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Investigation of the growth process of Si nanowires using the vapour–liquid–solid mechanism*

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Silicon nanowires have been grown by the thermal decomposition of silane via the vapour–liquid–solid (VLS) mechanism. Three different stages of VLS growth (eutectic alloy formation, crystal nucleation and unidirectional growth) were studied separately using a scanning electron microscope and a high-resolution transmission electron microscope. Very short silicon nanowires prepared under particular conditions provide direct evidence of the VLS mechanism on a nanometre scale. Our results will be very helpful for the controllable synthesis of Si nanowires.

Keywords: nanowires, vapour–liquid–solid mechanism
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1. Introduction

Miniaturization in electronic devices has motivated great efforts to synthesize nanoscale semiconductor materials.[1] Si nanowires (SiNWs) are an interesting nanoscale material due to the dominant role of bulk silicon in the modern semiconductor industry. Nanoscale diodes, transistors and logic gates using doped SiNWs as building blocks show that they still have typical rectifying, magnifying and logic computing behaviour, just as conventional planar devices.[2,3] On the other hand, red photoluminescence emission from thin SiNWs has been observed and has definitely been ascribed to the quantum confinement effect,[4] revealing that the electronic structure of SiNWs is different from that of bulk material. This remarkable progress makes SiNWs a promising candidate for nanoelectronics and optoelectronics.

Filamentary silicon structures have been synthesized via the vapour–liquid–solid (VLS) mechanism for more than three decades. This mechanism was first proposed to explain the anisotropic growth of a dislocation-free Si whisker by Wagner and co-workers with a three-step model[5,6] that is depicted briefly as below. The first step (alloy droplet formation) involves the formation of eutectic metal–silicon droplets at high temperatures. In the second step (crystal nucleation), Si atoms in the vapour phase are absorbed at the surface of the droplets and get into the droplets. The continuous absorption of Si causes Si supersaturation in the alloy droplets, and then Si crystals are precipitated from the droplets. In the third step (unidirectional growth), more Si atoms diffuse into the droplets and are stacked on the nucleation site in the Si-rich atmosphere, resulting in the continuous growth of long Si whiskers. Givargizov[7] later developed this model and discussed it within the framework of kinetics. He studied the dependence of the growth rate on the whisker diameter and found that VLS growth would terminate at a critical diameter $d_c \leq 0.1\mu$m due to the Gibbs–Thomson effect. Recently, Lieber *et al*[8] and Yu *et al*[9] have developed a novel approach for the synthesis of SiNWs with a diameter of less than 20 nm using laser ablation of silicon/metal powder; they have attributed the growth to the VLS mechanism. Some other similar techniques have also been used to grow SiNWs, such as chemical vapour deposition,[10] physical evaporation,[11] and the solution-based method.[12] The only evidence for VLS growth in all these experiments is the observation of solidified particles at the ends of the SiNWs, and a direct investigation of VLS growth at different stages has not yet been achieved. In this paper, we report on an investigation of the VLS

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growth process. The observation of crystal nucleation and growth directly confirms the validity of the VLS mechanism on a nanometre scale.

2. Experiments

The substrate used in our experiments was an n-type Si(111) wafer. It was ultrasonically cleaned in turns in pure petroleum ether and in ethanol for 5min, and leached in distilled water. The cleaned wafer was deposited on a thin layer of Ni (40 nm thick), using an e-beam evaporation system. The substrate was placed in a quartz tube that was heated in a tube furnace. An argon flow was introduced into the quartz tube at a rate of 40 sccm as the furnace temperature rose to 950°C. The substrate was then heated at this temperature in the ambient atmosphere of Ar, H_2 and SiH_4 (diluted to 5% with H_2) to investigate the different stages of the VLS process.

The morphology of the as-grown specimens was observed using an Amray FEG-1910 scanning electron microscope (SEM) with EDAX attachment. A Hitachi-9000 NAR high-resolution transmission electron microscope (HRTEM) equipped with energy dispersive spectrum (EDS) was used to characterize the microstructure and the chemical composition of the products.

3. Results and discussion

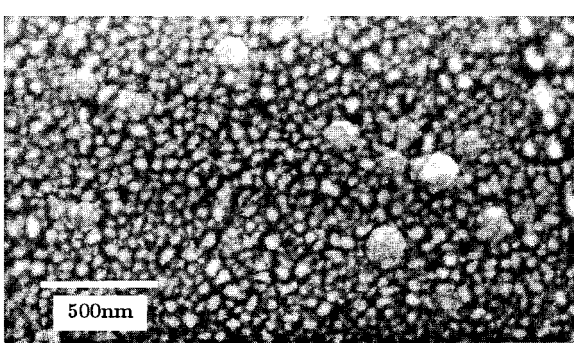


Fig.1. SEM image of nanoparticles formed on the substrate after annealing.

First, we studied the formation of eutectic alloy droplets in the VLS process. A metal catalyst plays an important role during VLS growth. The alloy droplets composed of metal and silicon act as the starting points of SiNW growth. Therefore, the eutectic point of the metal–silicon compound determines the lowest temperature for the nanowire growth. The silicon source for Ni–Si droplets may come from two places in our experiments: the Si substrate or silane. We believe that both these sources are effective. A substrate coated with a Ni film was heated at 950°C in the vacuum to examine the reaction between the Si substrate and Ni catalyst. The SEM image (Fig.1) shows the morphology of this annealed substrate. It is seen that the original continuous Ni film becomes isolated particles after heat treatment, and most particles have a diameter of about 50 nm, though some large particles are also formed. All particles are distributed uniformly on the substrate. EDAX analysis has revealed that the nanoparticles are composed of Ni and Si. This result shows that Ni–Si alloy droplets can be formed by directly heating the Ni film and Si substrate. The lowest temperature for droplet formation is 950°C in our experiments. From the binary Ni–Si phase diagram, however, it is known that in the silicon-rich region the lowest eutectic point at Ni–Si liquidus is 963°C. Because the thin nickel film shrinks into small islands during the heat treatment, the melting points of small-sized particles are lower than that of the corresponding bulk solid. As a result, Ni–Si alloy droplets can be formed at 950°C, which is a little lower than the eutectic point of Ni–Si. Annealing the substrate under pure Ar atmosphere does not affect particle formation obviously, whereas the diameter of Ni–Si particles decreases when a small amount of hydrogen is mixed into the ambient atmosphere.

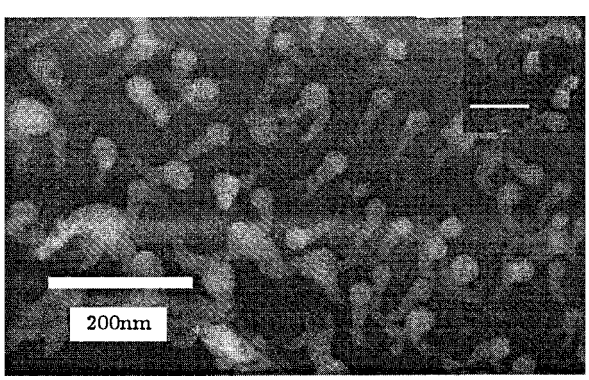


Fig.2. TEM image of SiNWs at the crystal nucleation step. The inset is a TEM image of solidified droplets with precipitated nanocrystal; the scale bar is 40 nm.

The surface of the Ni–Si eutectic droplets has a large accommodation coefficient and is therefore a preferred site for gas deposition. When silane is introduced into the reaction tube, Si atoms are generated by the decomposition of silane at a high temperature. The Ni–Si liquid droplets become supersaturated with the continuous absorption of Si from the vapour, and nanowire growth occurs by precipitation of the nanowire out of the droplet. This stage is

the key to VLS growth because it initiates the SiNW growth and determines the structure, composition and size of the SiNW. Particular attention was given to analysing this growth stage. A substrate was heated at 950°C in a gas mixture of Ar (36 sccm), H_2 (4 sccm) and SiH_4 (3 sccm) for 5 min. The system was then evacuated immediately and cooled down to room temperature quickly. The SiNWs at the crystal nucleation stage were scratched from the substrate and observed by TEM. Figure 2 shows that all SiNWs are in the shape of a mushroom, having round caps and very short stems. The round caps have a uniform diameter of 20 nm and the stems have a length less than 20 nm. Smaller and shorter SiNWs were prepared under conditions of a smaller flowing rate of silane and a shorter heating time. The TEM image of small particles with nanocrystals is shown in the inset of Fig.2, revealing that the Si crystal is really nucleated from the droplet. This result confirms the existence of a crystal nucleation stage and gives a direct evidence for the VLS model on a nanometre scale. It should be noticed that the caps of these SiNWs are significantly smaller than the particles in Fig.1. We think that this fact reveals the relation between the supersaturation and particle size. Because the surface/volume ratio of small alloy particles is much larger than that of large alloy particles, small droplets can dissolve more silicon atoms in unit volume than the large droplets under the same conditions, and indeed can have higher Si concentration. So SiNWs grown from small particles are easier to observe.

Once the short SiNW is precipitated from a droplet, a liquid–solid interface is created at the surface of the liquid droplets. Unidirectional growth is the consequence of an anisotropy in the solid–liquid interfacial energy. The dissolved Si atoms preferably diffuse out through the droplets and stack on the existing liquid–solid interface, because this process consumes less energy than that needed to form a new nucleation site in the droplet. Long SiNWs were grown at 950°C in the mixed atmosphere of Ar (36sccm), H_2 (4sccm) and silane (4sccm). The SEM image (Fig.3(a)) shows the morphology of a sample heated for 1h. It is seen that a large amount of SiNWs are formed on the substrate. The SiNWs have a diameter of 10–50 nm and a length up to several micrometres. Obviously, each SiNW has a large particle at its free end, which is a characteristic of VLS growth. A TEM image of a single SiNW is shown in Fig.3(b). The surface of a SiNW is quite smooth and clean. Further analysis shows that SiNWs are crystalline and are sheathed with a thin layer of amorphous silica. The inset in Fig.3(b) shows the selected area electron diffraction (SAED) pattern of the SiNW, revealing the monocrystalline nature of the SiNWs. A compositional analysis of this SiNW was conducted using energy dispersive spectrum (EDS). The analysis of the droplet shows that the tip is composed of Ni and Si. When the electron beam was moved away from the particle to the nanowire, only silicon and a trace amount of oxygen were detected.

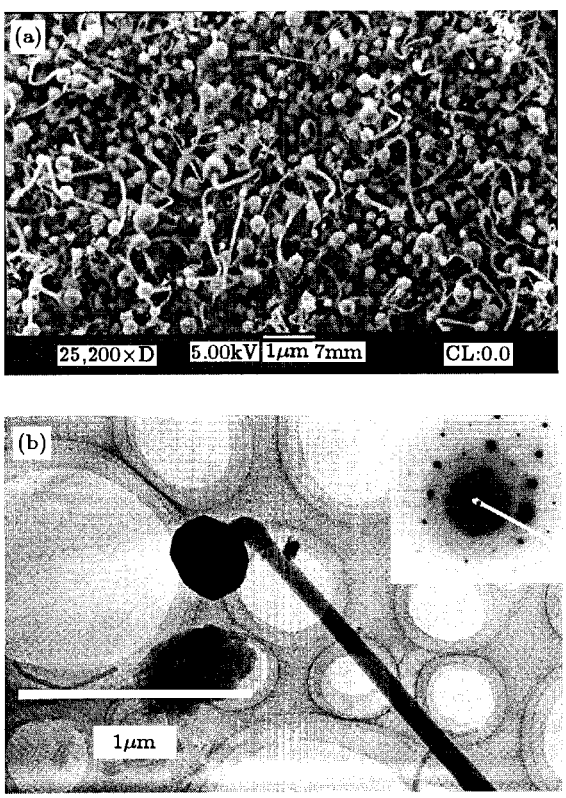


Fig.3. (a) SEM image of as-grown SiNWs. Large particles at the ends of SiNWs are a characteristic of the VLS mechanism. (b) TEM image of a single SiNW. The inset shows the SAED pattern of this SiNW, revealing its single crystalline structure.

SiNWs show some novel physical and chemical properties related to dimensionality.[4,13] Recent success in assembling nanoscale electronic devices and logic gates represents an important step toward integrated nanoelectronics built from a primarily bottom-up approach.[2,3] All these progresses need a precisely controllable synthesis of SiNWs. A detailed study of the VLS growth process can help us to control the SiNW growth. By optimizing the amount of silane and the growth period, we can prepare SiNWs with appropriate length, diameter and morphology. In addition, the observation of three different growth

stages (alloy formation, crystal nucleation and unidirectional growth) provides direct evidence for the VLS mechanism on a nanometre scale, showing that the VLS mechanism is valid for preparing other one-dimensional materials.

4. Summary

In summary, we have studied the VLS growth process of SiNWs. The three different stages of VLS growth (alloy formation, crystal nucleation and unidirectional growth) have been studied separately. Very short SiNWs at the crystal nucleation stage directly confirmed the validity of the VLS mechanism on a nanometre scale. The investigation of the VLS growth process is helpful for the controllable synthesis of SiNWs.

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