Fourier Transform Infrared Spectroscopy of Silicon Carbide Nanowires

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ABSTRACT

Silicon carbide (SiC) nanowires have been grown on by hexamethyldisilane (HMDS) using iron and nickel catalysts at temperatures between 900 and 1100℃ under H_2. The morphologies and bonding states were investigated by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). The results show that the as-synthesized nanowires are high-quality crystals with high aspect ratios. Moreover, high density of SiC nanowires have been successfully grown even at a low temperature of 900℃. Additionally, it has been observed that the phonon states of SiC nanowires are different from the bulk SiC. The SiC TO mode shifted to lower wavenumber compared to bulk SiC. Furthermore, the FWHM value of the TO mode absorption of the SiC nanowires is only 13cm^{-1}, which is lower than that of bulk SiC (59cm^{-1}). The sharp and consistent TO modes indicate very good bonding uniformity of the SiC nanowires.

Keywords: Fourier transform infrared spectroscopy, SiC nanowires, chemical vapor deposition

1 INTRODUCTION

One-dimensional (1D) nanostructures, particularly nanowires, have been proven to be promising materials for nanoelectronics, photocatalysis and other fields of modern nanotechnologies due to their unique physical, optical, mechanical, chemical, and electrical properties [1–2]. Silicon carbide (SiC), which is an important wide band-gap semiconductor, exhibits superior properties such as high thermal conductivity, excellent physical and chemical stability, high break down field strength, and high saturation drift velocity [3]. These excellent properties make SiC suitable for high frequency, high temperature and high power electronic and sensor applications [4]. The prominent mechanical properties of SiC nanowires make them excellent materials for the reinforcement of metal, ceramic, and polymer matrix composites. In addition, SiC nanowires also show enormous application potentials in field emission displays, nanoscale electronic devices, nanosensors and optoelectronic devices [5,6]. For example, SiC nanowire field effect transistors (SiC-NWFETs) are expected to be able to operate at temperatures higher than their Si-based counterparts. Furthermore, various methods for synthesizing SiC nanowires have been developed, such as chemical vapor deposition (CVD) method [7], thermal evaporation method [8], carbothermic method [9], high-frequency induction heating technology [10], and arc process [11].

Fourier transform infrared (FTIR) spectroscopy provides important and practical information about chemical bond states of materials. In this paper, SiC nanowires grown by CVD using hexamethyldisilane as the single source material with various catalyst materials at different temperatures are investigated by FTIR spectroscopy. Further, we will discuss the differences of phonon states of SiC nanowires compared to bulk materials. Moreover, the study also presents low temperature growth of high-density SiC nanowires and the decomposition temperature of the HMDS precursor with the presence of the catalysts.

2 EXPERIMENTAL DETAILS

SiC nanowires were grown on SiO_2/Si substrate with various catalyst materials, including iron and nickel film. The SiC nanowires were deposited in a resistively heated hot-wall 25-mm horizontal low pressure CVD reactor, employing hexamethyldisilane (HMDS) as the precursor. HMDS ($Si_2(CH_3)_6$) is a liquid metalorganic precursor. Fe-film and Ni-film were pre-deposited on SiO_2/Si and Si substrate by sputtering. The growth has been carried out between 900 and 1100ºC at a H_2 flow rate of 500 standard cubic centimeters per minute (sccm). The substrate was ultrasonically cleaned in acetone, isopropyl alcohol, de-ionized water and dried with nitrogen. A quartz boat containing the substrate was loaded into the CVD reactor. Then, the reactor was evacuated and purged with hydrogen (99.999%). After purging cycles, when the growth temperature is reached, HMDS was introduced to the reactor for typically about 15 min with a flow rate of 5 sccm. At the end of the growth, the HMDS precursor was shut off and the reactor cooled down under H_2 flow until 250ºC. Then, the furnace cooled down to room temperature.

FTIR spectroscopy is a valuable and rapid analytical technique that provides information about composition (qualitative) and bonding states of materials. Infrared spectroscopy was carried out by FTIR in absorption mode and the spectra were recorded in the range of 600-1000 cm^{-1}. From the FTIR spectra of the nanowires, the stretching-mode peak shift of the Si-C (TO) and Si-C (LO) bonds were investigated.

The grown nanowires have been characterized by scanning electron microscopy (SEM, JEOL JSM 6060 and JEOL 7600F SEM with Oxford Inca EDS) and Fourier

transform infrared spectroscopy (FTIR) (FTS 7000 Series DigiLab with UMA 600 microscope).

3 RESULTS AND DISCUSSION

Figure 1 shows SEM image of the dense SiC nanowires grown at 1100ºC with catalyst Ni-film. Large quantities of SiC nanowires with high aspect ratio have been synthesized with different catalysts.

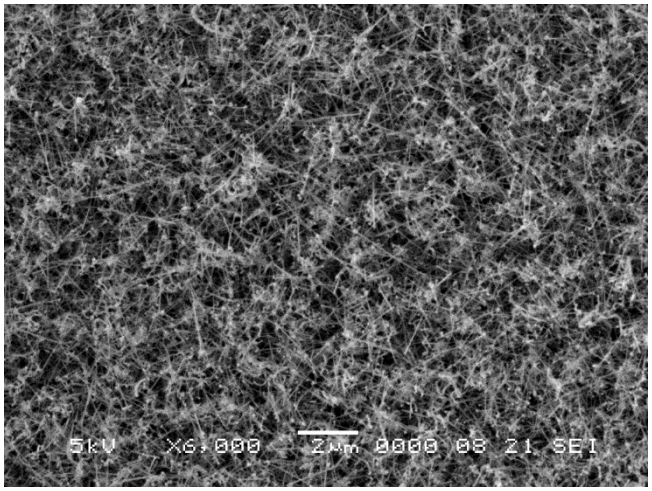

Figure 1. SEM image of high density of SiC nanowires grown at 1100 ℃ with catalyst Ni-film.

The SEM image shows that majority of SiC nanowires grown with Ni-film catalyst are straight and the SiC nanowire diameters are about 30 nm. Nanowires are relatively long with typical lengths of several tens of microns.

The metal catalysts were observed at the end of the nanowires, which demonstrates that SiC nanowire has been grown by vapor–liquid–solid (VLS) growth mechanism [12]. Furthermore, the growth of high density of SiC nanowires at 900ºC indicates that catalyst Ni promotes the formation of SiC nanowire.

High density of SiC nanowires have been produced at a relatively low temperature of 900ºC by decomposition of HMDS precursor. First, at temperatures below 1100ºC, HMDS decomposition has been shown to be first order forming $(CH_3)_3Si$ (trimethylsilane) radicals by breaking the silicon-silicon bond.

$$[CH_3]_3\ Si - Si\ [CH_3]_3 \rightarrow 2\ (CH_3)_3\ Si$$

Then, H_2, CH_4, C_2H_4, and Me_3SiH can form by extracting hydrogen from the $SiMe_3$ [13].

$$[CH_3]_3\ Si + H \rightarrow [CH_3]_2\ Si + CH_4$$

$$[CH_3]_2\ Si \rightarrow C_2H_4 + SiH_2$$

$$[CH_3]_2\ Si \rightarrow C_2H_2 + H_2 + SiH_2$$

$$H{+}[CH_3]_3\ Si - Si\ [CH_3]_3 \rightarrow [CH_3]_3\ Si\ H{+}[CH_3]_3\ Si$$

Then, due to the hydrogen in the carrier gas, SiC is formed by the reaction of carbosilanes [14].

$$H_2Si[CH_3]_2 + C_2H_4 \rightarrow SiC + 3CH_4$$

The reaction leads to the ralease of methane (CH_4), but consumes ethylene (C_2H_4). The amount of methane decreases rapidly at temperature above 1000℃ [14].

Figure 2 shows the FTIR spectra of the SiC nanowires formed on Si substrate with catalyst nickel film at temperatures of 1100℃, 1050℃, 1000℃, and 900℃, respectively. Table 1 shows the peak positions and full width at half maximum (FWHM) values of the main stretching transverse optical (TO) Si–C absorption band.

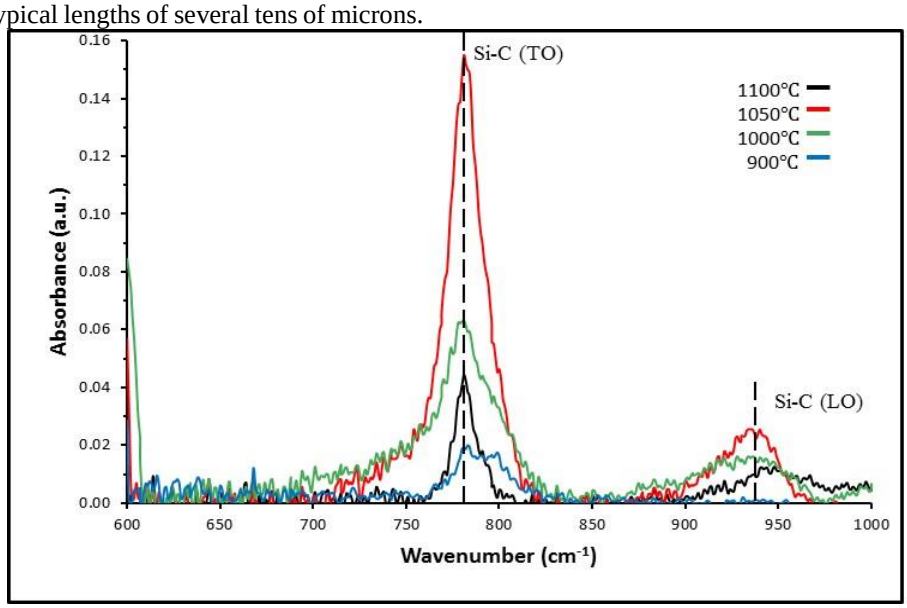

Figure 2. FTIR spectra of SiC nanowires grown with catalyst Ni-film at temperatures of 1100℃, 1050℃, 1000℃ and 900℃.

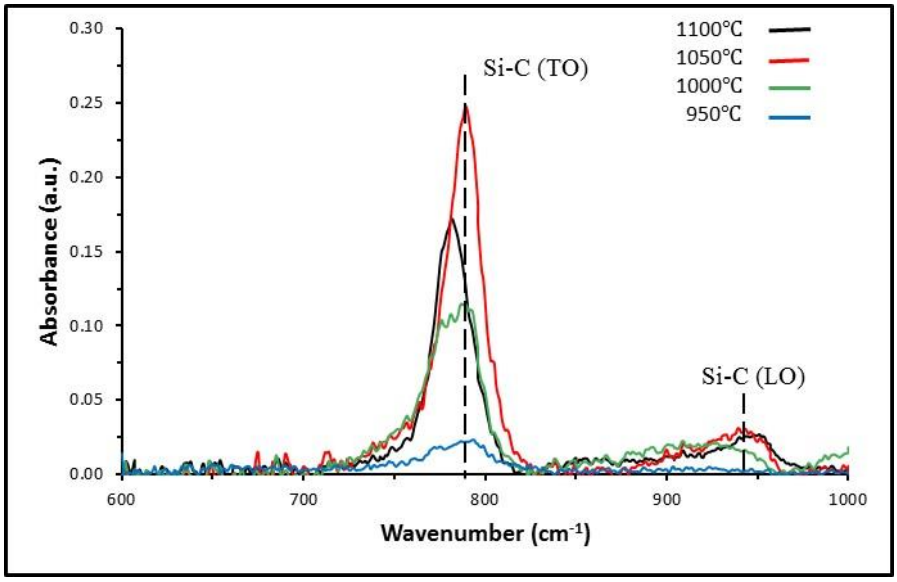

Figure 3. FTIR spectra of SiC nanowires grown with catalyst Fe film at temperatures of 1100℃, 1050℃,1000℃ and 950℃.

Growth Temperature	Peak position of the Si–C bond (cm^{-1})	FWHM of the Si–C absorption band (cm^{-1})
1100 ℃	782	13
1050 ℃	782	18
1000 ℃	782	22
900 ℃	784	31
3C-SiC single crystal [15]	800	59

Table 1. The peak positions and FWHM values of the SiC (TO) absorption band (SiC nanowires grown with Ni catalyst).

As seen in Fig. 2, the spectra of the SiC nanowires have revealed strong absorption bands with very small variations. In fact, the TO Si-C bond ranges from 782 to 784cm^{-1}, the broad longitudinal optical (LO) Si-C bond is located between 900 and 970 cm^{-1}.The FTIR spectra of the SiC nanowires consist of a broad main band at 780-790 cm^{-1}corresponding to strong absorption bands assigned to the stretching vibration of the Si-C (TO) bond positioned at about 782cm^{-1} at the temperatures of 1100℃, 1050℃ and 1000℃, and 784 cm^{-1} at 900℃, 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, which 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 SiC nanowires were improved by increasing of the growth temperature. It is important to note that the TO peaks shifted significantly towards the lower wavenumber region compared to the bulk SiC reported earlier (800cm^{-1}) [15]. 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}) [15] indicating better bonding uniformity and crystal quality of the SiC nanowires.

Figure 3 shows the FTIR spectra of the as-grown SiC nanowires with iron catalyst. The peak positions the FWHM values of the SiC (TO) mode are summarized in Table 2.

Growth Temperature	Peak position of the Si–C bond (cm^{-1})	FWHM of the Si–C absorption band (cm^{-1})
1100 ℃	783	21
1050 ℃	790	20
1000 ℃	790	27
950 ℃	793	36

Table 2. The peak positions and FWHM values of the SiC (TO) absorption band (SiC nanowires grown with Fe catalyst).

As shown in Figure 3, the spectra of the SiC nanowires revealed the presence of absorption band with maxima in the ranges of 783-793 cm^{-1} (TO) and 900-970 cm^{-1} (LO) . In the first band (783-793 cm^{-1}), a strong absorption peak corresponding to the stretching vibration of the Si–C bond is observed at 783 cm^{-1}, 790 cm^{-1}, 790 cm^{-1}, 793 cm^{-1} at temperatures of 1100℃, 1050℃, 1000℃, and 950℃, respectively. It is attributed to the transverse optical phonons of Si–C bonds in SiC. The changes in the position of IR absorption of the bond Si-C may arise due to intrinsic stress. The intrinsic stress in the SiC nanowires may induce strain in the chemical bonds of the IR absorber and cause a shift in the fundamental frequency of the IR absorption band. The

FWHM values of Si–C absorption band increasing from 21 cm^{-1} at temperature of 1100 ℃ to 36 cm^{-1} for SiC nanowires at temperature of 950℃ indicates that the bonding uniformity of the deposited SiC nanowires decreases by reducing the growth temperature. It demonstrates that better chemical order is achieved with higher temperature.

The Si-C (TO) stretching absorption band ranges from 783 cm^{-1} to 793 cm^{-1} with the FWHM values from 21 cm^{-1} to 36 cm^{-1} with Fe-film catalyst, while the Si-C (TO) stretching absorption band ranges from 782cm^{-1} to 784cm^{-1} with the FWHM values from 13cm^{-1} to 31cm^{-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}) [15].

4 CONCLUSION

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 presented. The SiC TO mode absorption shifted significantly towards the lower wavenumber region compared to the bulk SiC. Moreover, the FWHM values of the TO mode absorption of the SiC nanowires (13cm^{-1}) are significantly lower than that of bulk SiC (59cm^{-1}). Thus, both Ni and Fe catalysts result in high quality crystalline SiC nanowires with very sharp absorption peaks compared to bulk single crystal SiC. Therefore, FTIR spectroscopy provides valuable and practical information about the chemical bond states and crystal quality of the nanostructured materials.

REFERENCES

[1] Z.L. Wang, Z.R. Dai, Z.G. Bai, R.P. Gao, J.L. Gole, Applied Physics Letters. 77, 3349–3351, 2000.

[2] Z.W. Pan, Z.R. Dai, Z.L. Wang, Science. 291, 1947–1949, 2001.

[3] H.K. Seong, H.J. Choi, S.K. Lee, J.I. Lee and D.J. Choi, Applied Physics Letters. 85, 1256, 2004.

[4] W.J. Choyke, R.W. Halden, Diamond and Related Materials. 6, 1243, 1997.

[5] W.M. Zhou, L.J. Yan, Y. Wang, Y.F. Zhang, Applied Physics Letters. 89, 13105–13107, 2006.

[6] J.Wei, K.Z. Li, H.J. Li, Q.G. Fu, L.Zhang, Materials Chemistry and Physics. 95, 140–144, 2006.

[7] X.T. Zhou, H.L. Lai, H.Y. Peng, L.S. Liao, N. Wang, I. Bello, C.S. Lee, S.T, Lee, Chemical Physics Letter. 318, 58-62, 2000.

[8] R.B. Wu, G.Y. Yang, Y. Pan, L.L. Wu, J.J. Chen, M.X. Gao, R. Zhai, J. Lin, Applied Physics A. 88, 679–685, 2007.

[9] Y.J. Hao, G.Q. Jin, X,D. Han, X.Y. Guo, Material Letter. 60, 1334, 2006.

[10] W.M. Zhou, B. Yang, Z.X. Yang, F. Zhu, L.J. Yan, Y.F. Zhang, Applied Surface Science. 252, 5143–5148, 2006.

[11] Y.B.Li, S.S. Xie, X.P. Zou, D.S. Tang, Z.Q. Liu, W.Y. Zhou, G. Wang, Journal CrystalGrowth. 223, 125, 2001.

[12] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. 4, 89, 1964.

[13] T.H. Chiu and J.S. Hsu, Thin Solid Films. 252, 13, 1994.

[14] M. Miettimen, M. Johansson, J. Riikonen, U. Tapper, T.T. Pakkanen, V.P. Lehto, J. Jokiniemi, A. Lahde, Journal of Nanoparticle Research. 13, 4631-4645, 2011.

[15] F. Yan, Y.D. Zheng, P. Chen, L. Sun, and S.L. Gu, Opt. Mater. 23, 113, 2003.