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# Novel nanostructures: hole-patterned nanowires and nanotubes of silicon oxide

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## Abstract

Novel nanowires patterned with holes and nanotubes of silicon oxide have been fabricated on silicon substrates by a catalyst-assisted route. The diameters of these nanowires and nanotubes vary from 20 to 100 nm. The patterned nanowires have encapsulated holes along the longitudinal direction. High-resolution transmission electron microscopy reveals that the patterned nanowires and nanotubes are amorphous. The growth of the nanostructures is probably controlled by a modified vapour–liquid–solid process.

## 1. Introduction

In the past decade, nanoscale one-dimensional (1D) materials, such as nanotubes, nanowires, and nanorods, have attracted great interest in both scientific and technological areas of research [1–3], as they offer the opportunity to investigate the effect of dimensionality and size on a material's physical properties as well as potential applications in developing nanotechnologies. Many technologies have been developed to synthesize 1D nanostructures, such as catalytic vapour growth [4], solution growth [5], and template based design techniques [6]. The one-dimensional structures have been achieved in a wide range of materials, including metals [7, 8], semiconductors [9, 10], and oxides [11, 12]. But most of these 1D structures are solid inside, i.e., so-called nanowires. Although some materials have been fabricated in the form of nanotubes [13, 14], synthesizing hollow 1D structures in many materials is still a great challenge. Moreover, for manufacturing future electronic devices based on 1D nanostructures, compositional and structural modulation in a single 1D structure is necessary. It has been demonstrated that one-dimensional heterostructures and related devices can be achieved in the laboratory [15].

As a good candidate photoluminescence material, silicon oxide has attracted much attention. Amorphous SiO<sub>x</sub> nanowires have been synthesized by several methods, including

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thermal oxidation [16], laser ablation [17], and chemical vapour deposition [18]. Blue light emission from amorphous  $\text{SiO}_x$  nanowires has also been observed [19]. In this work, we report the synthesis of some unique 1D structures of silicon oxide, which are nanowires with penetrating holes along their axial directions, i.e., so-called hole-patterned nanowires, and nanotubes. To our knowledge, such 1D structures of silicon oxide have been not reported before. These interesting nanostructures of silicon oxide were grown on silicon wafers by heating  $\text{Ni}(\text{NO}_3)_2$  particles distributed on the surface of silicon wafers in an ammonia atmosphere. A modified vapour–liquid–solid (VLS) process was employed to grow the nanostructures. The distinguishing feature of the present method compared with the conventional VLS methods lies in one of the reactants (Si) coming from the solid substrate. It is believed that the present study may provide a new approach to fabricating composite or structure-modulated 1D nanostructures of other materials.

## 2. Experimental details

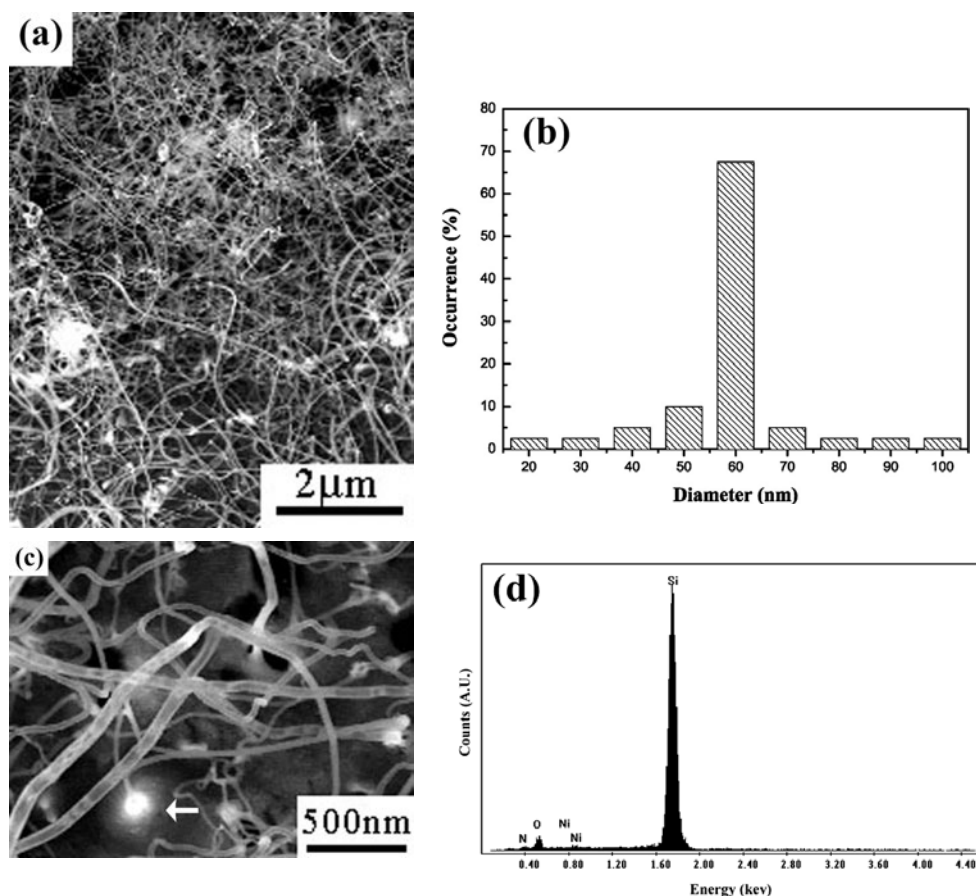
The synthesis of the product was carried out in a high-temperature tube furnace. First, a single-crystal intrinsic silicon wafer  $10\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$  in size was dipped in  $\text{Ni}(\text{NO}_3)_2$  ethanol solution with a concentration of about 0.1 M and dried in air. Then, the treated silicon wafer was placed into a long quartz tube which was inserted horizontally in the furnace. After the quartz tube had been evacuated to a base pressure of about 10 Pa by a mechanical rotary pump, an argon flow of 30 sccm was introduced. When the furnace was heated to  $1000\text{ }^\circ\text{C}$  at a rate of  $15\text{ }^\circ\text{C min}^{-1}$ , the argon flow was switched off, and a steady ammonia flow of 30 sccm was started and maintained for 4 h at this temperature. After the furnace had been naturally cooled down to room temperature in an argon atmosphere, the surface of the silicon wafer became grey and rough.

The morphology and the chemical composition of the products were characterized by a scanning electron microscope (SEM, Philips XL 30 FEG) with an energy-dispersive x-ray fluorescence (EDX) spectroscope attached. The microstructure was studied with a transmission electron microscope (TEM, Philips CM200 at 200 kV).

## 3. Results and discussion

A general overview of the morphology of the as-synthesized product was provided by an SEM image shown in figure 1(a). This indicates that the product mainly consists of a high density of wire-like structures. Those wires have lengths of up to tens of micrometres and diameters ranging from 20 to 100 nm, while a large part of them ( $\sim 70\%$ ) have diameters of about 60 nm. The diameter distribution of the wires obtained by SEM observation is shown in figure 1(b). The height and width of a histogram line represent the occurrence and measuring error for wires with the same diameter. Most of the wires have smooth surfaces and uniform diameters along their axial directions, although they are curved.

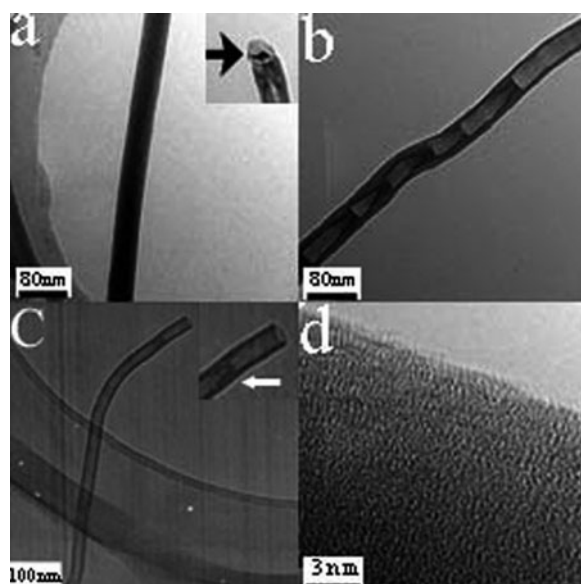
An SEM image with higher magnification is shown in figure 1(c), to reveal more clearly the morphologies of the wires. Besides the common solid nanowires, some unique nanowires with some holes encapsulated along their axial directions can be found. We call them hole-patterned nanowires. Such structures are found randomly in different regions of the substrate and amount to about 40% of all wires. Furthermore, small amounts of tube-like nanostructures (about 5%) were also found. As indicated by the arrow in figure 1(c), all wires have particles on their bottom ends and most of those particles adhere to the silicon surface. It seems that those wires grow from the substrate. A typical EDX spectrum (figure 1(d)) confirms that the



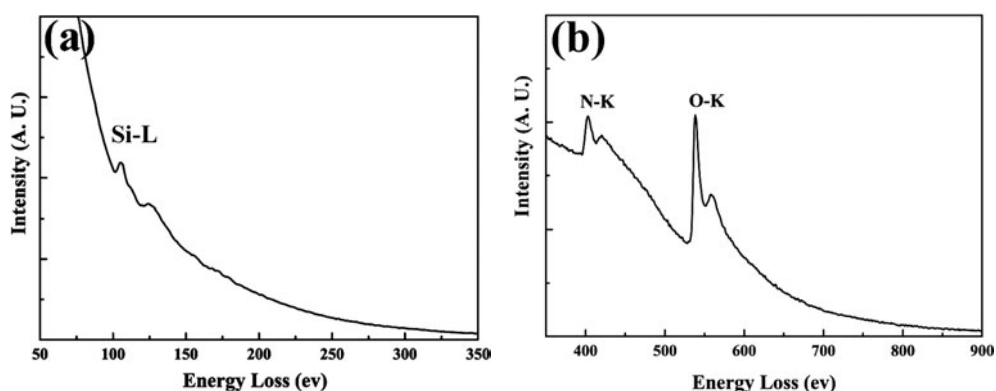
**Figure 1.** (a) A typical SEM image of the synthesized product with low magnification. (b) A histogram of the nanowire diameter distribution. (c) An SEM image of the product with a higher magnification. (d) A typical EDX spectrum identifying the composition of the product.

compositions of the wires include Si, O, N, and Ni. In this spectrum, the scattering intensity of Si becomes very strong due to the Si substrate and the weak signal of Ni should be arising from catalysts used in the synthesis. So, the wires mainly consist of Si, O, and N. The atomic ratio of O to N is about 1.5.

The morphology and microstructure of the product were further characterized by TEM. Figure 2(a) is a TEM image of a solid nanowire with a smooth surface and a diameter of about 50 nm. The inset of figure 2(a) shows a particle (indicated by an arrow) with an irregular shape attached to one end of a nanowire, implying that the VLS process may control the growth of the nanowires. A representative TEM image is shown in figure 2(b), revealing the unique morphology of hole-patterned nanowires. There are taper-like holes encapsulated in the wire along the axial direction and the sizes of the holes are different. Figure 2(c) exhibits a typical tubular morphology. The diameter and wall thickness of the nanotube are about 30 and 5 nm, respectively. The end of the nanotube is enlarged in the inset of figure 2(c). It can be seen that the nanotube has a smooth circular cross section and is open. It is worth noticing that the inner wall of the nanotube is rough (the white arrow in the inset of figure 2(c)). The high-resolution transmission electron microscopy (HRTEM) image (figure 2(d)) of a nanowire



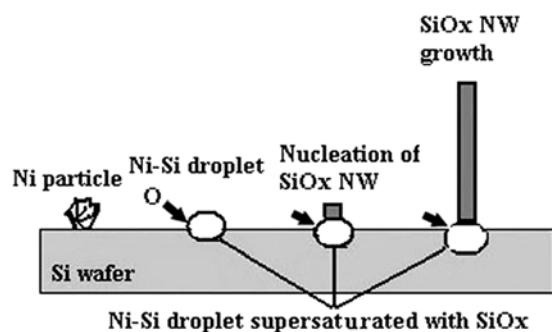
**Figure 2.** (a) A TEM image of a nanowire. Inset: a TEM image showing a particle on one end of a nanowire. (b) A TEM image of a hole-patterned nanowire. (c) A nanotube. Inset: an enlarged TEM image of the end of the tube. (d) An HRTEM image of one nanowire.



**Figure 3.** EELS spectra of a hole-patterned nanowire: (a) showing L-edge absorption for Si; (b) revealing K-edge absorption for N and O.

reveals its amorphous nature. Further observations reveal that the hole-patterned nanowires and nanotubes are both amorphous. Electron energy loss spectroscopy (EELS) was employed to identify the compositions of single nanostructures. Figures 3(a) and (b) show EELS spectra taken from the body of a hole-patterned nanowire; they reveal L-edge absorption for Si and K-edge absorption for N and O, respectively. The EELS results show that the solid nanowires, hole-patterned nanowires, and nanotubes have similar compositions, including Si, O, and N. The catalyst, Ni, cannot be detected in the bodies of those nanostructures. On the basis of the above investigations, we think that these 1D structures are of amorphous  $\text{SiO}_x$  doped with nitrogen.

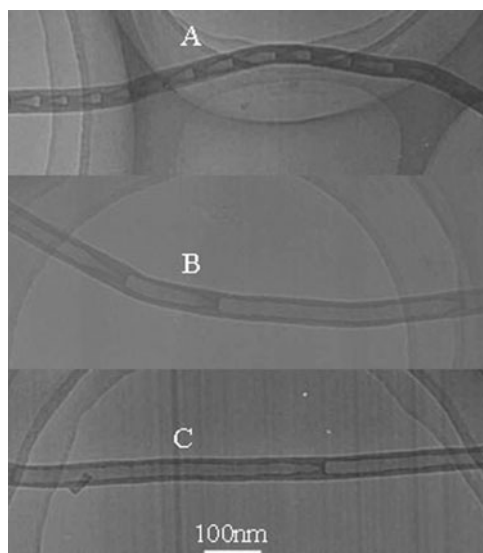
On the basis of the SEM and TEM observations, it is reasonable to think that the 1D nanostructures synthesized here undergo a VLS process. But, comparing with the conventional



**Figure 4.** A schematic illustration of the growth process for  $\text{SiO}_x$  nanowire grown on a Si wafer.

VLS mechanism, there are some distinct differences in our case. In usual VLS processes—for example, the growth of Si nanowires by Au-nanoparticle-assisted CVD [20]—the sources for the growth of the 1D structures are from the vapour phase, and pass through a liquid phase before finally forming solid nanowires or nanotubes. Here, one component in the final products, i.e., Si, comes from the Si substrate. It is known that  $\text{Ni}(\text{NO}_3)_2$  will decompose to NiO,  $\text{NO}_2$ , and  $\text{O}_2$  at high temperature [21]. Meanwhile,  $\text{NH}_3$  will partly decompose to  $\text{N}_2$  and  $\text{H}_2$  [22]. So, NiO should be further reduced to Ni by  $\text{H}_2$ . It functions as a catalyst in the synthesis. As for the oxygen source for the growth of the product, we think that the decomposition of  $\text{Ni}(\text{NO}_3)_2$  partly provides for it. The residual air in the system (about 10 Pa) is another possible oxygen source. According to the Ni–Si phase diagram [23], Ni and Si can form a perfectly mixed droplet over a broad composition range at  $1000^\circ\text{C}$ . The liquid Ni–Si droplet absorbs oxygen atoms and then forms  $\text{SiO}_x$  species. Upon the  $\text{SiO}_x$  becoming supersaturated in concentration in the Ni–Si melt, it is precipitated to gradually grow into  $\text{SiO}_x$  nanowires. The dissolving and diffusion of Si from the substrate to the Ni–Si melt continues due to the formation of  $\text{SiO}_x$  clusters, which sustains persistent growth of nanowires. The overall evolution of the growth process is illustrated schematically in figure 4. As mentioned above, SEM images reveal that many nanowires root on the Si wafer and TEM images show that there are particles adhering to those nanowires. Meanwhile, we also notice that there are some pits under the roots of nanowires. Hence, the growth mechanism presented here is consistent with all the experimental data shown above. Moreover, we heated the Si wafer without treating it with  $\text{Ni}(\text{NO}_3)_2$  solution under the same conditions, and found that there were no nanostructures formed. This demonstrates that the catalyst  $\text{Ni}(\text{NO}_3)_2$  is a key to our synthesis. Nitrogen atoms were introduced into the product as a dopant, due to the decomposition of  $\text{NH}_3$ . This is in agreement with the results of EDX and EELS studies, showing that N exists in these nanostructures.

Three hole-patterned nanowires (labelled A, B, and C) are shown in figure 5; these may give a clue as regards the question of the formation of the hole-patterned nanowires and nanotubes. It is clearly seen that many small tapering holes with similar size are regularly encapsulated in A, while the holes in B become fewer and bigger. In C, a nanotube seems to have developed. On the basis of the image, we speculate that the nanotubes and hole-patterned nanowires in our product probably evolve from solid nanowires. It is known that the suboxide of silicon is unstable at elevated temperature [24]. In our system, the partial pressure of oxygen is low due to there being no oxygen intentionally introduced. When the  $\text{SiO}_x$  nanowires grow from a Ni–Si melt (as discussed above), their surfaces may be further oxidized and become stable, while the centre parts of the nanowires cannot be further oxidized due to the insufficient supply



**Figure 5.** TEM images of three hole-patterned nanowires. The figure contains three independent images.

of oxygen. In addition, hydrogen present in the system from the decomposition of  $\text{NH}_3$  can retard  $\text{SiO}_x$  oxidization into crystalline  $\text{SiO}_2$ . Thus, sublimation of the unstable parts in the centres of the nanowires results in the formation of hole-patterned nanowires and nanotubes. Hence slow oxidation would be favourable for the formation of hole-patterned nanowires and nanotubes of  $\text{SiO}_x$ . When the synthesis was carried out under an Ar or  $\text{O}_2$  atmosphere, no novel morphologies were found—just the common solid nanowires. This indicates that ammonia (or hydrogen) plays an important role in the formation of hole-patterned nanowires and nanotubes. However, why do some nanowires evolve into tube-like structures, but not others? To fully understand this, more detailed and systematic studies are required.

#### 4. Conclusions

In summary, a novel 1D morphology, so-called hole-patterned nanowires, and nanotubes of  $\text{SiO}_x$  have been synthesized on silicon wafers by a catalyst-assisted route. The diameters of the nanowires and nanotubes range from 20 to 100 nm. The growth of the nanostructures is probably controlled by a modified VLS mechanism. The approach presented here may be extended to fabricate other composite 1D structures for potential applications based on their novel morphologies and structures.

#### Acknowledgments

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#### References

- [1] Iijima S 1991 *Nature* **354** 56
- [2] Dekker C 1999 *Phys. Today* **52** 22
- [3] Wu Y Y, Benjamin M and Yang P D 2001 *Adv. Mater.* **13** 1487



- [4] Chen X L, Li J Y, Cao Y G, Lan Y C, Li H, He M, Wang C Y, Zhang Z and Qiao Z Y 2000 *Adv. Mater.* **12** 1432
- [5] Justin D H, Keith P J, Doty R C and Korgel B A 2000 *Science* **287** 1471
- [6] Cheng G S, Zhang L D, Zhu Y, Fei G T, Li L, Mo C M and Mao Y Q 1999 *Appl. Phys. Lett.* **75** 2455
- [7] Sun Y G and Xia Y N 2002 *Adv. Mater.* **14** 833
- [8] Li J L, Liang X J, Jia J F, Liu X, Wang J Z, Wang E G and Xue Q K 2001 *Appl. Phys. Lett.* **79** 2826
- [9] Wang N, Tang Y H, Zhang Y F, Lee C S and Lee S T 1998 *Phys. Rev. B* **58** 16024
- [10] Liang C H, Chen L C, Huang J S, Chen K H, Huang Y T and Chen Y F 2002 *Appl. Phys. Lett.* **81** 22
- [11] Jian J K, Chen X L, Wang W J, Dai L and Xu Y P 2002 *Appl. Phys. A* **75** 695
- [12] Li J Y, Chen X L, Qiao Z Y, He M and Li H 2001 *J. Phys.: Condens. Matter* **13** 737
- [13] Ma R Z, Bando Y S and Sato T 2002 *Adv. Mater.* **14** 366
- [14] Du G H, Chen Q, Che R C, Yuan Z Y and Peng L M 2001 *Appl. Phys. Lett.* **79** 3702
- [15] Cui Y and Lieber C M 2001 *Science* **291** 851
- [16] Dai L, Chen X L, Jian J K, Wang W J, Zhou T and Hu B Q 2002 *Appl. Phys. A* **76** 1
- [17] Yu D P, Hung Q L, Ding Y, Zhang H Z, Bai Z G, Wang J J, Zhou Y H, Qian W, Xiong G C and Feng S Q 1998 *Appl. Phys. Lett.* **73** 3076
- [18] Zhu X C, Song W H, Wang K Y, Hu T, Zhao B, Sun Y P and Du J J 2001 *Chem. Phys. Lett.* **336** 53
- [19] Wang Y W, Liang C H, Meng G W, Peng X S and Zhang L D 2002 *J. Mater. Chem.* **12** 651
- [20] Cui Y, Lauhon L J, Gudiksen M S, Wang J F and Lieber C M 2001 *Appl. Phys. Lett.* **78** 2214
- [21] Lide D R 1997 *CRC Handbook of Chemistry and Physics* 78th edn (Cleveland, OH: CRC Press)
- [22] He M, Minus I, Zhou P, Mohammed S N, Halpern J B, Jacobs R, Sarney W L, Salamanca-Riba L and Vispute R D 2000 *Appl. Phys. Lett.* **77** 3731
- [23] Massalski T B, Okamoto H, Subramanian P R and Kacprozak L 1992 *Binary Alloy Phase Diagrams* 2nd edn (Materials Park, OH: ASM International) p 2859
- [24] Wang N, Tang Y H, Zhang Y F, Lee C S, Bello I and Lee S T 1999 *Chem. Phys. Lett.* **299** 237