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H_2-Assistance One-Step Growth of Si Nanowires and Their Growth Mechanism *

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Large-scale nanowires are grown on Si wafers by the catalyst-free one-step thermal reaction method in Ar/H_2 mixture atmosphere at 1000 °C. The x-ray diffraction and energy dispersive x-ray spectroscopy results reveal that the final nanowires are of silicon nanostructures. The field emission scanning electron microscopy shows that these self-organized Si nanowires (SiNWs) possess curly crowns with diameters varying from 10 to 300 nm and lengths of up to several hundreds of micrometers. The transmission electron microscopy indicates that the nanowires are pure Si with amorphous structures. All the measurement results show that no silicon oxide is generated in our products. The growth mechanism is proposed tentatively. Silicon oxide is reduced into Si nanoparticles under the Ar/H_2 mixture, which is the main reason for the formation of such SiNWs. Our experiments offer a method of preparing Si nanostructures by simply reducing silicon oxide at high temperature.

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Silicon nanowires (SiNWs) have higher carrier mobility, a larger surface-to-volume ratio and a longer minority carrier diffusion length than single-crystal bulk silicon materials and can bear large stress without pulverization, which make them suitable for fabricating high-performance nanoelectronic and nanophotonic devices.[12] Since SiNW-related nanodevices are compatible with the current Si-based microelectronics manufacturing process, many new nanodevices, such as field effect transistors (FET), solar cells, sensors, lithium battery and thermoelectric conversion devices, have been made in SiNWs.[2−7] To develop such nanodevices, SiNWs have been synthesized by using methods such as laser ablation,[8] chemical vapor deposition (CVD),[9−13] thermal evaporation,[14,15] solution synthetic method[16−18] and electroless etching method.[19] However, during the growth process of SiNWs, metal nanoparticles, especially gold, are generally used as the catalyst to direct the growth of SiNWs leading to the coexistence of gold nanoparticles and the SiNWs. These gold nanoparticles can induce deep levels in SiNWs and become trap canters, which could degrade the optical and electronic properties of such SiNW-based nanodevices. Moreover, most SiNWs are often surrounded by amorphous silicon oxide shells, which seriously influence the nanodevice applications. For example, the decrease of chemical sensitivity of SiNWs to the NH_3 gas and water vapor by the silicon oxide sheath has been reported by Zhou *et al.*[20] Therefore, the fabrication of high-quality SiNWs without an amorphous silicon oxide sheath and metal contaminations is the key issue to enhance the performance of nanodevices based on SiNWs. In addition, various materials, including Si powder, $SiCl_4$, SiH_4, SiO powder and diphenylsilane, have been used as the growth source to synthesize SiNWs. Few reports have concerned the preparation of SiNWs by Si wafers except that they are grown by chemical etching and laser ablation methods.[8] However, in Ref. [8], no SiNWs could be obtained when the laser target was fabricated by pure SiO_2. In this work, SiNWs with curly crowns are grown on Si wafers by simply heating Si wafers in the H_2/Ar mixture ambient. Our experiments show that Si oxide deposited on the surface of the Si wafers is the main reason for forming such SiNWs and a new mechanism will be proposed to explain its growth process.

SiNWs were synthesized by heating Si wafers without a catalyst. Before growth, the Si wafers were cleaned in an ultrasonic bath with acetone for 20 min, then rinsed with de-ionized water and dried under flowing nitrogen. Four pieces of Si (100) wafers were loaded onto a ceramic boat placed in the center of an alumina tube inside a horizontal tube furnace. After the reactor was purged with argon several times to remove residual oxygen and moisture, the system was elevated at a rate of 20℃/min under argon atmosphere. Once the temperature reached 1000℃, hydrogen was subsequently introduced into the chamber with a H_2/Ar volume ratio of 4:96 at a flux of 80 sccm. The working pressure of the alumina tube was maintained at normal pressure and the reaction proceeded

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for 2 h and then the furnace was cooled down slowly to room temperature in the argon atmosphere. White products were found deposited on the surface of the wafers.

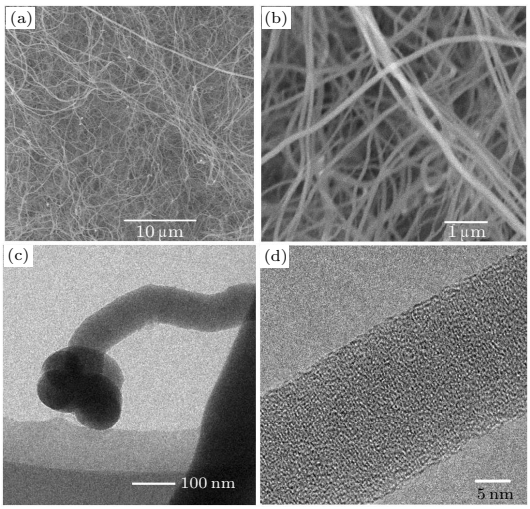


Fig. 1. SEM and TEM images of silicon nanowires: (a) low-magnification SEM (top view), (b) high-magnification SEM image, (c) low-resolution TEM image of one silicon nanowire with curly crown, (d) high-resolution TEM image of a single silicon nanowire.

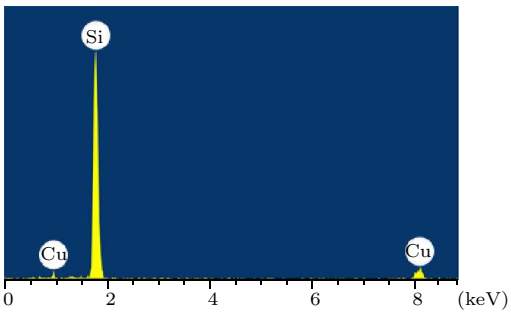


Fig. 2. (Colour online) EDX analysis of a single silicon nanowire.

The structure and morphology of the synthesized products were characterized by x-ray diffraction (XRD) with a Cu K_α radiation source (λ = 0.1542 nm), field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The composition was analyzed by energy dispersive x-ray spectroscopy (EDX), which is attached to the TEM system. All tests were performed at room temperature.

The FE-SEM and TEM images of the products shown in Fig. 1 reveal that the as-grown Si nanostructures possess a wire-like morphology with a curly crown. Figure 1(a) shows the low magnification top view of the sample, where a large number of SiNWs are observed. From the enlarged view of this sample (shown in Fig. 1(b)), we can see that diameters of the SiNWs exhibit wide distributions, which range from 10 to 300 nm, whereas most of the nanowires have diameters of 100–200 nm and the lengths are in the range of 200–500 μm. Figure 1(c) is a low-resolution TEM image of a single nanowire, where the curly crown located on the top of a nanowire is clearly exhibited. Figure 1(d) shows the high-resolution transmission electron microscopy (HRTEM) of a single Si nanowire, butm unfortunately, clear parallel fringes can not be observed, indicating that these SiNWs are of amorphous structures. Moreover, no amorphous oxide layer is observed in this picture.

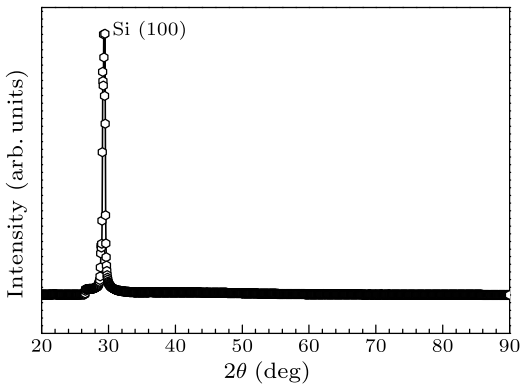


Fig. 3. The θ–2θ XRD diffraction pattern of the as-deposited silicon nanowires.

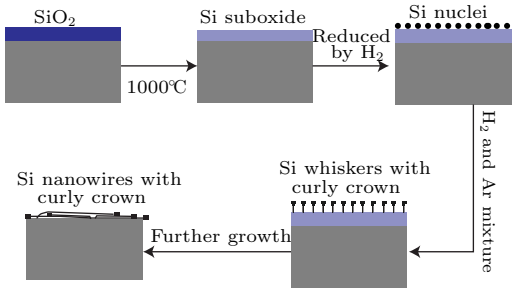


Fig. 4. Schematic illustration of the growth mechanism.

The EDX spectrum taken from a single nanowire is shown in Fig. 2. Three peaks corresponding to Cu and Si are found in this spectrum. Except the Cu peaks come from the Cu grid, no peak of O appears, which demonstrates that the compositions of these products are pure SiNWs without any oxide shells.

Figure 3 shows the XRD pattern of the SiNWs. It is clearly seen that only a peak indexed to (100) Si is observed in this pattern, demonstrating that the (100) direction is the preferred growth direction. No trace of SiO_2 or any other Si compound phases in the detection limit of the XRD exist, which suggests that no amorphous oxide shells are observed in these SiNWs. This is in agreement with the EDX result as shown in Fig. 2. In order to explain the reason for forming SiNWs on the Si wafers, two other experiments were carried out under the same growth conditions except that the wafers were cleaned by HF solution to remove the surface oxide layers and no hydrogen was introduced into the growth chamber, respectively. The

SEM results suggest that no nanowire can be observed in the above two conditions. Hence, silicon oxide on the surface of Si wafers and hydrogen may play an important role in the formation of wire-shaped nanostructures.

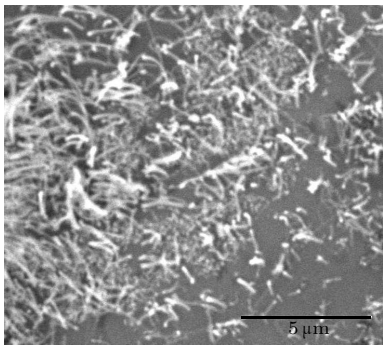


Fig. 5. SEM image of the Si nanorods grown at 1000°C in Ar/H_2 mixture for about 1 h.

Based on the above-mentioned results and compared with the previous reports about SiNWs grown by the laser ablation method, the possible growth mechanism of these SiNWs is tentatively proposed. The growth process of the SiNWs can be divided into three steps. Firstly, the top Si dioxide layer formed by natural oxidation Si wafer in air reacts with Si to form Si suboxide (SiO_x, $x \leq 2$), which decomposes thermally into Si nanoparticles and water vapor in the H_2/Ar mixture. The detailed reaction can be given by $SiO_x(s)+H_2(g)=Si(s)+xH_2O(g)$, where s and g represent solid and gas, respectively. Subsequently, the grown Si nanoparticles are deposited onto the lower layer of the Si suboxide. Then residual Si suboxide reacts continuously with H_2 to form more Si nanopaticles. These freshly formed Si nanoparticles deposited on the top of the Si nuclei or surrounded them, precipitating the growth of the SiNWs. Finally, Si nanowires are formed on the surface of the Si wafers. The possible growth mechanism is shown in Fig. 4. According to this growth mode, SiO_2 and H_2 are two important factors contributing to the formation of such SiNWs. In our experiment, SiO_2 acted as the source material and a special catalyst promotes the one-dimensional growth of SiNWs. H_2 is used as a reducing agent that can support Si nanopaticles to generate nanowires. To confirm the above deduction, the products grown for 1 h are shown in Fig. 5, SiNWs with crown are found to stand on a silicon wafer after synthesized under the same reaction conditions, which further support the deduction of the growth mechanism that the SiNWs firstly stand and then lie on the silicon substrate. In addition, the reason for forming a curly crown at the top of each silicon nanowire is unclear, different surface energies among the growth surfaces may lead to the bending of the initial silicon wafer. Further work is in progress.

In summary, large-scale SiNWs without amorphous silicon oxide sheath have been synthesized directly on Si wafers via a simple one-step thermal reaction method. The SiNWs are amorphous Si with diameters of 10–300 nm and the lengths of 200–500 μm. SEM and XRD results indicate that SiO_2 grown on the surface of Si wafers and H_2 may play critical roles in the formation and growth of SiNWs. The success of our experiment could offer opportunities for preparing SiNWs by reducing SiO_2 in Ar/H_2 mixture, as well as for further fundamental research. The growth mechanism is proposed tentatively and further experiments should be carried out in future.

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