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Silicon–Silica Nanowires, Nanotubes, and Biaxial Nanowires: Inside, Outside, and Side-by-Side Growth of Silicon versus Silica on Zeolite

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It was demonstrated that zeolite can be used as a pseudo-template to grow very fine and uniform silicon nanostructures via disproportionation reaction of SiO by thermal evaporation. Three distinct types of composite nanowires and nanotubes of silicon and silica were grown on the surfaces of zeolite Y pellets. The first type is formed by an ultrafine crystalline silicon nanowire sheathed by an amorphous silica tube (a silicon nanowire *inside* a silica nanotube). The second type is formed by a crystalline silicon nanotube filled with amorphous silica (a silicon nanotube *outside* a silica nanowire). The third type is a biaxial silicon-silica nanowire structure with *side-by-side* growth of crystalline silicon and amorphous silica. These silicon nanostructures exhibit unusually intense photoluminescence (in comparison to ordinary silicon nanowires).

Introduction

Silicon nanowires are important because they are totally compatible with Si-based microelectronics. Since the discovery of Si whiskers,[1] silicon nanowires (SiNWs) have attracted much attention in mesoscopic research and device applications as well as in fundamental research because of their highly interesting optical and electrical properties.[2−16] Several synthetic methods, including a metal-catalyzed vapor−liquid−solid (VLS) reaction[2] and oxide-assisted growth,[3−8] have been developed to grow SiNWs of different diameters.

SiNWs in the nanosize regime exhibit quantum confinement effects and are expected to play a key role as interconnects and functional components in future nanosized electronic and optical devices.[2−22] It has been suggested that semiconductor wires finer than 100 nm in diameter can be used to develop 1D quantum wire high-speed field-effect transistors and light-emitting devices with extremely low power consumption.[23]

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The control of the diameter and uniformity of SiNWs is a crucial factor in the design and fabrication of Si-based nanoscale devices.[17−21] Generally speaking, metal-free SiNWs produced by the oxide-assisted growth method are quite uniform and have average core diameters of about 20 nm.[3−8] In a recent communication,[24] we reported a new method for the preparation of very fine and uniform SiNWs using zeolites as templates and without metal catalysts. These SiNWs have a silicon core diameter of 1−5 nm with an average of 3 nm. The preparation involved the thermal disproportionation of SiO (in the gas phase) on zeolite substrates in an attempt to use the cages or the channels of zeolites to control the size (diameter) and uniformity of SiNWs. A closer examination of the products revealed that, although we succeeded in the preparation of very fine and uniform SiNWs, we also obtained a number of new nanostructures, including the known biaxial Si−SiO_2 nanowires and a new crystalline silicon nanotube structure (hereafter designated as cSiNTs) that may also be described as silicon nanotubes with their hollow interiors filled with silica. This paper reports the synthesis of these nanomaterials and their characterization by high-resolution transmission electron microscopy (TEM).

The fact that carbon and silicon belong to the same group (group IV) may have suggested that these two elements have similar properties. In reality, the two elements are very different in terms of their chemical and physical properties. For example, whereas carbon nanotubes (CNTs) are relatively easy to make, the corresponding silicon nanotubes (SiNTs), based on rolled-up graphitelike sheets, are yet to be synthesized. Several theoretical investigations have attempted to shed light on this disparity between carbon and silicon.[25−27]

As an interesting nanostructure, silicon nanotubes may open up new and exciting possibilities for making different kinds of nanosized heterostructures by filling the inside (hollow) space with one type of nanomaterial and/or by decorating the outside surfaces of the nanotubes with yet another type of nanomaterial. Such possibilities have been well demonstrated for CNTs.[28−35] It is hoped that these new silicon−silica nanostructures, with their intrinsic structural versatilities and/or their doped variants, either collectively or in combination with other materials, will form the material base for future Si-based nanodevice fabrications.[12,13,17−23,37−39]

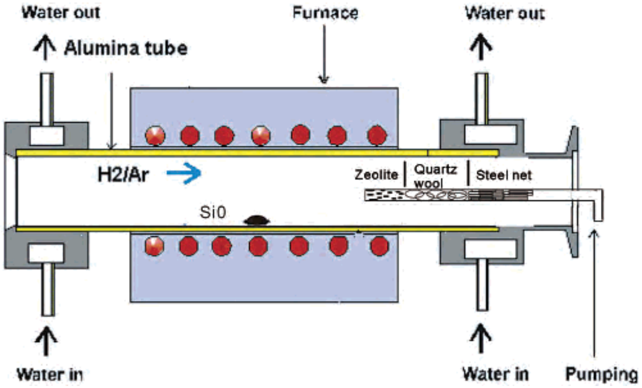

Figure 1. Schematic of the apparatus used in the synthesis.

Experimental Section

The schematic of the apparatus used in the present study is shown in Figure 1. An alumina tube (hereafter referred to as the outer tube) with an inner diameter of 5 cm was mounted inside a tube furnace. A separate alumina tube (hereafter referred to as the inner tube) with an inner diameter of 1 cm was mounted concentrically inside the outer tube. The open end of the inner tube was positioned 18 cm downstream from the center of the outer tube. The other end of the inner tube was connected to a mechanical vacuum pump.

Twenty grams of pure SiO powder (Aldrich, 325 mesh, 99.9%) was loaded onto an alumina boat and placed at the center of the outer tube. Two grams of the zeolite substrate (faujasite, zeolite Y) was packed and held in place at the open end of the inner tube by quartz wool and a steel net (Figure 1). The entire system was evacuated to a base pressure of 10^{-2} Torr (or lower) by the mechanical pump. A carrier gas consisting of 95% Ar and 5% H_2 was introduced at one end of the outer tube and maintained at a pressure of 400 Torr and a constant flow rate of 50 sccm (standard cubic cm per min). The carrier gas was forced to flow through the opening of the inner tube packed with the zeolite powder and was pumped out of the system via the mechanical pump mentioned above. The temperature of the furnace was increased gradually to 1250 °C (the SiO source temperature) and kept at this temperature for 1 h. The temperature at the opening of the inner tube was estimated to be ∼930 °C on the basis of a calibration curve. At the end of the reaction, the zeolite substrate at the opening of the inner tube, which changed from a white powder to green pellets, was collected.

The green pellets were first examined with a scanning electron microscope (SEM) (Philips XL 30 FEG), which was equipped with an energy-dispersive X-ray spectrometer (EDS). The greenish nanomaterials from the surface of the green pellets were dispersed onto holey carbon transmission electron microscopy (TEM) grids.

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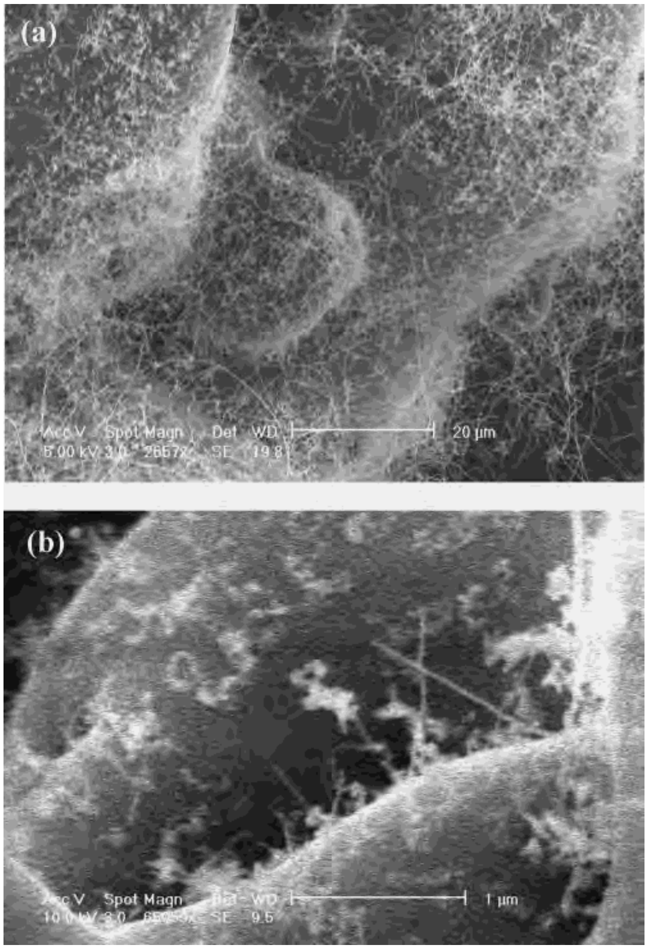

Figure 2. (a) Typical SEM image of the SiNWs. (b) Magnified image of a.

Detailed morphological and structural characterizations were carried out by using high-resolution transmission electron microscopy (HRTEM) (Philips CM200 FEG) operated at a 200-kV accelerating voltage. A micro-Raman spectrometer (Renishaw 2000) was used to characterize the photoluminescence (PL) properties of the sample at room temperature. The 514.5-nm emission from an argon ion laser was used to excite the luminescence.

Results and Discussion

The thermal disproportionation of SiO in the gas phase on the surface of the zeolite Y substrate was investigated in an attempt to use zeolites as templates to grow ultrafine silicon nanowires (SiNWs). Figure 2a is an overview of the SEM image of the SiNWs grown on zeolite Y. A large quantity of SiNWs was found on the surface of the zeolite pellet. Most of the SiNWs were anchored or attached to the surfaces of the zeolite pellets (Figure 2b). EDS results showed that SiNWs were mainly composed of Si, O, and a small amount of Al. The Al came from the zeolite and provided strong evidence for a proposed growth mechanism to be described later.

Three types of 1D nanostructures formed by crystalline silicon and amorphous silica were observed. These nanostructures may be described as three distinct classes of composite nanowires and nanotubes of silicon and silica depicted schematically in Scheme 1. The first type, portrayed in Figure 3, is formed by a crystalline silicon nanowire sheathed by an amorphous silica tube. This is the major product of the reaction. Although this nanostructure is commonly known as a silicon nanowire, it may also be considered to be “a silicon nanowire *inside* a silica nanotube”, which may be designated as $Si \subset SiO_2$ and represented schematically as **1** in Scheme 1. We note that silica nanotubes embedded with silicon nanocrystals have recently been reported by Wang et al.,[36] though their morphologies are very different.

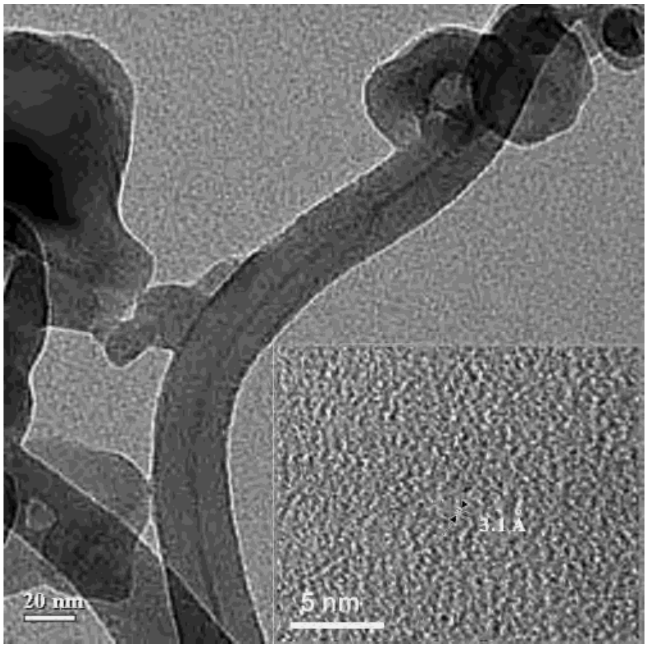

Figure 3. TEM image of a typical single SiNW with a Si core diameter of 3 nm covered with a SiO_2 layer of 28 nm. The inset is the HRTEM image of the same SiNW.

Scheme 1. Three Distinct Types of Composite Nanowires and Nanotubes of Silicon and Silica

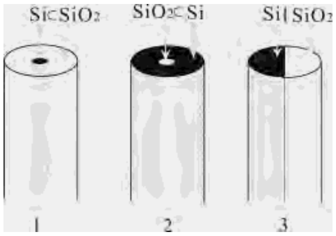

Figure 3 shows the TEM image (inset: HRTEM) of a typical SiNW (**1**). It can be seen that each SiNW has a very fine crystalline silicon core and a thick outer layer of amorphous silicon dioxide. The diameters of the Si cores range from 1 to 5 nm, with an average of 3 nm. These Si cores are very fine and uniform in diameter over the entire length (micrometers) of each wire. The diameter of the amorphous SiO_2 layer of the SiNWs ranges from 20 to 40 nm and is also quite uniform over the entire length of the wires. Many of the finest SiNWs observed in our samples had a central Si core 1.2 nm in diameter and a relatively thick SiO_2 outer layer 20 nm in diameter. Assuming a Si–Si bond length of 0.235 nm, this fine nanowire 1.2 nm in diameter contains only about six silicon atoms across the short dimension. To the best of our knowledge, this is the

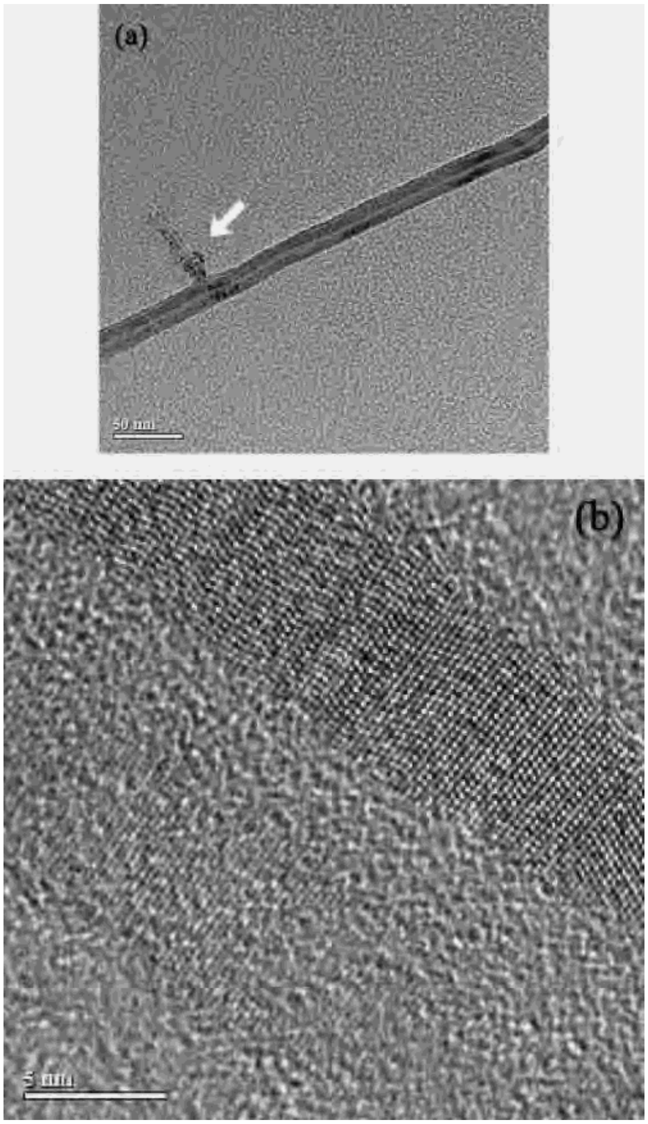

Figure 4. (a) TEM of a crystalline silicon nanotube. (b) Corresponding HRTEM image.

finest SiNW synthesized in bulk quantities to date. The HRTEM image (inset of Figure 3) of the same SiNW confirms that the core is crystalline silicon with 3.1-Å *d* spacing. The SiO_2 layer has a thickness of 12 nm on both sides of the central SiNW. The overall diameter of the nanowire is 25 nm.

The second type of nanostructure can be described as a crystalline silicon nanotube filled with amorphous silica. Typical TEM images are shown in Figure 4. Morphologically, this is a cable that may also be considered to be "a silica nanowire *inside* a silicon nanotube" and designated as $SiO_2 \subset Si$, which is represented schematically as **2** in Scheme 1. Equivalently, it can also be described as "a silicon nanotube *outside* a silica nanowire" or $Si \supset SiO_2$. Although this morphology represents a new silicon nanotube structure, it is different from the conventional rolled-up graphite-like sheet structures epitomized by the carbon nanotubes (CNTs). In this context, it is best described as a hollow crystalline silicon nanowire or nanorod. We prefer to label this type of silicon nanostructure as crystalline silicon nanotubes (cSiNTs). The particular cSiNT portrayed in Figure 4 has an inner diameter of 3 nm and an outer diameter of 15 nm. The crystalline silicon walls have a thickness of about 6 nm on each side. The crystal lattices on the two sides of the tube are almost parallel (within 10° in most cases). Independent work by Sha et al.[40] produced a somewhat different cSiNT structure, with the tube wall being made of polycrystalline silicon interlaced with amorphous silicon. These latter cSiNTs were prepared by chemical vapor deposition using a nanochannel Al_2O_3 substrate as a template (the channels were presputtered with gold, which served as a catalyst) and were believed to be hollow. The distinctive features of our cSiNTs are (1) single-crystalline tube walls, (2) uniform inner and outer tube diameters over the length of the wire, and (3) silica-filled tubes. Of particular importance is that we found no amorphous silicon within the tube walls. Furthermore, our method is simpler and requires no catalysts.

The third type of nanostructure is the biaxial silicon−silica nanowire structure with the side-by-side growth of silicon and silica, which may be designated as $Si|SiO_2$ and represented schematically as **3** in Scheme 1. One typical example is portrayed in Figure 5. This particular biaxial nanowire has an overall diameter of 10 nm with half of the wire (5 nm) being crystalline silicon and the other half (5 nm) being amorphous silica. Although this particular biaxial nanowire has a round-headed crystalline silicon tip, the majority of all three types of nanowires have flat-headed ends. The biaxial $Si|SiO_2$ nanowires also come in different sizes and shapes. One example is the T-shaped biaxial nanowire structure depicted in Figure 6.

A particularly interesting phenomenon was observed during the TEM examination of these nanostructures of silicon. As illustrated in Figures 4a and 5a, there were localized "explosions" of gaseous materials breaking through the walls of the nanotubes (Figure 4a) or nanowires (Figure 5a) (indicated by the arrows). These explosions can be likened to volcanic eruptions. They are believed to be caused by either the local heating or the production of gaseous materials as a result of intense electron irradiation during the TEM observation. In the latter case, it is possible that the reduction of silicon dioxide by the electron beam may have produced gaseous materials that cause the pressure within the walls to build up, leading to the eventual outbreak through the weak points in the walls.

It should be mentioned that we found very few, if any, of the so-called chainlike Si nanostrucures, often observed in the oxide-assisted growth of SiNWs.[7] The difference may be attributed to the use of zeolite as a quasi-template in our work. Furthermore, the major product (>90%) is the first type of nanostructure (ultrafine SiNWs), though the relative yields of the three types may vary with the experimental conditions. Also observed were very small numbers of crystalline ellipsoidal and cubic silicon nanodots (SiNDs, not shown) 2−4 nm in size as well as nearly perfect spherical

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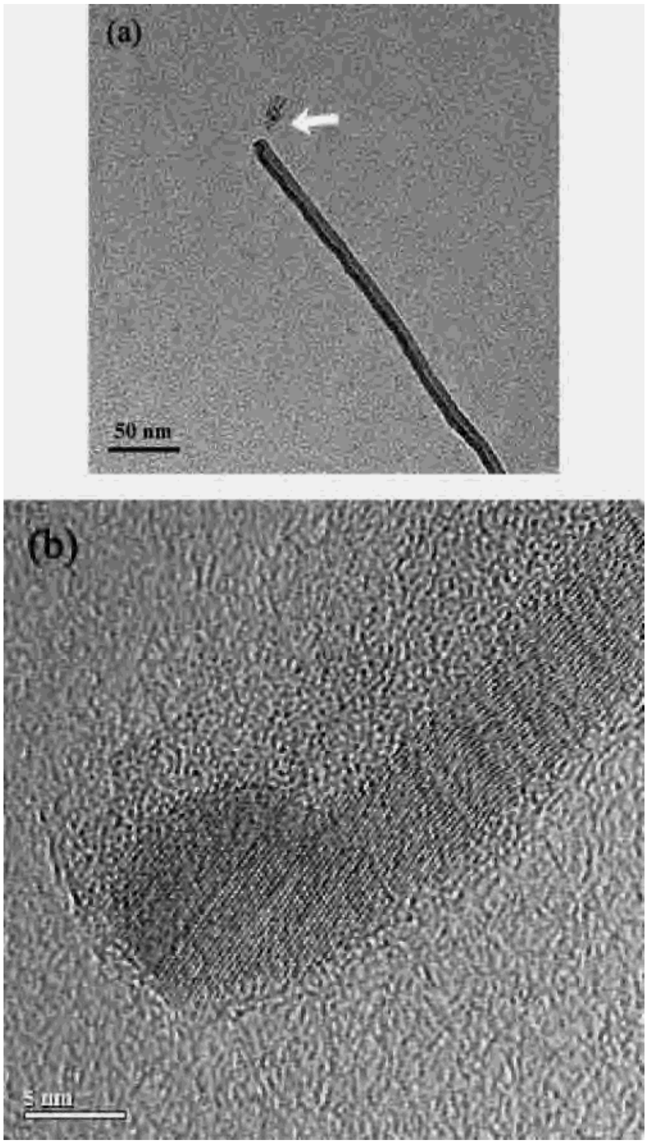

Figure 5. (a) TEM of a biaxial Si|SiO_2 nanowire. (b) Corresponding HRTEM image.

silica (not shown) measuring ~15 nm in diameter. These SiNDs may be precursors to the 1D silicon nanostructures.

Figure 7 shows a proposed mechanism for the formation of these nanostructures, illustrated here for the ultrafine and uniform SiNWs (**1**, $Si \subset SiO_2$) in a way similar to that of the previously described oxide-assisted growth mechanism.[11] The SiO powders were first sublimated at 1250 °C, forming nanoclusters in the vapor phase. In the present experiment, the zeolites were positioned downstream from the SiO starting material where the temperature was about 930 °C. The SiO nanoclusters in the vapor were subsequently deposited on the surfaces of zeolites, and some diffused into the channels or cages of the zeolites as shown schematically in Figure 7a. In this temperature regime, SiO nanoclusters disproportionated to form Si and SiO_2, resulting in the precipitation of silicon nanoparticles surrounded by silica. The silicon nanoparticles served as the nuclei for the subsequent growth of Si nanowires. In the channels or cavities of zeolites, however, the nucleation process was limited by the openings of the channels or the sizes of the cavities, and a large supply of SiO_2 from the zeolite retarded the disproportionation of SiO. In the case of zeolite Y, the 12-ring windows measure 0.74 nm in diameter, and the supercages have a free space of 1.18 nm (inscribed sphere diameter). Therefore, the crystalline silicon core of SiNWs was limited to 1−3 nm in diameter at the nucleation stage, and the zeolite supplied additional silicon oxide to form the silica shell of the SiNW, resulting in an oxide layer much thicker than that in normal SiNWs, as depicted in Figure 7b. The finding of Al in SiNWs provides strong evidence that the oxide layer of SiNWs comes partially from the zeolite. Because the silicon oxide outer layer plays a key role in the growth process of SiNWs, the thick oxide layer limited the lateral growth of the Si nucleation core. At this point, the oxide-assisted growth process became operative, with the oxide being primarily supplied in situ by the zeolites. The increased SiO_2 local concentration (from the zeolite) at the $Si-SiO_2$ interface again limits the growth of the wires to larger diameter. The net result is a very fine (1−5 nm diameter) and uniform SiNW sheathed by a thick (20−40 nm diameter) and uniform oxide layer. Each SiNW has a "root" in the zeolite, as shown in Figure 7c. This growth

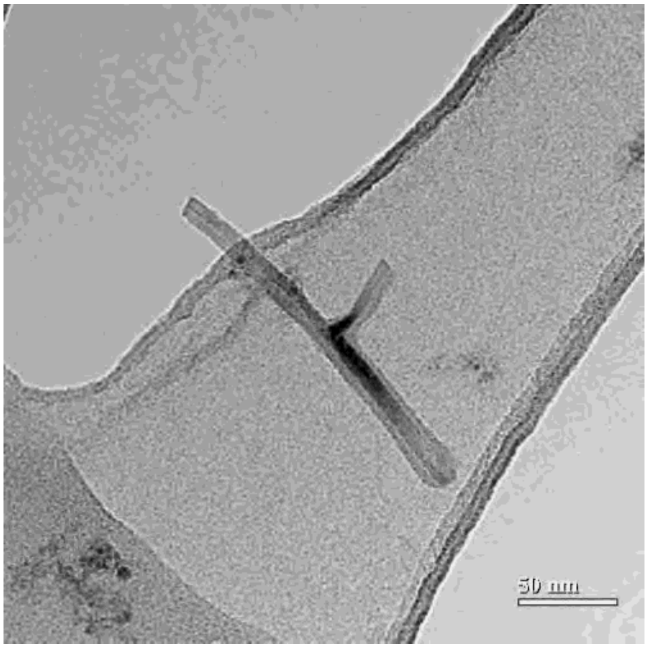

Figure 6. TEM image of a T-shaped biaxial nanowire.

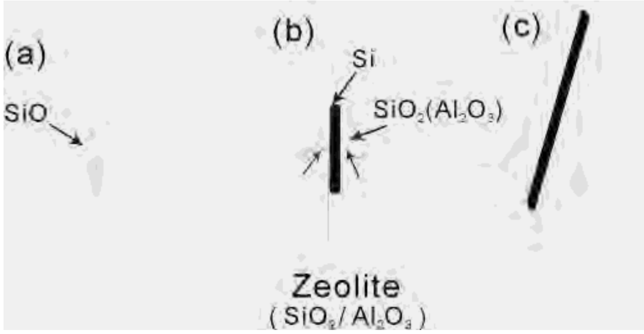

Figure 7. Proposed growth mechanism for the very fine and uniform SiNWs on zeolite surfaces.

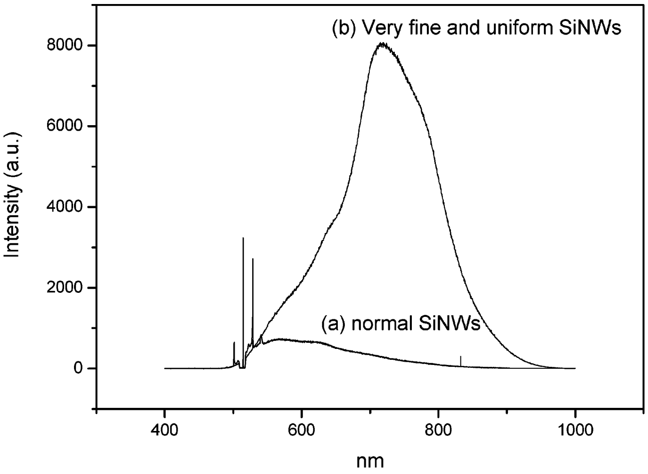

Figure 8. Photoluminescence spectra from (a) normal SiNWs 20−50 nm in diameter and (b) very fine and uniform SiNWs 1−5 nm in diameter synthesized with zeolite Y.

process is consistent with the SEM results (Figure 2b) showing that the SiNWs were attached to the surface of the zeolites. (We should note that we cannot rule out the possibility of the coalescence of adjacent SiNWs during the nucleation stage or in the early stages of growth. Indeed, the fact that the observed SiNWs (average 3 nm) are, in general, wider than the channels (0.74 nm) or cavities (1.18 nm) of zeolite Y used in this experiment may be taken as an indication that such a secondary mechanism is operative.)

The mechanisms for the growth of the other types of nanostructures may be similar to that proposed in Figure 7 for SiNWs (**1**, $Si \subset SiO_2$). In the case of the cSiNTs (**2**, $SiO_2 \subset Si$) shown in Figure 4, the coalescence of SiNWs around a central nanowire of silica may have resulted in the formation of a crystalline silicon nanotube with a silica core of 3-nm inner diameter. The crystalline silicon walls have a thickness of 6 nm on each side, giving rise to an outer diameter of 15 nm. As in the case of the formation of the SiNWs (**1**), such a coalescence process, either during the nucleation step or in the early stages of the growth of cSiNTs (**2**), is made possible by the dimensions of the unit cell of zeolite Y (cubic crystal system, $a = 2.467$ nm), which are comparable to the lateral dimensions of the cSiNTs. A similar argument applies to the formation of the biaxial silicon/silica nanowires, $Si|SiO_2$ (**3**), depicted in Figure 5.

The photoluminescence (PL) of these very fine SiNWs was measured at room temperature. Very weak PL intensity was obtained from the normal SiNW sample 20−50 nm in diameter (Figure 8, curve a). The PL peak is centered at around 600 nm. However, the very fine SiNW samples reported in this paper exhibited very intense (at least 1 order of magnitude higher) luminescence in the PL measurement (Figure 8, curve b). The PL peak is centered around 720 nm. The strong PL intensity probably arises from the quantum size effect of the ultrafine Si core (<5 nm in diameter)[22] in conjunction with impurity or interface states.[41]

In summary, we have demonstrated that zeolites can be used as a pseudotemplate/precursor to grow ultrafine and uniform silicon nanostructures via the disproportionation reaction of SiO by thermal evaporation. Three distinct types of composite nanowires and nanotubes of silicon and silica were synthesized. The first type is formed by a crystalline silicon nanowire sheathed by an amorphous silica tube (silicon nanowire inside a silica nanotube). The second type is formed by a crystalline silicon nanotube filled with amorphous silica (silica nanowire inside a silicon nanotube). The third type is the biaxial silicon−silica nanowire structure with the side-by-side growth of silicon and silica. Although the first type of nanostructure is the major product, work is in progress to shed light on the factors (e.g., temperature, pressure, carrier gas, zeolite type, etc.) that affect the formation of these three types of products with the hope of controlling their relative yields.

Further work is planned to fabricate heterostructures involving silicon by filling the hollow space of the silicon nanotubes with one material and/or coating or decorating the outside surface with yet another material to produce integrated nanodevices. Such strategies are particularly important in view of the fact that these silicon nanostructures exhibit unusually strong photoluminescence in comparison with that of the conventional SiNWs. It is hoped that the combination of SiNWs, cSiNTs, and biaxial $Si|SiO_2$ nanowires, along with dopants and other surface modifications, will build the materials foundation for future Si-based nanodevices.[12,13,17−23,37−39]

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(41) In a separate experiment, we measured the photoluminescence (PL) of Al-doped (5−10%) as-prepared SiNWs 20 nm in diameter (silicon core) and observed no significant enhancement in PL over that of the corresponding undoped SiNWs. EDX of SiNW samples prepared with zeolite Y as quasi-template (this work) gave atomic ratios of Al/Si in the range of 4−10%. This suggests that the order-of-magnitude enhancement in the PL of the latter samples may not arise primarily from the Al ions in the silicon oxide layer of SiNWs prepared with zeolites. We caution, however, that such an indirect test experiment cannot completely rule out the effect of Al. Note also that the Al/Si ratio in zeolite Y is 1:2.25.