Growth of β-SiC nanowires on Si(100) substrates by MOCVD using nickel as a catalyst

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Available online 23 July 2004

Abstract

We have deposited β-SiC nanowires on nickel-covered Si(100) substrates using a single molecular precursor at deposition temperature in the range of 800–1000 °C by metalorganic chemical vapor deposition (MOCVD) method and analyzed their surface and structural characteristics. Nickel played an important role in a catalyst as growing β-SiC nanowires. Dichloromethylvinylsilane (CH2CHSiC(CH3)Cl2) was used as a single molecular precursor without any carrier or bubbler gas. The working pressure was fixed at about 50 mTorr, and the growth of β-SiC nanowires was carried out for 0.5–3 h. SEM images clearly showed that straight nanowires were randomly grown on the substrate with a high density. The lengths of the nanowires were up to several micrometers and their diameters were about 30–50 nm depending on deposition temperature. In order to identify their structure and composition, analyses of X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscope (TEM) combined with energy dispersive X-ray (EDX) were performed. XRD data showed a well-crystallized structure with highly oriented nanowires to (111) and (200) planes. Through TEM and EDX analyses as well as XPS study, we can suggest that as-deposited β-SiC nanowires are wrapped with very thin carbon outer layer, and the wire was grown to [111] direction with well-crystallized structure. This means that our SiC nanowires can be one of the candidate materials for both nanoelectronic device applications and a field emitter due to carbon-rich composition.

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PMCs: 81.07.-b
Keywords: β-SiC; Nanowires; MOCVD; Ni catalyst; Single molecular precursor

1. Introduction

Silicon carbide (SiC) is a wide band gap semiconductor with many superior characteristics such as high breakdown field strength, high thermal conductivity, and high saturation drift velocity [1]. These excellent physical properties make SiC a promising semiconductor material for the fabrication of electronic devices [2]. Moreover, as an important wide band gap semiconductor with high electron mobility, cubic silicon carbide (β-SiC) nanowires would be favorable for applications in high temperature, high power, and high frequency nanoelectronic devices [3]. In addition, SiC wires exhibit good field-emitting properties [4]. A lot of methods have been developed to synthesize SiC nanorods or nanowires. Dai et al. [5] first succeeded in the synthesis of SiC nanorods in 1995 through the reaction of carbon nanotubes with SiO or Si + I2. Meng et al. [6] synthesized β-SiC nanorods by carbothermal reduction reaction, and Zhou et al. [7] fabricated SiC nanowires by the hot filament CVD method. Recently, Li et al. [8] synthesized SiC nanowires by using an SiC rod as the anode to arc-discharge. However, because these methods use various reactants and require high reaction temperatures (usually above 1200 °C), there are several difficulties at reaction process to synthesize SiC nanorods and nanowires on silicon substrates directly. Even though some groups synthesized SiC nanowires at low temperatures, they applied a high pressure [9]. Also, syntheses of SiC nanowires using metal as a catalyst have been reported [10,11].

In this study, therefore, we first deposited β-SiC nanowires on nickel-covered Si(100) substrates using a single molecular precursor at deposition temperature in the range of 800–1000 °C by high vacuum metalorganic chemical
vapor deposition (MOCVD) method and analyzed their surface and structural characteristics.

2. Experimental

Growth of \(\beta\)-SiC nanowire was achieved in homemade metalorganic chemical vapor deposition (MOCVD) system. First, nickel thin film of about 40–50 nm thickness was deposited on Si(100) substrate using radio frequency (RF) magnetron sputtering system. Nickel played an important role as a catalyst in growing \(\beta\)-SiC nanowires. The nickel-deposited Si(100) substrate was pretreated in an ultrasonic cleaner in the order of methanol, diluted HF, DI water, and acetone. Dichloromethylvinylsilane (\(\text{CH}_2\text{CHSiC(CH}_3\text{)Cl}_2\)), 97%) was used as a single molecular precursor that contains silicon and carbon atoms in the same molecule. Since there are Si-C bonds in our precursor, additional activation energy to make Si-C bond is not necessary. Moreover, dichloromethylvinylsilane is very volatile at low temperature, so it is not necessary to use any carrier or reactive gas. Therefore, this metalorganic source is very suitable for synthesis of \(\beta\)-SiC nanowire at low temperature. The base pressure of the MOCVD apparatus was \(5 \times 10^{-5}\) Torr, and the working pressure was kept at about 50 mTorr. The deposition temperature was 800–1000 °C, and the deposition was carried out for 0.5–3 h. Additional post-sintering process of the obtained nanowires was not demanded in this experiment.

The as-grown nanowires were first characterized by X-ray diffraction (XRD), and we could then confirm the shape of the \(\beta\)-SiC nanowires through scanning electron microscope (SEM) and transmission electron microscope (TEM) images. In order to identify their chemical composition, analyses of X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray (EDX) were performed. By means of the TEM images and transmission electron diffraction (TED) pattern, the structures of synthesized \(\beta\)-SiC nanowires were also analyzed.

3. Results and discussion

The structure of the nanowires has been characterized by using X-ray diffraction (XRD). Fig. 1 shows XRD patterns of deposited nanowires on the nickel-deposited Si(100) substrate at 50 mTorr and 900 °C for different reaction times. The noticeable thing was that the nanowire crystallinity, as well as length and diameter of nanowires, are not dependent on the growth time over 1 h. Only the deposition temperature was affected by the crystallinity, length, and diameter of nanowires. For example, by increasing growth temperature to 1000 °C, the crystallinity and initial growth rate are increased, and nanowires with longer lengths and wider diameters have been obtained at 1000 °C rather than those at 800 °C. The XRD patterns exhibit characteristic peaks of \(\beta\)-SiC at \(2\theta = 35.6^\circ, 41.4^\circ, \) and \(60.0^\circ, \) which are attributed to diffraction of \(\beta\)-SiC(111), (200), and (220) planes, respectively. These values are almost identical with the known values for \(\beta\)-SiC [JCPDS card No. 29-1129]. Peaks originating either from other phases of SiC or nickel were not observed. Conclusively, our XRD analysis showed that all deposited SiC nanowires have a zinc-blende structure.

Further evidence for the formation of \(\beta\)-SiC can be obtained through the X-ray photoelectron (XP) spectroscopy analysis. Fig. 2(a) shows the typical XP survey spectrum of an as-deposited \(\beta\)-SiC nanowire at 900 °C. It shows the strong XP peaks of Si2p and C1s as well as O1s. We infer that the O1s peak at binding energy of 531 eV is mainly attributed to the SiO2 and/or CO2 that formed by both oxidation reaction and adsorption at air condition. Fig. 2(b) and (c) show the Si2p and C1s high-resolution XP spectra of obtained \(\beta\)-SiC nanowire. For the case of Si2p (Fig. 2(b)), the spectrum can be decomposed to two Gaussian components located at 101.4 and 103.4 eV. These two Si states are attributed to SiC and SiO2. The spectrum of C1s (Fig. 2(c)) consists of three components centered at 282.5, 284.2, and 286.6 eV. The peaks at 282.5 eV correspond to C1s for SiC, and the other two C1s peaks can be attributed to a small amount of both the residual carbon originated from the metalorganic precursor and adsorbed CO2 on the SiC nanowire surface, respectively [11,12]. With these XPS quantification analysis, we thus obtained that \(\beta\)-SiC nanowire has an Si and C atomic ratio of about 1.0:1.2. Fig. 3 shows the typical scanning electron microscopy (SEM) images of the obtained \(\beta\)-SiC nanowires grown on (a) Ni powder-coated Si(100) substrate and (b) Ni thin film-deposited Si(100) substrates, respectively. It can be seen clearly that straight nanowires were randomly grown on the substrate with a high density, and the surface of deposited \(\beta\)-SiC nanowires looked rough. The average diameter of the nanowires was about 30–50 nm and their...
length was estimated at about several micrometers depending on growth temperature and packing density of catalyst on Si(100) surface. Through SEM images, we could confirm that the obtained β-SiC has a shape of nanowire.

To investigate in more detail the structure of as-deposited β-SiC, transmission electron microscope (TEM) combined with energy dispersive X-ray (EDX) analyses were performed. For TEM experiments, the β-SiC nanowires grown at 900 °C for 2 h were prepared by mechanically peeling off pieces of the nanowire samples from the substrate and dispersed into the methanol using ultrasonic cleaner and put on TEM grids for observation. Fig. 4(a) shows a typical TEM image obtained from a β-SiC single nanowire. The diameter of this wire was about 50 nm and it was decreased to 30 nm with decreasing deposition temperature. The lengths were also varied from about 5 to about 15 μm depending on growth temperature, and the body part of nanowire has numerous stacking faults. The inset image in Fig. 4(a) shows the corresponding selected area electron diffraction (ED) pattern obtained from the same sample of Fig. 4(a). The electron beam was injected into [110] direction that is perpendicular to the [111] growth direction. The ED pattern shows bright spots as well as streaks, indicating a single crystalline nature with some defects. It is known that since the electron diffraction pattern streaks are always perpendicular to the stacking fault, the existence of (111) stacking faults is confirmed by aligning the electron beam along the [110] direction of the β-SiC nanowires [9,13,14]. These stacking faults are generally thought to originate from thermal stress during the growth process [15]. The remarkable thing is that our β-SiC nanowire is wrapped with an amorphous layer with a thickness of about 1.5 nm. In previous published papers, this amorphous layer was reported to be a SiO₂ layer [9,16,17]. Li et al. [3] reported that the thick SiO₂ shell-wrapped β-SiC nanowire would not only reduce the electronic conductivity between the nanowires and their contacting electrodes, but also be unfavorable to the transmission of excitons and photoluminescence. In our EDX analysis (Fig. 4(b)), oxygen hardly appeared in the EDX spectrum. Because the metalorganic source used in this experiment does not have an oxygen component, there was no possibility of forming SiO₂ originating from the precursor. However, from the outer layer of β-SiC nanowire, the C peak is shown predominantly, while the Si peak is observed slightly. Atomic percentage ratio of Si and C in the surrounding layers was estimated to be 8.1:91.9, indicating a carbon-rich layer formation. Since the thickness of this wrapping layer was very thin (about 1.5 nm), C and Si contents were not obtained accurately. However, we can suggest that this layer is mostly composed of not amorphous SiO₂ but amorphous carbon or amorphous SiC. This means that our SiC nanowires could be one of the candidate materials for a field emitter due to carbon-rich stoichiometry.

Fig. 4(c) showed that EDX spectrum corresponding to the stem of a β-SiC nanowire. There are three peaks due to Si, C, and Ni. The peak originating from O is not observed again.
Through quantification analysis of the stem of a \(\beta\)-SiC nanowire, the average atomic percentage ratio of Si and C is estimated about 1.0:1.2. To understand the role of Ni as a catalyst, we attempted to grow SiC nanowires without metal catalyst under the same MOCVD conditions. Only an amorphous SiC thin film was deposited on Si(100) substrates. We thus confirm that the Ni metal should play an important role as a catalyst in growing \(\beta\)-SiC nanowires on Si(100) substrates. Furthermore, we can suggest that dichloromethylvinylsilane as a single MO source is very suitable for growing \(\beta\)-SiC nanowires at relatively low temperature (below 1000 °C) compared with separate sources.

### 4. Conclusions

Cubic silicon carbide (\(\beta\)-SiC) nanowires have been deposited on both nickel powder-coated Si(100) and nickel thin film-covered Si(100) substrates using a single molecular precursor at deposition temperatures in the range of 800–1000 °C by the metalorganic chemical vapor deposition (MOCVD) method. Dichloromethylvinylsilane (\(\text{CH}_2\text{CHSiC(CH}_3\text{)}\text{Cl}_2\)) was used as a single molecular precursor without any carrier or reactive gas to increase mass transportation or to remove contaminants in the nanowires. The initial growth rate of nanowires is strongly dependent on the deposition temperature. The length and width of nanowires are mainly controllable with deposition temperature rather than deposition time. XRD pattern showed that as-

![Fig. 3. Typical SEM images of the obtained \(\beta\)-SiC nanowires grown on (a) nickel powder-coated Si(100), and (b) nickel thin film-deposited Si(100) substrates.](image)

![Fig. 4. (a) High-resolution TEM image of a \(\beta\)-SiC nanowire grown at 50 mTorr and 900 °C for 2 h. Inset shows the electron diffraction pattern of the same sample; (b) and (c) show EDX spectrum obtained from (b) the border and (c) stem parts of \(\beta\)-SiC nanowire corresponding selected area.](image)
deposited SiC nanowires were cubic silicon carbide ($\beta$-SiC). Through TEM analysis, we can suggest that an amorphous carbon layer surrounds the as-deposited $\beta$-SiC nanowires, and the $\beta$-SiC nanowire has [111] growth direction with well-crystallized structure. XPS and EDX analyses showed that the as-obtained SiC nanowire has an atomic Si and C composition of about 1.0:1.2, suggesting possible applications for both electronic devices and field emitters.

Acknowledgements

This work was supported by the BK21 project of the Ministry of Education, Korea and the Ministry of Science and Technology in Korea (project No. M1021400278-02B1500-04211).

References