocrystal, porous silicon, quantum well, and nanowire,[3] have stimulated great interest among scientists because of their peculiar physical properties, such as light emission, field emission, and quantum confinement effect. In this communication we report on the synthesis of *single-crystal silicon ribbons* of nano dimensions achieved by thermal evaporation of silicon monoxide (SiO) without using any templates or catalysts. The nanoribbons have a thickness of only about 10 nanometers, widths of several hundreds of nanometers, and lengths of many micrometers. This new type of nanostructure, distinctive in shape from nanofilms, -wires, -tubes, -chains, and -particles, might be explored for physical property studies and interesting applications as a new kind of nanoblock.

Free-standing quasi-two-dimensional silicon nanoribbons have been realized in the present work by using an oxide-assisted growth method, which has been previously applied to the growth of one-dimensional silicon nanostructures.[4] The remarkable growth of silicon nanoribbons was carried out in a tube furnace, in which SiO powder as the source was placed at the center zone where the temperature was 1150 °C. The evaporated material was carried down the tube by a gas mixture of 5% hydrogen in argon at a flow rate of 50 standard cubic centimeters per minute at a total pressure of 0.5 Torr. Si nanoribbons were abundantly grown on substrates placed down the tube where the temperature was 900 °C. Untreated alumina plates were usually used as substrates, although ribbon growth was also observed on other substrates. Typical growth process lasted for 2 h.

From the synthesized material of light-yellow color, two kinds of morphology of the nanoribbons have been observed from a low-magnification TEM overview image (Figure 1A). Most of the ribbons have rippling edges (Figure 1B), and a small portion of the ribbons has smooth edges (Figure 1C). The thickness of the ribbons can be deduced from the ribbons imaged edge-on, as marked by arrows in Figure 1, B and C, and were estimated to be 10−20 nm. Support for this estimate is found in the transparency of the ribbons to the 200 keV electrons used for the TEM imaging (Figure 1C). It is worthwhile noting that the thickness of the ribbons is nearly uniform from ribbon to ribbon with different width and morphology and also is remarkably constant within an individual ribbon. Analysis of a number of nanoribbons with different widths reveals that the average thickness is about 15 nm. The widths of the various ribbons vary from 50 to 450 nm as determined from the TEM images. It can also be observed that the widths exhibit little change over the length of individual ribbons. Using a representative ribbon as an example (Figure 1C), the thickness is about 14 nm, and the width is about 370 nm. Statistically, the ratio of thickness to width varies from 4 to 22. The rippling and curling features at the edge of most ribbons also further confirm that the nanoribbons are a quasi-two-dimensional structure and are distinctly different in shape from the one-dimensional silicon nanowires with a smooth surface.

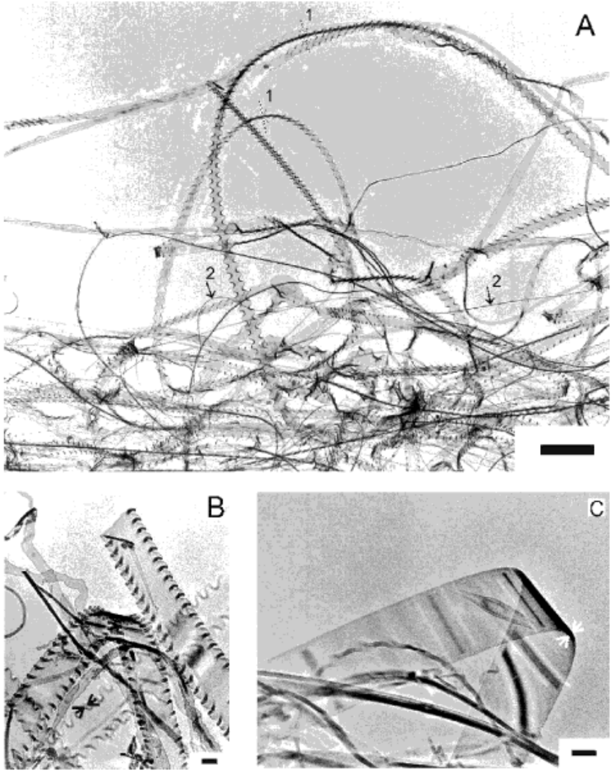

Figure 1. TEM images (TEM, Philips CM 20 TEM at 200 kV) of **(**A**)** silicon nanoribbons collected from the substrate. Arrows 1 indicate the edge-on position, and arrows 2 indicate silicon nanowires grown together with nanoribbons. **(**B**)** Some rippling-edge ribbons, and **(**C**)** a smooth-edge ribbon. The thickness of the ribbons estimated from the arrows indicating parts in B and C are 13 and 14 nm, respectively. Scale bars: 1 μm in A, and 100 nm in B and C.

A high-resolution TEM image (Figure 2) of a single nanoribbon revealed that the ribbon has a crystal core nipped by amorphous layers with atomically sharp interfaces. The fact that the distance between atomic planes (indicated by lines in Figure 2) is identical to that of (110) lattice planes of bulk silicon suggests that the in-plane layers of the nanoribbon are silicon (110) facet with a perfect atomic, defect-free, single-crystal structure grown along

---

[*] Corresponding author. E-mail: apannale@cityu.edu.hk. Fax: 852-2784-4696. Telephone: 852-2788-9606.

[†] On leave from Technion Israel Institute of Technology, Solid State Institute, Technion City, Haifa 3200, Israel.

[‡] Current address: Physics Department, the Hong Kong University of Science and Technology, SAR, China.

(1) (a) Iijima, S. *Nature* **1991**, 354, 56. (b) Hu, J.; Odom, T. W.; Lieber, C. M. *Acc. Chem. Res.* **1999**, *32*, 435. (c) Kondo, Y.; Takayangi, K. *Science* **2000**, *289*, 606. (d) Stevens, R.; Nguyen, C.; Cassell, A.; Delzeit, L.; Meyyappan, M.; Han. Jie *Appl. Phys. Lett.* **2000**, *77*, 3453. (e) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947. (f) Guo, L. J.; Leobandung, E.; Chou, S. Y. *Science* **1997**, *275*, 649.

(2) (a) Wang, Z. L.; Dai, Z. R.; Gao, R. P.; Bai, Z. G.; Gole, J. L. *Appl. Phys. Lett*. **2000**, *77*, 3349. (b) Zhang, Y.; Suenaga, K.; Colliex, C.; Iijima, S. *Science* **1998**, *281*, 973. (c) Vigolo, B. et al. *Science* **2000**, *290*, 1331.

(3) (a) Choi, S. H.; Elliman, R. G. *Appl. Phys. Lett.* **1999**, *75*, 968. (b) Wei, J.; Buriak, J. M.; Siuzdak, G. *Nature* **1999**, *399*, 243. (c) Balchin, G. A.; Amirtharaj, P. M.; Silvestre, C.; Thompson P. *J. Appl. Phys.* **1999**, *85*, 2875. (d) Wang, N.; Tang, Y. H.; Zhang, Y. F.; Lee, C. S.; Bello, I.; Lee, S. T. *Chem. Phys. Lett.* **1999**, *299*, 237.

(4) (a) Lee, S. T.; Wang, N.; Zhang, Y. F.; Tang, Y. H. *Mater. Res. Bull.* **1999**, *24*, 36. (b) Lee, S. T.; Zhang, Y. F.; Wang, N.; Tang, Y. H.; Bello, I.; Lee, C. S.; Chung. Y. W. *J. Mater. Res.* **1999**, *14*, 4503. (c) Shi, W. S.; Peng, H. Y.; Zheng, Y. F.; Wang, N.; Shang, N. G.; Pan, Z. W.; Lee, C. S.; Lee, S. T. *Adv. Mater*. **2000**, *12*, 1343.

10.1021/ja0162966 CCC: $20.00

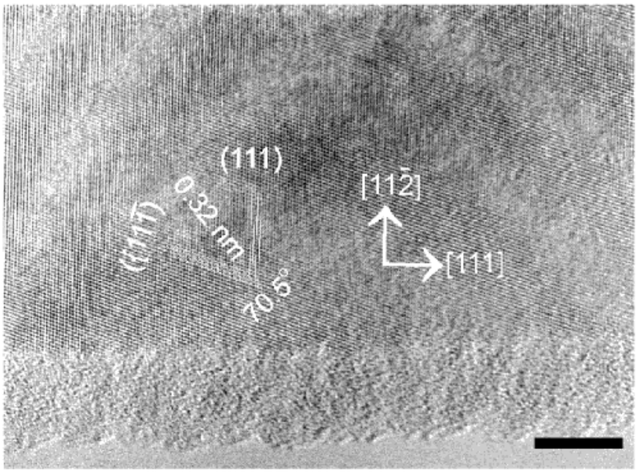

Figure 2. High-resolution TEM (Philips CM200 FEG TEM, at 200 kV) image of an individual silicon nanoribbon. Scale bar: 10 nm.

the ⟨111⟩ direction. This direction is different from the predominant ⟨112⟩ and ⟨110⟩ direction of silicon nanowires synthesized similarly by the oxide-assisted method.[5] However, it is the same as the growth direction of Si nanowires synthesized by the metal-catalyzed vapor–liquid–solid (VLS) method.[6] From the high-resolution lattice image shown in Figure 2, we can also conclude that the wide part of the ribbon is along the ⟨112⟩ direction. The chemical components of the amorphous edges of the ribbon consist of silicon oxide (SiO_x) as determined by using an electron energy loss spectrometer and an energy-dispersive X-ray spectrometer attached to the TEM. The width of the amorphous edge is about 10 nm. Analysis of a number of nanoribbons with different widths shows that the width of the oxide edges varies from 3 to 25 nm, which are similar to the thickness of the amorphous silicon oxide shell of the nanowires synthesized by the oxide-assisted growth.[4] The width of these oxide edges is larger than the typical thickness of a native silicon oxide layer on a silicon wafer and was found to be related to the width of the ribbons. Of course, there are also oxides coated on the flat surfaces of the silicon ribbons. Taking account of the thickness of the ribbons observed in the above TEM investigations, we concluded that the thickness of the oxide layer covering the flat surfaces of the ribbons is much less than the width of the oxide edges; that is, the thickness of the oxide layers is anisotropic. This result may be understood in terms of the oxide-assisted growth process, in which the silicon oxide shell was formed by the reaction of $SiO + SiO = Si + SiO_2$, and subsequently separated from the silicon core during growth.[4] According to this reaction, the amount of segregated silicon oxide is proportional to the amount of the silicon at the same place. In other words, the anisotropic growth of the nanoribbons also contributes to the anisotropic thickness of the silicon oxide shell.

Evidently, the growth of Si nanoribbons differs markedly from that of silicon nanowires, and the conditions for nanoribbon growth are quite restrictive. Where nanoribbons were produced, a few nanowires were also observed (indicated by arrows in Figure 1A). However, in the same experiment at the higher-temperature zone (about 950 °C) only nanowires and no ribbons were observed. If the temperature of the furnace and the pressure of the system (up to 1250 °C and 400 Torr, respectively) was increased, only wires and no ribbons could be observed in the deposited product. It has been reported that the growth of micro-sized ribbons (size in micrometer to millimeter) via metal-catalyzed VLS method could be interpreted by a twin-plane growth mechanism, according to which the growth of the microribbons was controlled by a twin plane parallel to the flat surface of the microribbons.[7] However, for Si nanoribbons, it is impossible for the existence of (110) twin plane parallel to the flat face of the nanoribbons according to crystallographic knowledge. Indeed, no twins were observed in the present nanoribbons. Therefore, the nanoribbon growth cannot be explained by the twin-plane growth mechanism. Although the precise growth mechanism of the nanoribbons is not yet clear, it is likely that the anisotropy in growth kinetics along different crystallographic directions due to the particular growth conditions is responsible for the peculiar growth reported here.

The growth conditions for achieving Si nanoribbons need to be optimized, and the growth mechanism requires further study. In particular, once the sideways growth can be controlled, it may be possible to synthesize, by this method, *2D extremely thin single-crystal Si nanosheets*. The discovery of the existence of well-ordered, defect-free, and extremely thin narrow single-crystal silicon nanoribbons described here not only extends the understanding of crystal growth in nanoscale but is also scientifically interesting and technologically promising. The proximity of atomic planes in nano dimension in nanoribbons may offer unprecedented opportunities for exploring novel devices.

Acknowledgment. This work was supported by the Research Grants Council of Hong Kong SAR (Project no. 9040637).

JA0162966

---

[5] Wang, N.; Tang, Y. H.; Zhang, Y. F.; Lee, C. S.; Lee, S. T. *Phys. Rev. B* **1998**, *58*, R16024.

[6] Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.

[7] Wagner, R. S.; Treuting, R. G. *J. Appl. Phys.* **1961,** *32*, 2490.