

A wurtz-like reaction to silicon nanowires

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Abstract

Silicon nanowires have been successfully synthesized via wurtz-like reaction, using silicon tetrachloride and sodium in the presence of Co/Ni catalyzer at 500 °C. In this process the sodium was used as reductant and flux. Transmission electron microscopy (TEM) shows that the nanowire cluster is about 10 nm in diameter and length up to several microns, and well aligned along their longitude direction. High-resolution transmission electron microscopy (HRTEM) images demonstrate that as-synthesized nanowires interlayer spacing are around 0.31 nm, corresponding well to the (111) lattice parameter of diamond-like crystalline silicon. Based on the experimental results, the possible wurtz reaction mechanism of the silicon nanowires (SiNWs) has been properly proposed.

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1. Introduction

Wurtz coupling reaction has been well known widely used method for preparing high molecular weight rodlike, flexible and semiflexible linear polysilanes since 1920s. These polysilanes are promising candidates of building blocks of molecular electronics and optoelectronics due to their remarkable semiconducting property [1]. A simple wurtz reaction as shown in Eqs. (1) and (2), involving metallic sodium and an alkyl halide,



presumably a sodium alkyl is firstly formed and then reacts with additional alkyl halide to yield the coupled products [2].

In the past decades, wurtz-like reactions have been applied to synthesis various inorganic materials. Such as, hexagonal-shaped silicon single crystals [3], multi-wall carbon nanotubes [4], diamond powder [5], and silicon nanocrystals were synthesized via wurtz type coupling reaction [6].

As silicon is of great technological importance, much research and development have been aimed at producing high quality crystalline and polycrystalline Si, and because of the advantage of technical compatibility, compared with other semiconducting nanowires, much more efforts have been made to produce silicon nanowires (SiNWs). Different methods have been developed to synthesize SiNWs including vapor–liquid–solid (VLS) method [7], photolithography technique combined with etching [8], molecular-beam epitaxy (MBE) [9], laser ablation [10], supercritical fluid–liquid–solid [11], arc-discharge in de-ionized water [12]. Although the existing methods can synthesize well-defined SiNWs, some of them are still expensive, complicated for operating or need high synthesis temperatures. Seeking simple and economical routes for facile synthesis of SiNWs still remains a challenge for the future Si-based nanoelectronic application. Here, we report a new method for preparation SiNWs via wurtz-like reaction.

2. Experimental

The typical experimental procedure was designed as follows: 5 ml of $SiCl_4$ was put into a stainless steel autoclave with 30 ml capacity, and an excess of 20 g metal Na was added. After that, 5 mg of catalyzer precursor was added. The sealed autoclave was maintained at 500 °C for 24 h and then air-cooled to room

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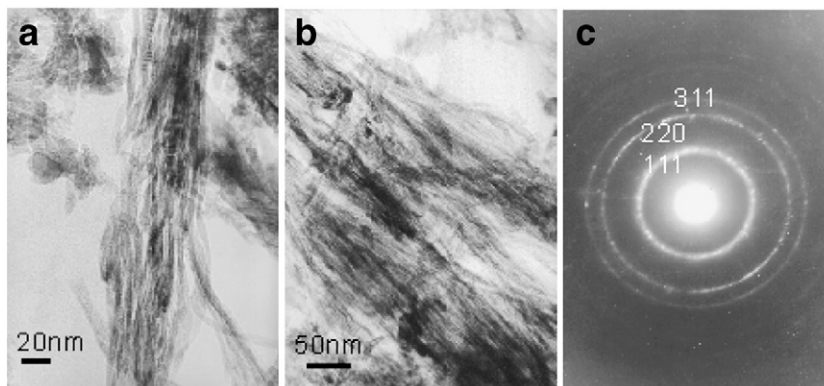


Fig. 1. a) TEM image of SiNWs bundle, b) a denser region of the nanowires. c) SAED pattern of SiNWs.

temperature naturally. The obtained product was washed with absolute ethanol, dilute acid, distilled water, respectively, to remove residual impurities, and then the product was dried in a vacuum at 80 °C for 6 h. The morphology and structure of the synthesized products were investigated by transmission electron microscopy (TEM, Hitachi H-800) and high-resolution transmission electron microscopy (HRTEM, JEOL-2010) both with an accelerating voltage of 200 kV.

3. Results and discussion

Fig. 1a and b show TEM images of the SiNWs. Which indicates the product consists of clusters of high aspect ratio nanowires. In Fig. 1a, we can see a typical nanowire bundle that has a diameter around 10 nm, length up to several microns. It is worth noting that the nanowires are rather uniform along the entire length in diameter and well aligned in their longitude direction.

A selected-area electron diffraction (Fig. 1c) pattern taken from nanowires bundle shows continuous diffraction rings which match well with the (111), (220), (311) diffraction rings of silicon with diamond-like structure, indicating cubic-phase Si.

The energy dispersive spectroscopy of SiNWs was shown in Fig. 2, which indicates that the product consists of Si, except the background of O and micro-grid Cu. The absence of Co or Ni in the SiNWs suggests that current growth mechanism is different from conventional

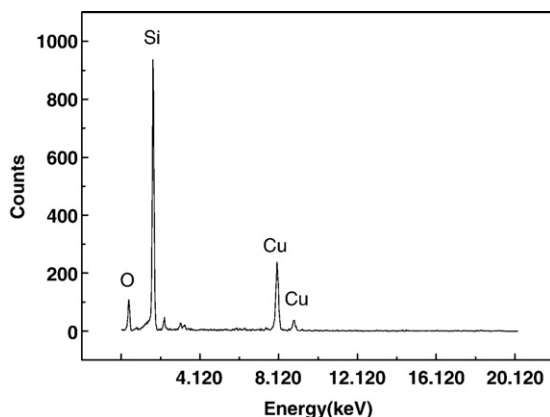


Fig. 2. EDS spectrum of SiNWs, only elements Si, O and Cu of product and the background can be distinguished.

VLS process, in which metal-catalyst is often found at the tips, roots, or middle of the products [13].

Fig. 3a shows a high-resolution TEM image and accordingly Fourier transformation (inset) of one typical SiNWs produced in this way. The measured spacing of the lattice plane is about 0.31 nm, which matches well with the (111) plane of the cubic diamond structure silicon (0.31 nm). Observation from Fig. 3a, it is found that the (111) plane is perpendicular to the nanowire axis, which means the SiNWs grow along [111] direction. This growth direction is also observed in those thick SiNWs synthesized through the VLS approach [14]. In the OAG mechanism, the predominant growth directions are [112] and [110] [15], these can be ascribed to the crystal dislocations which are important factors for nanowires growth. In a low seed particle supersaturation, the main growth directions are [112] and [110] according to an atom stability criteria model [16]. Besides [111] growth direction, some [112] growth direction are also observed (in Fig. 3c), and note the amorphous shell that coat the crystalline core.

Some stacking faults (Fig. 3b) and twins (Fig. 3d) are observed in the as-synthesized SiNWs, which is consistent with a previous report

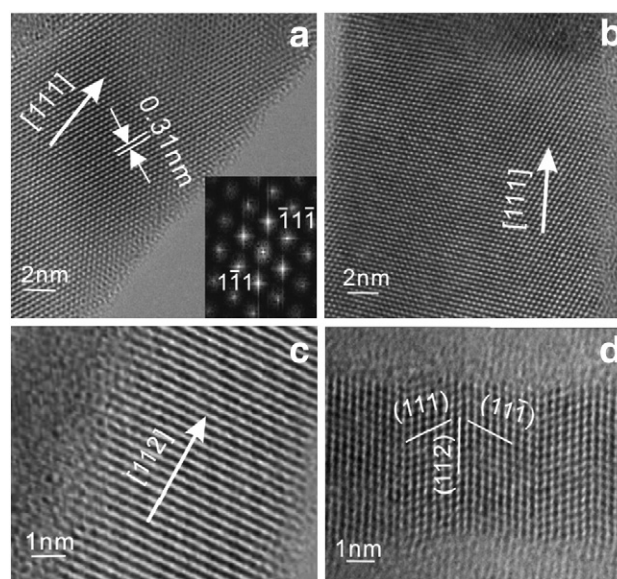


Fig. 3. a) HRTEM images of SiNWs, spacing between the fringes is about 0.31 nm, corresponding to the (111) lattice parameter of diamond-like crystalline silicon. b) a typical SiNW with SF defects. c) SiNWs with [112] growth direction. d) the twin boundary structure of a nanowire.

that micro-twins occur usually in the kinks of SiNWs [17]. In Fig. 3b, the stacking sequence alteration of (111) plane caused stacking faults are indicated as white line. Fig. 3d shows the twin structure of SiNWs with (1–11) boundary, in which lattice planes of (111) and (11–1) are symmetrical to the twin boundary. The bending character of SiNWs (Fig. 1a, b) may be caused by the crystalline defects like stacking faults or twins.

In previous reports, metal-catalyzed (such as Au) SiNWs growth was explained by the VLS mechanism. According to this mechanism, Si (from the decomposition of silicides) and catalyzer (Au) will form a liquid alloy when the reaction temperature is higher than the eutectic point. The liquid surface has a large accommodation coefficient, which is a preferred deposition site for incoming Si vapor. SiNWs growth occurs at the solid–liquid interface after the liquid alloy becomes supersaturated with Si. In the VLS process, the temperature is the key parameter to sustain nanowires formation and it need to be higher than the metal–Si eutectic point (for example, the eutectic point Au/Si is 363 °C). However, in our experiment, Ni/Co was used as catalyzer. The liquid eutectic point shown on the binary diagram for Ni/Si and Co/Si is much higher than the experimental temperature of 500 °C [18]. So the details of the growth of SiNWs are likely to be different from the metal-catalyzer VLS process. Herein, we believed that traditional wurtz reaction mechanism is effective to explain the transformation of silicon precursors into a nanowire. Metal sodium serves as reductant and flux, which can exchange metal sodium cation for halide on silicon. The reductive product is NaSi. Then it reacts with another silicon halide to provide a Si–Si bond. This can explain both an additive atom needed in the intermolecular formation of Si–Si bonds to add an atom to grow cluster, and the intramolecular bond formation required to close the six-membered rings of the silicon diamond structure [5].

4. Conclusions

In conclusion, the present work has demonstrated a facile and economical wurtz-like reaction route to synthesize high aspect ratio, well-aligned SiNWs, and the diameter of as-synthesized SiNWs about 10 nm, using reduction of SiCl₄ by metallic sodium in the presence of Co/Ni catalyzer at a moderate temperature. The SiNWs have predominant growth direction of [111]. The possible growth mechanism, different from the conventional metal-catalytic VLS mechanism, has also been discussed.

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