Growth of 3C-SiC nanowires on nickel coated Si(100) substrate using dichloromethylvinylsilane and diethylmethylsilane by MOCVD method

B.-C. Kang, J. S. Hyun and J.-H. Boo

Department of Chemistry, Sungkyunkwan University, Suwon 440-746 South Korea
chemcvd@skku.edu, memoriesed@skku.edu, jhboo@skku.edu

ABSTRACT

We have grown 3C-SiC nanowires on nickel coated Si(100) substrates using single source precursors by thermal metal-organic chemical vapor deposition (MOCVD) method. Dichloromethylvinylsilane ($CH_2CHSi(CH_3)Cl_2$) and diethylmethylsilane ($CH_3SiH(C_2H_5)_2$) were used as a single precursor without any carrier and bubbler gas. 3C-SiC nanowires with 40 ~ 100 nm diameter could grow on substrates at temperature as low as 900 ^oC. XRD pattern showed that SiC nanowires were cubic silicon carbide. TEM analysis showed that an amorphous carbon layer surrounds the as-deposited SiC nanowires, and the 3C-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.

Keywords: 3C-SiC, nanowire, MOCVD, Ni catalyst

1 INTRODUCTION

3C-SiC is an important material for the fabrication of electronic devices because it has a high thermal conductivity, high hardness, high wear resistance and excellent chemical resistance. Therefore it can operate at high power, high temperature and in harsh conditions. In the meantime, the miniaturization of devices is an irresistible trend for both industrial manufacture and academic research. Nanowires are interesting building blocks for the fabrication of various devices on nanometer scale. Therefore, the fabrication and understanding of the properties of SiC nanowires are thus decisive for the development of SiC based nanodevices. Various methods have been used to grow SiC nanowires. Among them, the easiest way is a chemical vapor deposition (CVD) method. However, conventional SiC CVD process requires high deposition temperature. Therefore, many research groups have tried to find suitable metal-organic (MO) precursors for growing SiC nano materials [1-7].

In this study, therefore, we have deposited 3C-SiC nanowires on nickel thin film deposited Si(100) substrates at as low as 900 ^oC by thermal MOCVD method using two kinds of single molecular precursors ; dichloromethylvinylsilane ($CH_2CHSi(CH_3)Cl_2$) and diethylmethylsilane ($CH_3SiH(C_2H_5)_2$). This paper will be present that the structural characteristics, compositions and surface morphologies of deposited 3C-SiC nanowires on nickel coated Si(100) substrates.

2 EXPERIMENTAL

Growth of 3C-SiC nanowires were performed in homemade vertical metal-organic chemical vapor deposition (MOCVD) system. We expected that nickel thin film plays an important role in growing 3C-SiC nanowires, so we prepared the nickel thin film as a catalyst of about 20 nm on Si(100) substrate using rf magnetron sputtering method. Si(100) substrate was pretreated in an ultrasonic cleaner in order of methanol, DI water, and acetone. Dichloromethylvinylsilane ($CH_2CHSi(CH_3)Cl_2$) and diethylmethylsilane ($CH_3SiH(C_2H_5)_2$) were chosen as a single molecular precursor because they have already Si-C bonds in them and are very volatile at low temperature. We can suggest that these two kinds of single molecules are very suitable for growing 3C-SiC nanowires at low temperature. The base pressure of the MOCVD system was 5×10^{-5} Torr, and the deposition pressure was kept at 50 mTorr. The deposition was carried out at 900 ^oC for 1 ~ 3 h. The as-grown nanowires were firstly characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). In order to further define the structure of the 3C-SiC nanowires, transmission electron microscope (TEM) images and transmission diffraction (TED) patterns were obtained. To identify the composition of the 3C-SiC nanowires, x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray (EDX) analysis were also carried out.

3 RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of the 3C-SiC nanowires deposited on nickel deposited Si(100) substrates under 50 mTorr, 900 ^oC for 3 h. using (a) dichloromethylvinylsilane and (b) diethylmethylsilane. They show the crystalline peaks at 2θ = 35.6^o, 41.4^o and 60.0^o, which are good attributed to diffraction of the 3C-SiC(111), (200) and (220) planes, respectively. Peaks from either the other phases of SiC or the nickel catalyst are not appeared. The SiC nanowires grown by two different kinds of precursors show the same diffraction pattern and tendency. However, the 3C-SiC nanowire grown by dichloromethylvinylsilane shows a good crystallinity than that of the SiC nanowire deposited by diethylmethylsilane. Conclusively XRD analysis show that the deposited 3C-SiC nanowire on nickel deposited Si(100) substrate has a poly crystalline zinc-blende structure at 900 ^{o}C, and the 3C-SiC nanowire from dichloromethylvinlysilane as a precursor has good crystallinity than that from diethylmethylsilane precursor.

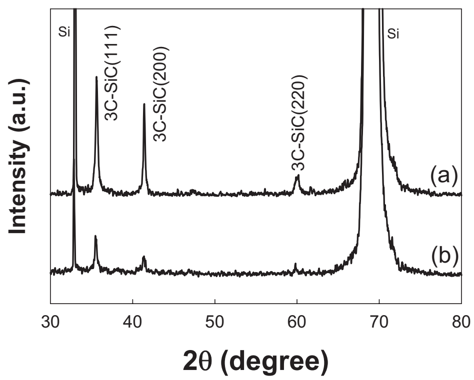

Fig. 1. XRD patterns of the 3C-SiC nanowires deposited on nickel deposited Si(100) substrates under 50 mTorr, 900 ^{o}C for 3 hr. using (a) dichloromethylvinylsilane and (b) diethylmethylsilane.

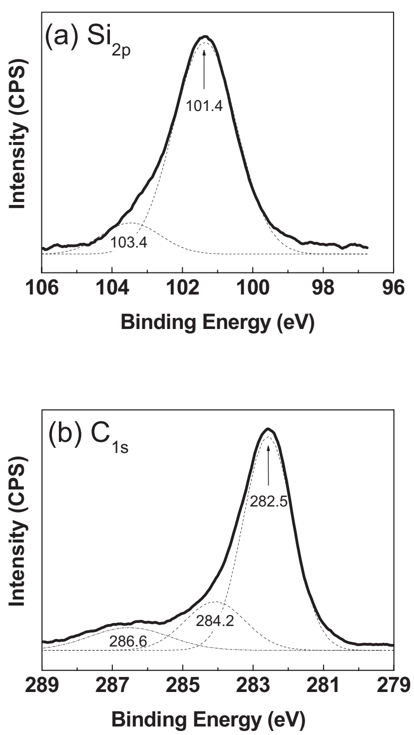

Fig. 2. Typical XPS high resolution spectra of the 3C-SiC nanowires grown on nickel covered Si(100) at 900 ^{o}C : (a) and (b) show Si_{2p} and C_{1s} peaks, respectively.

Further evidence for the formation of 3C-SiC can be obtained through the XPS analysis. The typical XP survey spectrum (not shown here) of an as-deposited 3C-SiC nanowire at 900 ^{o}C shows the strong XP peaks of Si_{2p} and C_{1s} as well as O_{1s}. We infer that the O_{1s} peak at binding energy of 531 eV is mainly attributed to the SiO_2 and/or CO_2 that formed by both oxidation reaction and adsorption at air condition. Fig. 2(a) and 2(b) show the Si_{2p} and C_{1s} high-resolution XP spectra of obtained 3C-SiC nanowires. For the case of Si_{2p} (Fig. 2(a)), the spectrum can be decomposed to two Gaussian components located at 101.4 eV and 103.4 eV. These two Si states are attributed to SiC and SiO_2. And the spectrum of C_{1s} (Fig. 2(b)) consists of three components centered at 282.5 eV, 284.2 eV, and 286.6 eV. The peaks at 282.5 eV correspond to C_{1s} for SiC, and the other two C_{1s} peaks can be attributed to a small amount of both the residual carbon originated from the metalorganic precursor and adsorbed CO_2 on the SiC nanowire surface, respectively. With these XPS quantification analysis, we thus obtained that 3C-SiC nanowire has an atomic ratio of Si and C to be about 1.0:1.2.

Fig. 3 shows the typical SEM images of the obtained 3C-SiC nanowires grown by (a) dichloromethylvinylsilane and (b) diethylmethylsilane at 900 ^{o}C. It can be seen clearly that straight nanowires are randomly grown on the substrate with a high density. The differences of two SEM images are the thickness and length of grown SiC nanowires. In the case of dichloromethylvinylsilane as a precursor (Fig. 3(a)), about 40 ~ 100 nm diameter and over 10 μm nanowires can grow easily. However, in the case of diethylmethylsilane (Fig. 3(b)), deposited SiC nanowires show that the thicker and shorter SiC nanowires, and the surface roughness looks very high than that do Fig. 3 (a).

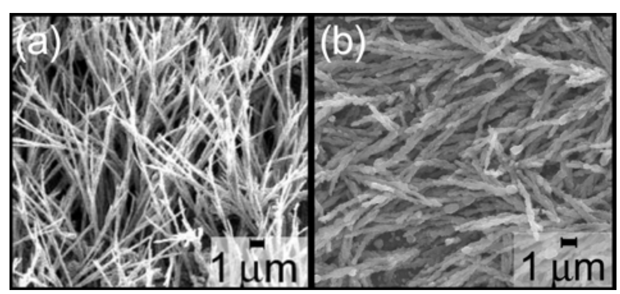

Fig. 3. Typical SEM images of the obtained 3C-SiC nanowires grown by (a) dichloromethylvinylsilane and (b) diethylmethylsilane at 900 ^{o}C.

To investigate more detail structure of as-deposited β-SiC nanowire, TEM combined with EDX analyses were performed. For TEM experiments, the 3C-SiC nanowires grown at 900 ^{o}C were prepared. Fig. 4 shows a typical TEM image obtained from a 3C-SiC single nanowire. TEM analysis results exhibit the grown 3C-SiC nanowires with a diameter of about 100 nm, and these are wrapped with an amorphous layer with the thickness of about 2 nm. We can confirm that this layer is amorphous carbon by EDX data. Because the metal-organic sources used this experiment contains lots of carbon contents, we could guess that this amorphous carbon layer was originated from the precursor. Also, TEM image of this nanowire shows that they are crystalline, but showing that they have defects, including numerous stacking faults, etc. We speculate that the nanowire was grown via the vapor-liquid-solid (VLS) process from a nickel-containing catalytic droplet, although the catalytic droplet was not observed at the ends of the nanowire because the nanowire was broken and the droplet was removed during the ultrasonic treatment. Based on this speculation, we can thus guess that changes in diameter and well-defined facets can be recognized from the 3C-SiC nanowire grown via the VLS process from catalytic droplet. Theses two features indicate that stick-slip motion occurred during the growth; when sticking, the diameter, which was defined by the area of the LS interface, increased to form energetically favorable facets. When growing along the facets, the diameter became larger, then the wetting angle became smaller and the component of VL interface tension in the LS interface became larger. Eventually the droplet slipped driven by LS and VL interface tensions resulting in an abrupt decrease in diameter [8]. The inset image (left) of Fig. 4 shows the corresponding selected area electron diffraction (ED) pattern obtained from the same sample. It shows the bright spots corresponding to 3C-SiC(200) and (111), and streaks, which are perpendicular to the stacking faults. These stacking faults are generally thought to originate from thermal stress during growth process [7]. EDX spectrum corresponding to the stem of a 3C-SiC nanowire was also investigated. There are only three peaks due to Si, C, and Ni. Through quantification analyses of the stem of a 3C-SiC nanowire, an average atomic % ratio of Si and C is estimated about 1.0:1.2, while that of surface regime wrapped with carbon is observed about 1.0:11.5, respectively.

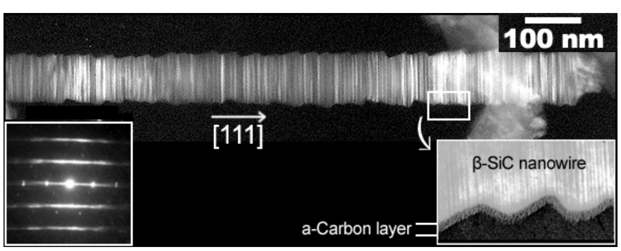

Fig. 4. Typical TEM image of single 3C-SiC nanowire grown at 900 ^{o}C. Inset (left) shows the electron diffraction pattern of the same sample, and insert (right) shows a zoom-image of 3C-SiC nanowire.

4 CONCLUTIONS

Cubic silicon carbide (3C-SiC) nanowires have been deposited on nickel thin film deposited Si(100) using a single molecular precursor at 900 ^{o}C by the metal-organic chemical vapor deposition (MOCVD) method. Dichloromethylvinylsilane ($CH_2CHSi(CH_3)Cl_2$) and diethylmethylsilane ($CH_3SiH(C_2H_5)_2$) were used as a single precursor without any carrier and bubbler gas to increase mass transportation or to remove contaminants in the nanowires.

XRD and SEM analyses show that the deposited 3C-SiC nanowire on nickel deposited Si(100) substrate has a poly crystalline zinc-blende structure at 900 ^{o}C, and the 3C-SiC nanowires from dichloromethylvinylsilane as a precursor have good crystallinity and narrow nanowires with smooth surface than that from diethylmethylsilane. High-resolution TEM analysis showed a detailed structure that amorphous carbon layer surrounds the as-deposited 3C-SiC nanowires, and the 3C-SiC nanowire has [111] growth direction with well-crystallized structure. Based on the XPS and EDX analyses, near same atomic composition ratio of Si to C (1.0:1.2) was obtained, indicating carbon rich species on surface regions, suggesting possible applications to both electronic devices and field emitter.

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