Single source fabrication of SiC nanowires and FTIR spectroscopy

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Silicon carbide (SiC) nanostructures continue to attract interest due to their applications in optoelectronic devices, sensors, and high-power/high temperature electronics. SiC nanowires have been fabricated by chemical vapor deposition using hexamethyldisilane (HMDS) as the source material with various catalysts including iron, nickel, and cobalt at temperatures between 900 and 1100°C under H_2. The SiC nanowire diameters are in the range of 8 nm to 90 nm. High density of SiC nanowires have been successfully grown even at a low temperature of 900°C. SiC nanowire growth mechanism (VLS) and a reaction scheme for the low temperature growth have been discussed. A comprehensive FTIR spectroscopy investigation of the SiC nanowires grown with various catalyst materials at different temperatures has been provided. Further, the differences of phonon states of SiC nanowires compared to the bulk SiC have been studied. The SiC TO mode absorption shifted significantly towards the low wavenumber region compared to bulk SiC. Moreover, the FWHM values of the TO mode absorption of the SiC nanowires (12cm^{-1}) are significantly lower than that of bulk SiC (59cm^{-1}). These results suggest that FTIR provides valuable and practical information about the chemical bond states and crystal quality of the nanostructured materials.

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1. Introduction

Silicon carbide is a wide band-gap semiconductor material with many superior properties, such as high electron mobility, high thermal conductivity, high mechanical strength, and high radiation resistance [1-4]. These superior properties make SiC an excellent material for applications in many areas including optoelectronics, thermoelectric devices, microelectronics (high temperature, high power, and high frequency as solid state transformers and inverters), and biomedical applications [5]. Furthermore, nanoscale materials exhibit unique properties differing from bulk materials. Due to these unique properties, SiC nanostructures present even more advantages in some applications such as gas sensors, blue LEDs, UV photodetectors, field emission devices [6-8], and field-effect transistors [9] due to their superior properties at nanoscale. However, integration of these nanostructures to the large-scale manufacturing is still a major challenge for researchers and engineers. Owing to the very promising applications, significant research has been devoted to the synthesis of 1D-SiC nanostructures with various fabrication methods. These fabrication methods include chemical vapor deposition [10-11], carbon thermal reduction [12], metalorganic chemical vapor deposition (MOCVD) [13-14]. CVD has been the most widely used method to fabricate nanostructured materials due to its low cost, high yield, simplicity of operation, and possibility of enabling direct device fabrication on pre-patterned substrates.

This paper presents CVD growth of SiC nanowires using hexamethyldisilane as the single source material with various catalyst materials. We will provide a comparative Fourier transform infrared spectroscopy investigation of the SiC nanowires grown with various catalyst materials. FTIR provides valuable and practical information about the chemical bond states of materials. Further, we will discuss the differences of phonon states of SiC nanowires compared to bulk materials. Furthermore, the study also presents low temperature growth of high-density SiC nanowires.

2. Experimental details

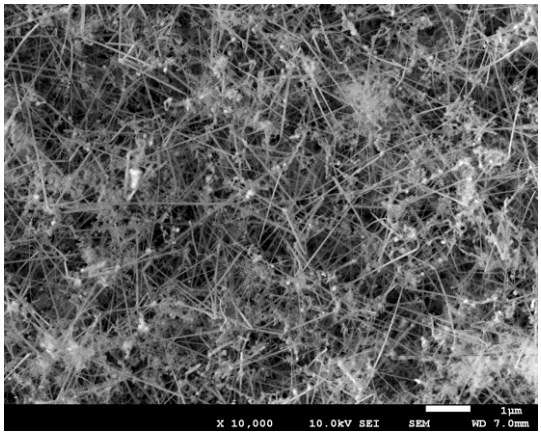
SiC nanowires were grown in a resistively heated hot-wall 25-mm horizontal low pressure CVD reactor. Si and SiO_2/Si substrates were used for growth. Various catalyst materials, including iron film (0.8 nm), nickel film (20 nm), and cobalt nanoparticles (25 nm) have been used. Fe-film and Ni-film were pre-deposited on SiO_2/Si and Si substrate by sputtering, respectively. Cobalt nanoparticle solution was applied to the Si substrate by micropipette. The growth runs have been carried out at temperatures between 900 and 1100°C under H_2 as both carrier and source dilution gas at atmospheric pressure. The substrate was ultrasonically cleaned in acetone, isopropyl alcohol,

de-ionized water and dried with nitrogen. Nanoparticle solution was applied to the substrate surface and dried. A quartz boat containing the substrate was loaded into the CVD reactor. Then, the reactor was evacuated and purged three times with hydrogen (99.999 %). After purging cycles, the reactor was heated to targeted growth temperature (typically between 900 and 1100^{o}C) under carrier gas. Then, the HMDS was introduced to the reactor for typically about 15 min. HMDS ($Si_2(CH_3)_6$) is a liquid metalorganic precursor. The HMDS and H_2 gas flow rates were controlled by mass flow controllers and set to 5 and 500 standard cubic centimetres per minute (sccm), respectively. After the growth, the HMDS precursor was shut off and the reactor cooled down under H_2 flow until 250^{o}C. Then, the furnace cooled down to room temperature.

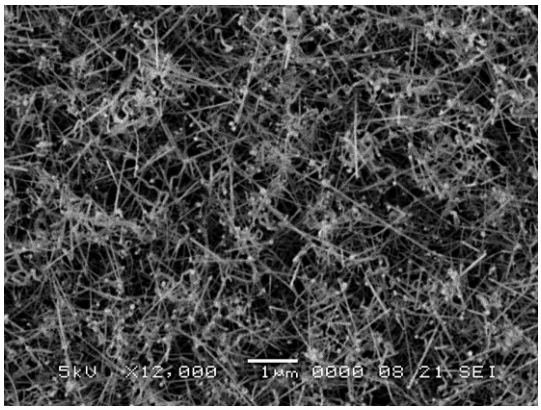
The samples have been characterized by scanning electron microscopy (SEM, JEOL JSM 6060 and JEOL 7600F SEM with Oxford Inca EDS), x-ray diffraction (XRD, Rigaku 300 and Bruker D8 Discover), transmission electron microscopy (TEM, JEOL JEM 1011), and Fourier transform infrared spectroscopy (FTIR) (FTS 7000 Series DigiLab with UMA 600 microscope).

3. Results and discussion

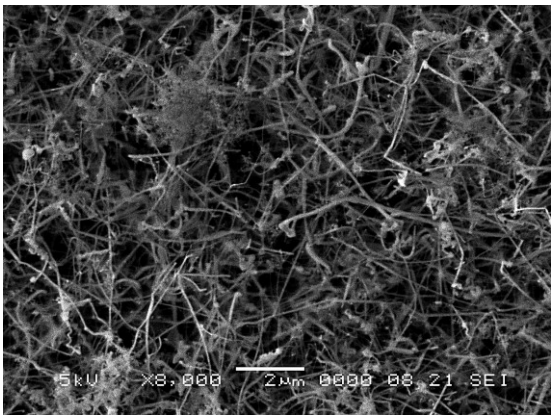
Fig. 1 shows SEM images of dense SiC nanowires grown at 1100^{o}C on Fe-film, Ni-film, and Co nanoparticles on SiO_2/Si and Si substrates. The SEM images show that large quantities of SiC nanowires with high aspect ratio have been synthesized with different catalysts. Majority of SiC nanowires grown with Fe and Ni-film catalysts are straight, while the majority of the nanowires grown with Co nanoparticles are curved. Nanowires are relatively long with typical lengths about ten microns. The SiC nanowires mean diameter grown on Fe is about 31.5 nm with a standard deviation of 4.9. Similarly, the SiC nanowires mean diameter grown on Ni is about 29.5 nm with a standard deviation of 6.1. However, the SiC nanowires mean diameter grown on Co nanoparticles is about 49.5 nm and occasionally nanowire diameter can reach to 90 nm. It is crucial mentioning that the metal catalysts were observed at the end of the nanowires. This observation indicates that SiC nanowire growth has taken place via vapour–liquid–solid (VLS) growth mechanism [15]. In the VLS mechanism, the metal droplet acts as a catalyst for decomposing the crystalline constituents. As the constituents for nanostructures become supersaturated within the liquid solution, crystal growth proceeds by precipitation of source materials from the solid/liquid interface. In general, the VLS mechanism results in highly anisotropic nanostructures, since nucleation and growth process is mainly controlled by the liquid catalyst droplet.



(a)



(b)



(c)

Fig. 1. SEM images of high density of SiC nanowires grown at 1100^{o}C with different catalysts: (a) Fe-film, (b) Ni-film, and (c) Co nanoparticles.

Next, XRD measurements were carried out using Cu K_α radiation (λ = 0.154 nm) to determine the structure of the SiC nanowires and typical spectra are shown in Figure 2. The diffraction peaks in the spectrum were indexed to a cubic zinc blende crystal structure. The lattice constant derived from the peak position is 0.437 nm, which agree well with the reported values of SiC crystals [JCPDS card No. 29-1129]. The main diffraction peak and its position from SiC nanowires is (111) at 35.65^{o}. Furthermore, the two intense peaks which exist at 32.9^{o} and 69.3^{o} in the diffraction pattern are related to Si substrate. No

characteristic peak associated with other crystalline forms or phases was detected in the XRD spectrum. This suggests that the grown SiC nanowires consist of only one crystalline phase.

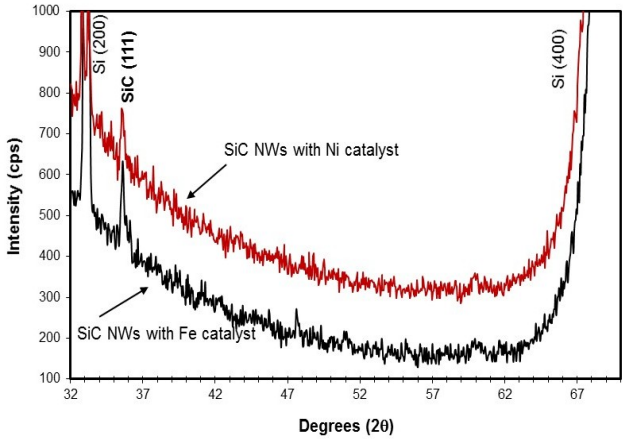


Fig. 2. XRD spectra of the SiC nanowires grown with Fe and Ni catalysts indicating cubic zinc blende structure (using Cu K_α radiation).

Next, in attempts to lower the growth temperature, the deposition has been carried out at 900°C. Figure 3 shows SEM image of the SiC nanowires grown at 900°C with Ni-film catalyst. It is very important to emphasize that high density of SiC nanowires have been achieved at a relatively low temperature of 900°C with respect to the decomposition temperature of HMDS precursor. The possible reaction scheme for the low temperature deposition of the SiC nanowires from the HMDS precursor can be described as follows: First, HMDS is decomposed at temperatures below 1100°C and primarily forms $(CH_3)_3Si$ (trimethylsilane) radicals by breaking the silicon-silicon bond. Then, $SiMe_2CH_2$ radical is formed by extracting hydrogen from the $SiMe_3$ [16]. The $SiMe_2CH_2$ radical eliminates CH_4 to form MeSiCH. Then, the MeSiCH radicals could form SiC by undergoing several decomposition steps through eliminating CH_4, C_2H_4, and H_2. Furthermore, the growth of high density of SiC nanowires at 900°C suggests that Ni promotes SiC nanowire formation acting as a very efficient catalyst.

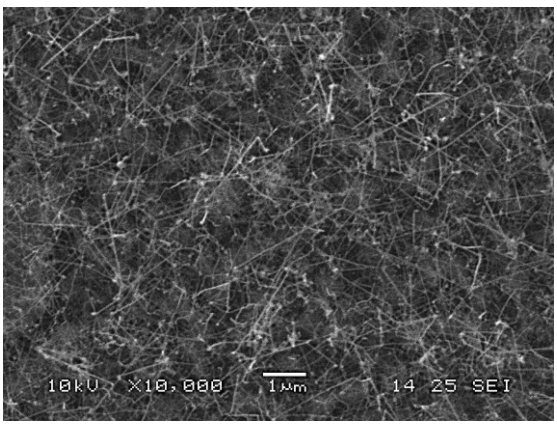


Fig. 3. SEM image of high-density SiC nanowires grown at 900°C with Ni-film catalyst.

Transmission electron microscopy was performed to characterize the morphology and diameter of the nanowires. The TEM specimen was prepared by scraping nanowires from the substrates to the carbon-coated copper grids. Figure 4 shows the TEM images of the SiC nanowires with diameters ranging from 8 nm to 60 nm. It is worth noting that particularly the straight nanowires have high density of planar defects observed by the dark lines perpendicular to the axis of the nanowires.

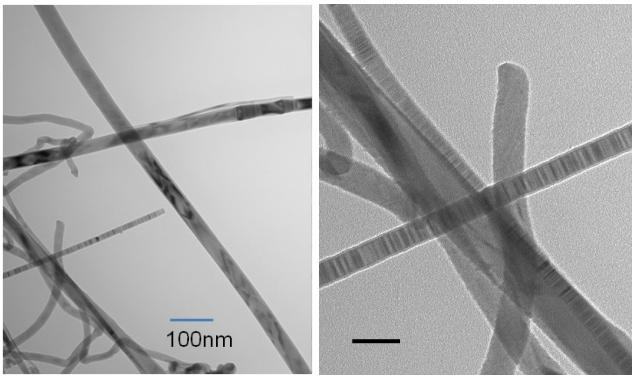


Fig.4. TEM images of the SiC nanowires showing the planar defects perpendicular to the axis of the nanowires (scale bar in Fig. 4b is 40 nm).

The {111} planes are the faces with lower energy in cubic zinc blende structures promoting the growth of nanowires along {111} planes. Planar defects like stacking faults in <111> oriented nanowires form perpendicular to the growth direction. These defects release the local stresses which are caused by any kind of disturbances in growth conditions.

FTIR provides valuable and practical information about the chemical bond states of the materials. Fig. 5 shows the FTIR spectra of the SiC nanowires grown on Si substrate with Ni-film catalyst at the temperatures of 1100°C, 1050°C, 1000°C, and 900°C, respectively. Table 1 shows the peak positions and full-width-at half-maximum (FWHM) values of SiC transverse optical (TO) mode absorption. As seen in Figure 5, the spectra of the SiC nanowires have revealed strong absorption bands with a very small variation. In fact, the TO Si-C bond ranges from 782 to 784cm^{-1}; the broad longitudinal optical (LO) Si-C bond located between 900 and 970cm^{-1}. The Si-C (TO) bond positioned at about 782cm^{-1} at the temperatures of 1100°C, 1050°C and 1000°C, and 784 cm^{-1} at 900°C, respectively. It can be seen that there is no obvious shift, while broadening of the peak is observed as the growth temperature is lowered. As noted in Table 1, the FWHM values of the Si–C absorption band are increasing ranging from 13cm^{-1} to 31cm^{-1} by decreasing the growth temperature. This suggests a slight reduction in the crystal quality of SiC nanowires as the growth temperature is reduced. Therefore, the Si–C bonding structure and the crystallinity of the SiC nanowires were improved with the increase of the growth temperature. It is important to note that the TO peaks shifted significantly towards the low wavenumber region compared to the bulk SiC reported

earlier (@ 800cm^{-1}) [17]. This could be due to the confinement effects of 1D nanostructures. Moreover, the FWHM values of the SiC nanowires are significantly lower than that of bulk SiC (59 cm^{-1}) [17] indicating better crystal quality of the SiC nanowires.

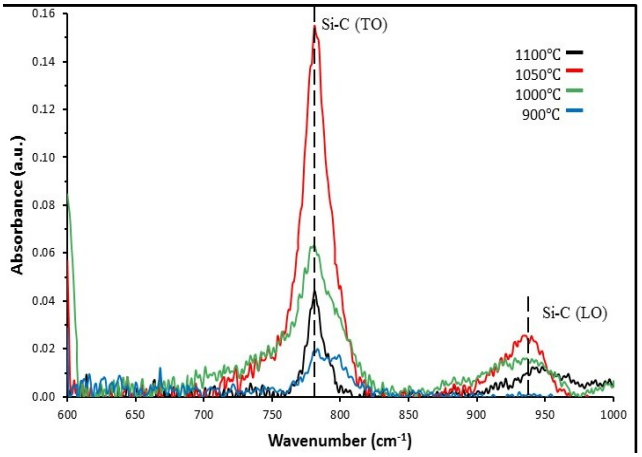


Fig. 5. Infrared spectra of SiC nanowires grown with Ni-film catalyst at temperatures of 1100°C, 1050°C, 1000°C, and 900°C.

Table 1. The peak positions (TO) and FWHM values of SiC absorption band obtained by FTIR spectrum measurements of the SiC nanowires grown with Ni-film catalyst.

Growth Temperature (°C)	SiC TO peak positions (cm^{-1})	FWHM of the SiC (TO) absorption band (cm^{-1})
1100	782	13
1050	782	18
1000	782	22
900	784	31
3C-SiC single crystal [17]	800	59

Fig. 6 shows typical FTIR absorption spectra of the as-grown SiC nanowires grown with Fe-film catalyst. The peak positions and the FWHM values of the main absorption band of Si-C bond are summarized in Table 2. As shown in Fig. 6, the spectra of the SiC nanowires revealed the presence of strong absorption band with maxima in the ranges of 783-793 cm^{-1} (transverse optical (TO) Si-C bond) and 900-970 cm^{-1} (longitudinal optical (LO) Si-C bond). The SiC TO band is observed at 783 cm^{-1}, 790 cm^{-1}, 790 cm^{-1}, 793 cm^{-1} at temperatures of 1100°C, 1050°C, 1000°C, and 950°C, respectively. The FWHM values of Si–C absorption band increasing from 21 cm^{-1} at the temperature of 1100°C to 36 cm^{-1} for SiC nanowires at the temperature of 950°C indicates that the bonding uniformity of the deposited SiC nanowires decreases by reducing the growth temperature.

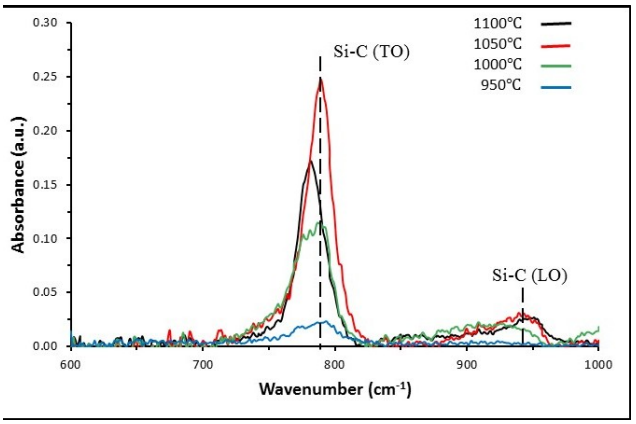


Fig. 6. Infrared spectra of SiC nanowires grown with Fe-Film catalyst at growth temperatures of 1100 °C, 1050 °C, 1000 °C, and 950 °C.

Table 2. The peak positions (TO) and FWHM values obtained by FTIR spectrum measurements of the SiC nanowires grown with Fe-film catalyst.

Growth Temperature (°C)	SiC TO peak positions (cm^{-1})	FWHM of the SiC (TO) absorption band (cm^{-1})
1100	783	21
1050	790	20
1000	790	27
950	793	36

The Si-C (TO) stretching absorption band ranges from 783 cm^{-1} to 793 cm^{-1} with the FWHM values from 20 cm^{-1} to 36 cm^{-1} with Fe-film catalyst, while the Si-C (TO) stretching absorption band ranges from 782 cm^{-1} to 784 cm^{-1} with the FWHM values from 13 cm^{-1} to 31 cm^{-1} with Ni-film catalyst. It can be seen that the variation of the Si-C TO peak positions of the SiC nanowires with Fe catalyst is slighly higher than that of with Ni catalyst. Moreover, the FWHM values of the Si–C bond of SiC nanowires with Fe catalyst are slightly higher than that of with Ni catalyst. Nevertheless, both Ni and Fe catalysts result in high quality SiC nanowires with very sharp absorption peaks compared to bulk single crystal SiC (FWHM 59 cm^{-1}) reported previously [17].

In addition to the Fe and Ni catalysts, the FTIR measurements were conducted on SiC nanowires grown with Cobalt catalyst. The results are very similar to the aforementioned catalysts such that strong and sharp absorption peak corresponding to the stretching vibration of the SiC TO mode is observed at 781cm^{-1} with the FWHM value of 12cm^{-1} indicating very high crystal quality of SiC nanowires. It is also worth mentioning that a broad SiC LO mode absorption has been observed from the FTIR measurements, that is unique to small size diameter nanowires. Since, electromagnetic waves cannot

interact with longitudinal phonons in an infinite crsytal. However, it is expected to see longitudinal optical resonances from the SiC nanowires, when the diameter of nanowires is small compared to the incoming wavelength of the radiation [18]. These results show that FTIR provides important and practical information about the chemical bond states and crystal quality of the nanostructured materials.

4. Conclusions

The synthesis of SiC nanowires by chemical vapor deposition using hexamethyldisilane as the source material with various catalysts has been presented. High density of SiC nanowires have successfully been grown even at a low temperature of 900^{o}C. SiC nanowire growth mechanism (VLS) and a reaction scheme for the low temperature growth have been discussed. A comprehensive FTIR spectroscopy investigation of the SiC nanowires grown with various catalyst materials at different temperatures has been provided. Further, the differences of phonon states of SiC nanowires compared to the bulk SiC have been observed. The SiC TO mode absorption shifted significantly towards the low wavenumber region compared to the bulk SiC. Moreover, the FWHM values of the TO mode absorption of the SiC nanowires (12cm^{-1}) are significantly lower than that of bulk SiC (59cm^{-1}). In brief, FTIR provides valuable, practical, and quick information about the chemical bond states and crystal quality of the nanostructured materials.

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