Materials Science in Semiconductor Processing 29 (2015) 155–160

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

$FeCl_2$-assisted synthesis and photoluminescence of β-SiC nanowires

Feng Wang [a,*], Xiaofang Qin [a], Dongdong Zhu [a], Yanfeng Meng [a], Lixia Yang [a], Lixiang Sun [a], Yongfei Ming [b]

[a] School of Chemistry and Materials Science, Ludong University, Yantai 264025, China
[b] School of Life Science, Ludong University, Yantai 264025, China

ARTICLE INFO

Available online 20 February 2014

Keywords:
SiC
Nanowires
Carbothermal reduction
Photoluminescence

ABSTRACT

β-SiC nanowires were synthesized by the carbothermal reduction of the carbonaceous silica xerogel prepared using tetraethoxysilane (TEOS) and sucrose as sources, and ferrous chloride as an additive. The products were obtained by heating the xerogel at 1300 °C for 6 h in argon flow (200 ml/min). The products were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR), scanning electron microscope (SEM), high-resolution transmission electron microscope (HRTEM), energy-dispersive X-ray spectroscopy (EDS), and selected area electron diffraction (SAED). The results show that the products mainly consist of crystalline β-SiC nanowires with an amorphous SiO_2 shell. The SiC nanowires have a diameter of 100–300 nm and a length from tens to hundreds of micrometers. The vapor–liquid–solid (VLS) mechanism was proposed to explain the formation of β-SiC nanowires, and the nanowires mainly grow along [1 1 1] direction. The photoluminescence (PL) spectrum of β-SiC nanowires at room temperature shows two emission peaks at 405 nm and 436 nm.

1. Introduction

One-dimensional (1D) nanomaterials, such as nanowires, nanotubes, nanorods, nanobelts, nanowhiskers and nanocables, have attracted considerable attention owing to their excellent mechanical, optical, electronic, physical and chemical properties and widely potential applications [1–3]. Among the various nanomaterials, the potential applications of nanowires are truly impressive in alternative energy, computational technology, communications, spectroscopic sensing, and the biological sciences [4]. Over the past several years, various methods have been used to synthesize 1D nanowires, including chemical vapor deposition (CVD) [5], thermal evaporation method [6], carbothermal reduction [7], hydrothermal synthesis [8], direct nitridation method [9], template-based method [10], and so on.

As a well-known wide band gap (2.3–3.3 eV for different crystalline phases) semiconductor material, silicon carbide (SiC) possesses outstanding physical properties, such as high mechanical strength, good chemical stability at high temperatures, high wear-resistance, and high thermal conductivity [11–13]. Recently, 1D SiC nanowires have attracted considerable attention because of their high strength, low density, high stiffness and high temperature stability, and wide applications in sensor, high frequency nanodevices, composite reinforcements, and electronic nanodevices [14–16], etc. Up to now, 1D SiC nanowires have been synthesized by many routes, such as thermal evaporation, carbothermal reduction, polymer pyrolysis, CVD, solvothermal synthesis, molten salt synthesis, etc.

* Corresponding author. Tel.: +86 535 6672176.
E-mail address: wf200818@126.com (F. Wang).

http://dx.doi.org/10.1016/j.mssp.2014.02.007
1369-8001

For example, Khongwong et al. [6,14] reported the synthesis of β-SiC/SiO_2 core–shell nanowires through simple thermal evaporation of Si powder among flowing CH_4 gas. Pan et al. [17] synthesized SiC/SiO_2 nanocables decorated with laminated porous silicon oxycarbide (SiOC) ceramics by pyrolysis at low temperature, using cellulosic materials (filter paper) as a biomorphic template and silicon resin as a polymeric precursor. Li et al. [18] fabricated β-SiC nanowires arrays on a 6H-SiC substrate from a simple chemical vapor reaction by using Ni as the catalyst. Chen et al. [19] prepared hierarchical SiC nanowires by a simple thermal evaporation of carbonaceous silica xerogel. Li et al. [20] synthesized SiC nanowires starting from SiO_2, C_2H_5OH, and Mg in an autoclave at 200 °C. Gao et al. [21] reported triangular prism-shaped *p*-type 6H-SiC nanowires via the pyrolysis of polymeric precursors. Wei et al. [22] synthesized hexagonal-shaped SiC nanowires by a simple thermal reaction method between ball-milled activated carbon and vaporized silicon at 1600 °C without catalyst assistant. Besides, Wu et al. [23] also reported the synthesis of SiC nanowires by a reaction of multiwall carbon nanotubes (MWCNTs) and silicon vapor from molten salt medium at 1250 °C. However, it is essential to employ a simple route with low cost, low temperature, high yield for the synthesis of SiC nanowires.

In this paper, we report the $FeCl_2$-assisted synthesis of β-SiC nanowires by the carbothermal reduction of carbonaceous silica xerogel. The PL property of β-SiC nanowires was investigated.

2. Experimental procedure

2.1. Preparation of β-SiC nanowires

All chemical reagents were of analytical grade and used without further purification. A detailed synthesis process was described as follows. Firstly, 10 g of sucrose and 1.28 g of ferrous chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, AR) were dissolved in distilled water (30 ml) under electromagnetic stirring. Twenty-five milliliters of tetraethoxysilane (TEOS, AR) and oxalic acid solution (4.8% 4 ml) were slowly added into the above solution. A carbonaceous silica (C–Si) sol was obtained by stirring the solution at room temperature for 24 h. Hexamethylenetetramine solution (35.7% 2 ml) was added to speed up the gelation of the C–Si sol, and then the C–Si gel was obtained. The C–Si xerogel was obtained after drying the gel at 110 °C for 12 h. An alumina boat with the xerogel was placed in an alumina tube furnace, and heated to 1300 °C under a flowing argon atmosphere (200 ml/min) and maintained at this temperature for 6 h. Then the system was cooled down to room temperature naturally under the protection of argon. Finally, the white cotton-like products were obtained in the alumina boat.

2.2. Characterization

The crystalline phase of the white cotton-like products was characterized by X-ray powder diffraction (XRD) with a Rigaku D/max2500VPC diffractometer using CuKα radiation. IR spectrum of SiC was recorded on a Fourier transform infrared (FTIR, MAGNA550, KBr) spectrometer from the 400 to 2400 cm^{-1} range. The morphology and structure of the products was examined by scanning electron microscopy (SEM, JSM-5610LV) and high-resolution transmission electron microscopy (HRTEM, JEM-2010) equipped with energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED). Photoluminescence (PL) spectrum of the products was measured in a LS55 fluorescence spectrometer with a Xe lamp at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of the products prepared by carbothermal reduction of silica xerogel without and with $FeCl_2$ additives at 1300 °C for 6 h. From the XRD patterns, it can be seen that the diffraction peaks of the products have obvious difference. Fig. 1a indicates that the products prepared without $FeCl_2$ additives are amorphous SiO_2 phase [24], while SiC phases are not formed. This reveals that carbothermal reaction cannot occur at 1300 °C without $FeCl_2$ additives, and only SiO_2 and carbon are produced via the pyrolysis of xerogel. As Fig. 1b, the products have the strong and sharp diffraction peaks, which indicate that the product is well crystalline. The diffraction peaks at 35.8°, 41.5°, 60.2°, 71.9°, and 75.8° can be indexed as (1 1 1), (2 0 0), (2 2 0), (3 1 1), and (2 2 2) planes of β-SiC, respectively. The lattice constant of the SiC samples calculated from the XRD data is 4.354 Å for a, which is consistent with the known value of β-SiC (a=4.359 Å, JCPDS Card No. 29-1129) [17]. A strong diffraction peak at 45.6° marked with ⁎ in the XRD pattern is ascribed to the characteristic diffraction peak of Fe_3Si [25], which acts as a catalyst during the formation of SiC nanowires. In addition, a weak broad peak marked with AS at about 2θ=22° can be attributed to amorphous SiO_2 [24]. The XRD results suggest that $FeCl_2$ has an important effect on the formation of SiC in present experiment. Previous studies show that SiC was formed via vapor–solid (VS) mechanism in carbothermal reaction of SiO_2 xerogel without metal catalyst [26,27]. In VS mechanism, SiC was prepared through the following reactions:

$$SiO_2(s)+C(s)\rightarrow SiO(g)+CO(g) \tag{1}$$

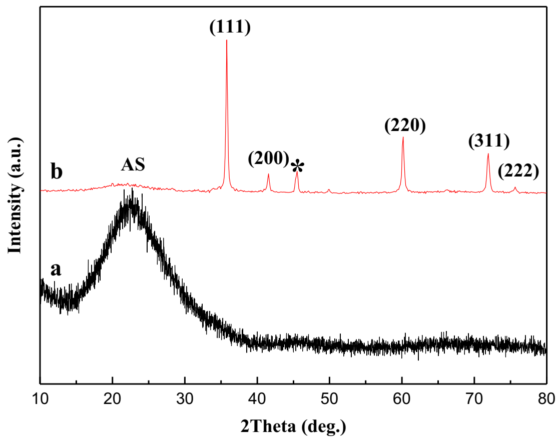

Fig. 1. XRD patterns of the products prepared by carbothermal reduction of silica xerogel without $FeCl_2$ additives (a) and with $FeCl_2$ additives (b).