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Aloetic-Shaped SiC Nanowires: Synthesis and Field Electron Emission Properties

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Novel ordered aloetic-shaped SiC nanowires were synthesized on a Si (100) substrate by reacting methane with silicon dioxide using iron as a catalyst. Their structure and chemical composition were studied by scanning electron microscopy (SEM), X-ray diffraction (XRD), and transmission electron microscopy (TEM). The wires have a tapered aloetic structure with a top diameter about 50–80 nm and a length about 10 μm. The field emission properties of the aloetic nanowires were investigated. A stable emission with current density of 0.525 mA/cm^2 at an applied electric field of 2.2 V/μm and a low turn-on electric fields of 1.4 V/μm were observed. The excellent field emission properties indicate that the aloetic-shaped SiC nanowires may have potential applications in flat panel displays and electron field-emitting devices.

Keywords: SiC Nanowires, Aloetic-Shape, Synthesis, Field Emission Characteristic.

RESEARCH ARTICLE

1. INTRODUCTION

The pioneering work by Iijima in making carbon nanotubes has aroused much research interest worldwide in the synthesis of one-dimensional materials. As an important wide bandgap semiconductor, silicon carbide appears to be the most promising material for blue and ultraviolet light emitting devices:[1] high power and high frequency electronic devices that can be operated at high temperature and in harsh environment.[2] In addition, SiC nanowires and microwires have always been a research focus because of their high strength, low density, and high thermal stability that enabled them to serve as a reinforcing phase in ceramic, metal, and polymer matrix composites.[3] In particular, the field emission properties of SiC nanowires have been investigated by many researchers, and the results show low turn-on and threshold electric field values, which indicate potential applications in electron field-emitting devices.[4,5]

So far, several techniques have been developed for synthesizing SiC nanowires, such as reaction between carbon nanotubes and SiO or SiI_2,[6] carbothermal reduction of sol–gel-derived silica xerogel,[7] controlling the reaction between silicon halides and CCl_4,[8] laser ablation,[9] arc-discharge,[10] and chemical vapor deposition (CVD).[11]

In this paper, we report a simple but efficient gas-solid reaction method for fabricating well-ordered high density aloetic-shaped SiC nanowires. The method is based on the reaction of methane with silicon dioxide powders in the presence of $FeCl_3$ nanoparticles catalysts. The possible growth mechanism and the field emission properties have been discussed. The result shows that this type of SiC nanowires is well-suited to field emission.

2. EXPERIMENTAL DETAILS

2.1. Sample Preparation

The growth of aloetic-shaped SiC nanowires was carried out in a horizontal tube furnace system. The system contained an alumina tube inside a furnace, and the gas flow was controlled by a mass flow controller. Methane (purity 99.99%), SiO_2 powder (spectrally pure), and $FeCl_3 \cdot 5H_2O$ powder (analytically pure) were used to supply C, Si precursors, and catalysts, respectively. 1 g SiO_2 and 0.8 g $FeCl_3 \cdot 5H_2O$ powders were mixed with 5 ml deionized water. Then 20 μl of the solution, measured using a pipette, was spread uniformly over the surface of the Si (100) substrate, which had been cleaned using trichloroethylene, acetone, and ethanol for 10 min in turn by ultrasonic agitation. After the substrate had been dried in a vacuum oven at a temperature of 120 °C for

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2 h, a thin layer film of the mixed powders was formed. An alumina boat supporting the substrate was placed in the constant temperature zone of the alumina tube.

A two-step process was used to synthesize the aloetic-shaped SiC nanowires. First, the system was purged with 300 sccm of argon (purity 99.999%) while the constant temperature zone was heated to 600 °C. This was followed by raising the furnace temperature to 1,250 °C in a hydrogen atmosphere with a flow rate of 300 sccm to eliminate the remaining chloric ions and enhance the activation of the formed iron particles. Second, after the constant temperature zone reached growth temperature, methane and hydrogen (purity 99.999%) with gas flows of 20 sccm and 50 sccm, respectively, were used to fabricate aloetic-shaped SiC nanowires. Hydrogen played two roles in the reaction process. One was to deoxidize the catalyst ion and maintain the catalyst at high activity. The other was to improve the crystalline qualities of the nanowires. During the growth, the constant temperature zone was kept at 1,250 °C in a normal pressure atmosphere. After 10 min of growth, the furnace was cooled to room temperature in an argon atmosphere, and the gray-white product was found on the surface of the Si substrate (approximately 0.2 cm^2).

2.2. Measurements

The as-grown products were characterized by scanning electron microscopy (SEM, Hitachi S-4800) and X-ray diffraction (XRD, Ricoh). In addition, transmission electron microscopy (TEM, JEM-2010) was used to further characterize the products.

Field emission experiments were carried out in a vacuum chamber with a base pressure of about 9×10^{-5} Pa at room temperature. The sample, as a cathode, was attracted to a copper cylinder stand with conductive glue. The indium-tin-oxide (ITO)-coated glass was adopted as an anode. A quartz spacer of 500 μm thickness was placed on the substrate to isolate the cathode from the anode. The emission current was monitored by a picoammeter (Keithley 237).

3. RESULTS AND DISCUSSION

3.1. Morphology and Structure

Figure 1(a) shows a typical SEM image of the SiC nanowires. It can be seen that a large quantity of distributed nanowires has been formed on the Si substrate. The nanowires have a pronounced tapered aloetic shape structure diameter about 200–500 nm and length about 10 μm. Meanwhile, the nanowires are not slick, but have lots of smaller nano-size wires (about 30–80 nm) on the surface and tip, as shown in Figure 1(b). The nanowires are not oriented vertically to the substrate but have some slant from the vertical direction. When the density of SiC nanowires reaches a high value, SiC nanowires grown in directions other than the vertical direction are prohibited from growing due to steric hindrance from adjacent nanowires and then change the growth direction for further vertical growth.

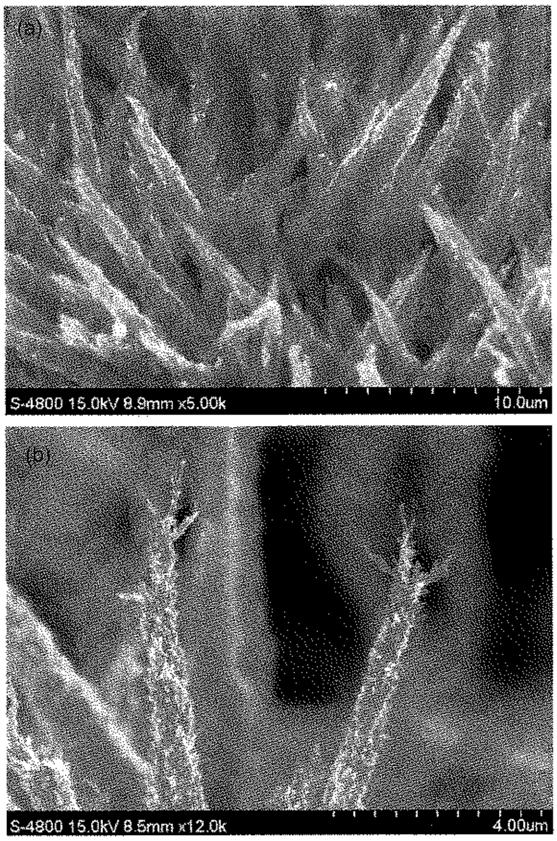

Fig. 1. (a) A typical SEM images of the aloetic-shaped nanowires on the Si substrate and (b) high-resolution SEM images of top of nanowires.

The XRD result of the nanowires on Si (100) substrate is shown in Figure 2. Three SiC peaks at 35.7°, 41.4°, and 60° (2θ) are observed that can be attributed to the diffraction of SiC (111), (200), and (220) planes, respectively, and indicate the formation of β-SiC. In addition, a strong diffraction peak of FeSi at $2\theta = 45.3°$ has been detected, indicating that a large amount of FeSi phase was formed on the surface of the Si (100) substrate in the above reaction process.

Further characterization was carried out using transmission electron microscopy (TEM). Some products from the Si (100) substrate were peeled off, ultrasonically dispersed in ethanol, and dropped on a copper grid covered with holey carbon film. Figure 3 shows a typical TEM top image of the nanowires. Iron particles are observed at the tips of the nanowires.

3.2. Growth Mechanism

The growth mechanism may follow the conventional metal-catalyst vapor-liquid-solid (VLS) process.[9] $FeCl_3$ nanoparticles were employed as catalysts to fabricated

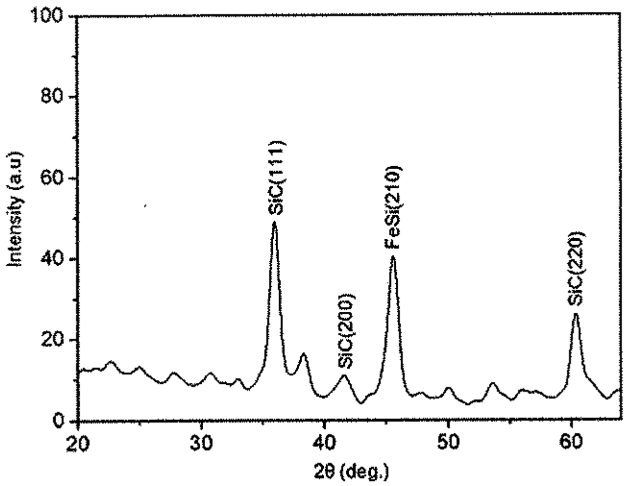

Fig. 2. XRD pattern for the SiC nanowires on Si (100) substrate.

SiC nanowires. Synthesis of the nanowires without $FeCl_3$ nanoparticles has been attempted, but no nanowires can be grown on the surface of the Si (100) substrates using the same growth system at the same conditions. This fact suggests that the $FeCl_3$ nanoparticles play a key role in the formation of nanowires, and a VLS mechanism is the most probable growth mechanism. Moreover, TEM also detects the existence of iron at the tips of the nanowires. Thus, we suggest that the growth mechanism follows the "tip growth model" as shown by Amelinckx et al.[12] The growth process may be proposed as follows: First, with the temperature up to 1,250 °C, the carbonthermal reduction of SiO_2 takes place,[11] and the Fe particles start to melt. The melted Fe becomes liquid and flows on the surface of Si substrate, and it may combine with Si and C in the vapor to form nanoliquid droplets of Fe, Si, C and O alloys.

$$SiO_2 + C \rightarrow SiO + CO, \quad (1)$$

$$SiO + 2C \rightarrow SiC + CO, \quad (2)$$

$$2SiO + 3C \rightarrow 2SiC + CO_2. \quad (3)$$

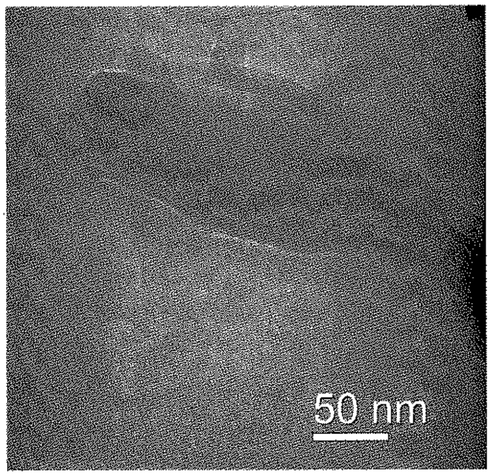

Fig. 3. A typical TEM top image of the nanowires.

As the above three reactions progressed, a large amount of SiC nanowires formed.

3.3. Field Emission Characteristic

The characteristic of emission current versus electric voltage for the typical SiC nanowires and carbon nanotubes (CNTs) grown by our group are shown in Figure 4(a). Compared with the carbon nanotubes, the field emission characteristic of aloetic-shaped SiC nanowires has obviously improved and shows excellent field electron emission. The emission current density can be up to 0.525 mA/cm^2 at applied electrical field 2.2 V/μm. At the same applied electrical field, the emission current density of CNTs is 0.32 mA/cm^2. The electron emission turn-on field of the nanowires, defined as the macroscopic field required to produce a current density of 10 μA/cm^2, is about 1.4 V/μm. This Fowler–Nordheim plot is shown in Figure 4(b). The linearity of this curve shows a conventional field emission mechanism for our SiC nanowires.

Compared with conventional CNT emitters fabricated on substrates, it is suggested that there are three reasons

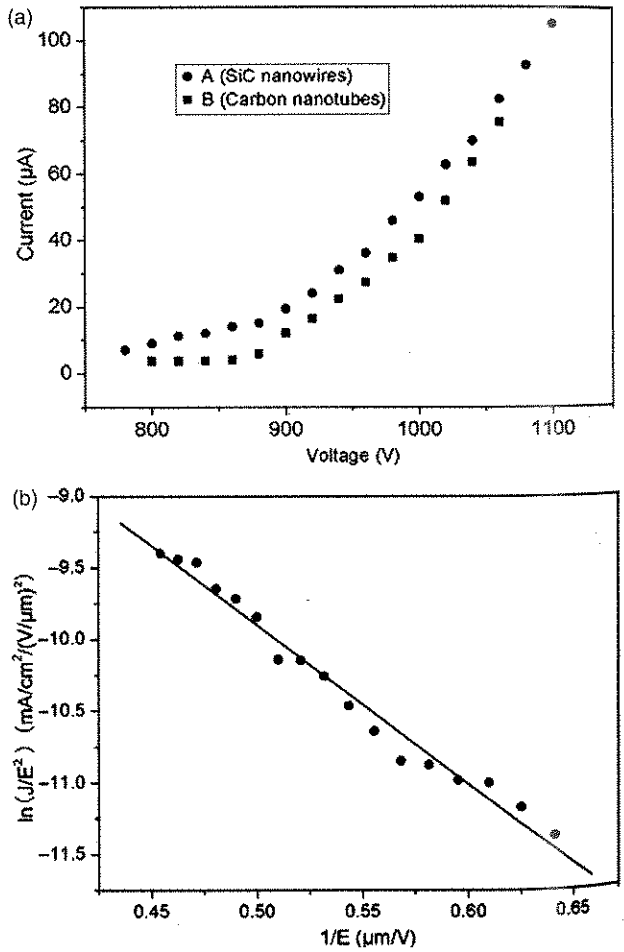

Fig. 4. (a) Field electron emission direct current-voltage characteristic of SiC nanowires and (b) corresponding Fowler–Nordheim plot.

for enhanced field emission properties of nanowires. First, there are large numbers of thorns and sub-size nanowires on the surfaces and tips of these nanowires, which will form lots of efficient electron emitting sites, leading to better field emission properties. Second, strong local electric fields can be easily formed on the tips of the thorns and sub-size owing to their smaller tip size. This electric field will make the electron overcome the surface barrier to the air with ease and then greatly enhance the electron emission. Third, the nanowires are nearly vertical with the Si substrate, which will effectively decrease the field-screening effect from adjacent nanowires.

4. CONCLUSIONS

In summary, we have synthesized aloetic-shaped SiC nanowires at 1,250 °C in a normal pressure atmosphere in a catalyst-assisted process using iron as a catalyst by reacting silicon dioxide with methane. The growth mechanism follows the metal-catalyst VLS process, and the $FeCl_3$ nanoparticles play a key role in the formation of SiC nanowires. The emission current density of these nanowires can be up to 0.525 mA/cm^2 at an applied electric field of 2.2 V/μm and a turn-on electric field of only 1.4 V/μm. The excellent field emission properties indicate that the aloetic-shaped SiC nanowires may have potential applications in flat panel displays and electron field-emitting devices.

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