



CHARACTERIZATION OF SILICON CARBIDE NANOTUBE SYNTHESIZED USING MICROWAVE HEATING

V. C. S. Tony¹, C. H. Voon¹, C. C. Lee², B. Y. Lim³, U. Hashim¹, W. Rahman², A. R. Ruslinda¹, M. K. Md Arshad¹, K. L. Foo¹, W. W. Liu¹, R. M. Ayub¹, Saeed S. Ba Hashwan¹, Munirah Majid¹ and V. Thivina¹

¹Institute of Nanoelectronics Engineering, Universiti Malaysia Perlis, Taman Pertiwi Indah, Jalan Kangar-AlorSetar, Seriab, Kangar, Malaysia

²School of Manufacturing Engineering, Universiti Malaysia Perlis, Kampus Alam Pauh Putra, Arau, Perlis, Malaysia

³School of Materials Engineering, Universiti Malaysia Perlis, Jejawi, Arau, Perlis, Malaysia

E-Mail: chvoon@unimap.edu.my

ABSTRACT

Currently available conventional methods for the synthesis of silicon carbide nanotubes are highly demanding in terms of the energy consumption, temperature and reaction duration. Synthesis of silicon carbide nanotube through microwave irradiation is thought to be more efficient considering shorter time and lower energy consumption is needed. In this paper, for the first time the synthesis of silicon carbide nanotubes was reported through microwave heating of mixture of carbon nanotubes and silicon dioxide in argon atmosphere at temperature of 1400 °C. Silicon dioxide and carbon nanotube in the ratio of 1:3 as suggested by previous study were mixed in ultrasonic bath for 2 hour using ethanol as medium. The mixture was dried on hot plate and cold pressed into a 3mm pellet. The pressed pellet was then placed in an alumina crucible filled with silica sand acted as heat insulator and SiC susceptor. The pellet was heated to 1400 °C at heating rate of 30 °C/min and hold at 1400 °C for 40 minute. X-ray diffraction analysis verified that silicon carbide nanotubes were produced after the mixture was subjected to the microwave irradiation. Scanning electron microscopy analysis revealed the tubular structure of carbon nanotubes was retained after the microwave irradiation by formation of silicon carbide nanotubes which have tubular structure. Fourier transform infrared (FTIR) spectroscopy show that Si=C bond has the absorption bands around 900cm⁻¹ to 700cm⁻¹ and band gap of silicon carbide nanotube was found out to be 2.76 eV.

Keywords: silicon carbide nanotubes, carbon nanotubes, microwave assisted synthesis, X-Ray diffraction.

INTRODUCTION

Silicon carbide (SiC) is one of the most promising and attractive ceramic that can be applied in many applications including reinforcement of composite, electronic devices, optic devices and many other applications. Promising properties of SiC nanomaterials such as excellent thermal stability, high mechanical strength, chemical inertness and unique optical properties of SiC has lead the major improvement to properties of others material with SiC filler (Li, Shirai and Fuji, 2013), (Alfano, 2011), (Senthil and Yong, 2008), (Wu *et al.*, 2004).

In the last decade, the main method of SiC production is Acheson process which involves very high temperature of carbothermal reduction of SiO₂ by coke at 2200-2500 °C (Zheng *et al.*, 2008). Since then, numerous other synthesis route have been developed for production of SiC including mechanical milling (Chaira, Mishra and Sangal, 2007), sol-gel processess (Xin *et al.*, 2012), chemical vapor deposition (CVD) (Cao, 2010), rapid carbothermal synthesis (Pan *et al.*, 2008) and thermal plasma (Karoly *et al.*, 2014). All these method have similar limitations and drawbacks such as high energy consumption, large impurities of oxygen in the SiC, low uniformity of grain size and time consuming reaction.

Recently, scientists and researchers have employed microwave heating to synthesize material with uniform grain size at high heating rate and reduced

reaction time. Microwave heating is superior than conventional heating considering microwave heating can volumetrically heat materials with favourable dielectric properties while conventional heating rely on the external radiant energy to heat materials (Cho and Lee, 2010). The heat was generated from the inside of the material when exposed to the microwave irradiation and this can accelerate the heating process and enhance the diffusion. Li, Shirai and Fuji (Li, Shirai and Fuji, 2013) has reported that nanostructured β-SiC particles and whickers were successfully synthesized in microwave cavity filled with argon atmosphere with short heating duration. Microwave heating was proven to be an efficient approach for synthesis SiC in terms of low consumption energy and time saving.

Considering carbon nanotube has excellent microwave absorbing properties, the aim of this study is to produce silicon carbide nanotubes (SiCNTs) by exposing the mixture of silicon dioxide and carbon nanotube in the ratio of 1:3 to microwave irradiation to attain 1400 °C with heating rate of 30 °C/min and hold for 40 minutes.. Previous study has suggested that 1:3 ratio of silicon dioxide to carbon source (graphite) was able to produce silicon carbide nanowires without any excess carbon and consisted of single β-SiC phase (Ding *et al.*, 2014). To the best of the authors' knowledge, there is no study reported on the synthesis of silicon carbide nanotubes by microwave heating of mixture of carbon



nanotubes and silicon dioxide. Therefore, in this study, SiCNTs were synthesized by microwave heating of mixture of silicon dioxide and carbon nanotubes in the ratio of 1:3. SiCNTs were then characterized using scanning electron microscopy, x-ray diffraction, energy dispersive x-ray, photoluminescence spectroscopy and fourier transform infrared in order to investigate the morphology, composition and optical properties of the SiCNTs.

EXPERIMENTAL

Sample preparation

The carbon nanotubes used in this experimental are multi walled carbon nanotubes (MWCNTs) which were supplied by Sigma Aldrich. These MWCNTs were mixed with the silicon dioxide (SiO₂) purchased from Sigma Aldrich in the ratio of 3:1 ratio according to previous study (Ding *et al.*, 2014). Ethanol was used as medium for ultrasonic mixing to properly mix the MWCNTs and SiO₂ for 2 hours. Mixture MWCNTs and SiO₂ was then dried using hot plate until ethanol was completely evaporated left only the mixture of MWCNTs and SiO₂. The mixture was cold pressed into a 3mm pellet using a hydraulic press.

Synthesis of SiCNTs by microwave heating

Microwave heating was carried out in a multi mode cavity in which microwave irradiation of 2.45GHz was introduced through a waveguide. Pellet of MWCNTs and SiO₂ was placed in an alumina crucible filled with silica sand acted as heat insulator and SiC susceptor in microwave cavity as shown in Figure-1. Temperature was increased to 1400 °C with heating rate of 30 °C/min and maintained at this temperature for 40 minute.

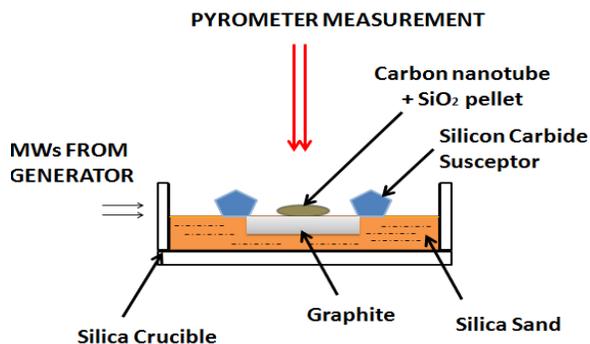


Figure-1. Schematic diagram of setup for microwave assisted synthesis.

Characterization of silicon carbide nanotubes

After the SiCNTs were synthesized, characterization was conducted using scanning electron microscopy (SEM), energy-dispersive x-ray (EDX), x-ray diffraction (XRD), photoluminescence spectroscopy (PL) and fourier transform infrared spectroscopy (FTIR).

Phase characterization of SiCNTs was done by powder XRD measurements carried out with Siemens Diffractometer Model D-5000, using Cu K α radiation source in $\theta/2\theta$ mode. Measurement made with fast duration scan (1s) and small step size (0.02°).

The morphology of the SiCNTs was observed by scanning electron microscopy (SEM JEOL JSM6010LV) at magnification of 30000X and accelerating voltage of 20 kV while energy-dispersive x-ray spectroscopy (EDX JEOL JSM6010LV) equipped together with SEM was used to confirm the presence of the carbon and silicon in silicon carbide nanotube.

Optical properties of SiCNTs such as band gap and absorption band were identified using the photoluminescence spectroscopy (PL FL3-11 J81040) with xenon lamp at 400 watt and excitation wavelength at 325 nm while for fourier transform infrared spectra was recorded using FTIR MAGNA550 kBr spectroscopy with wavelength ranged from 500 to 4000 nm⁻¹.

RESULTS AND DISCUSSION

Scanning electron microscopy (SEM)

Figure-2 shows images of scanning electron microscopy for the MWCNTs, mixture of MWCNTs and SiO₂ and SiCNTs respectively. The tubular structure of carbon nanotube can be observed in Figure-2 a). In Figure-2 b), the tubular structure of carbon nanotube was retained after the ultrasonic mixing process. White particle in the micro size range in Figure-2 b) is the SiO₂ particles. As in Figure-2 c), the structure of nanotube is retained after the mixture in Figure-2 b) was exposed to microwave irradiation at 1400 °C for 40 minute through the formation of silicon carbide nanotube with average diameter of 88 nm. SiO₂ particle was not observed in Figure-2 c) after exposing to microwave irradiation. It is postulated in this stage that the tubular structure in Figure-2 c) is silicon carbide nanotubes. Reaction of MWCNTs and SiO₂ was dependent on the microwave heating. Microwave heating depends on the interactions of material with electric field of electromagnetic radiation. These interactions caused the materials to heat up from the inside of material and lead to more uniform and stable distribution of heat within the heated material (Méndez, Kharissova and Rodríguez, 2003). In the same manner, MWCNTs in the mixture were heated from inside of the pellet and heat was transferred to the entire mixture. At high temperature of 1100 °C and above, SiO₂ particles were vaporized to form SiO gas that reacted with MWCNTs to form SiCNTs (Ding *et al.*, 2014). These reaction can be represented by following:



Since the SiO vapor reacted with MWCNTs to form SiCNTs, the nanotube structure of carbon nanotube was retained after the reactions. Similar observation was reported by Keller *et al* (Keller *et al*, 2003) in their study of synthesis of SiCNTs by conventional heating of mixture



of CNT and SiO₂. They found that the tubular morphology of carbon was retained after the carburization process. This proved that silicon carbide nanotube can be produced

with the conservation of the starting shape of carbon material.

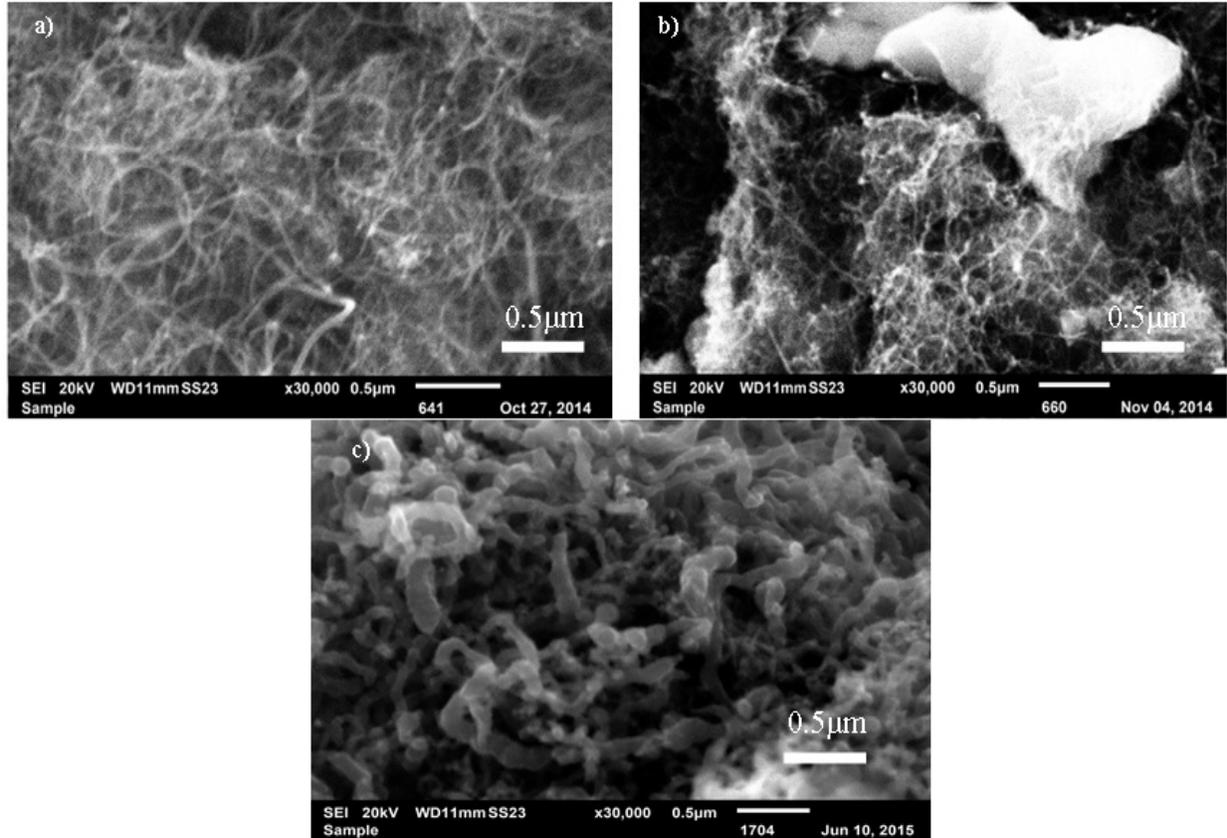


Figure-2. Scanning electron microscopy (SEM) results for a) carbon nanotubes (CNTs), b) Mixture of silicon dioxide and carbon nanotube and c) Silicon carbide nanotubes (SiCNTs).

Energy-dispersive X-ray spectroscopy (EDX)

Figure-3 shows the result of energy dispersive x-ray spectroscopy (EDX) analysis for MWCNTs, mixture of MWCNTs and SiO₂ and SiCNTs respectively. It can be observed that peak corresponded to carbon was present in the EDX result for the presence of MWCNTs. While in Figure-3 b), the EDX results of the mixture of MWCNTs and SiO₂ show peaks corresponded to carbon, silicon and oxygen which were due to the presence of MWCNTs and SiO₂. EDX results in Figure-3 c) shows the presence of peaks correspond to Si and C only with the absence of peak corresponded to O. It is postulated that the absence of O peak was due to the vaporization of SiO₂ during microwave heating that led to the formation of SiCNTs. This is in good consistence with the absence of SiO₂ particles in the SEM image in Figure-2 c) after the microwave heating which shows that the SiO₂ was completely vaporized become SiO vapor and then reacted with MWCNTs to produce SiCNTs (Pham-Huu *et al*, 2001).

X-ray diffraction (XRD)

Figure-4 shows the X-ray diffraction patterns for as received MWCNTs and SiCNTs formed after exposing to microwave irradiation at 1400 °C for 40 minute respectively. The presence of peaks corresponded to β-SiC in Figure-4 b) confirmed the silicon carbide nanotube was successfully formed after exposing the mixture of MWCNTs and SiO₂ to microwave irradiation. The peaks corresponded to β-SiC in XRD pattern are 35.6°, 43.2°, 60.2° and 71.7° respectively (JCPDS Card No 29-1129) and these 2 theta values of peaks also corresponding to cubic reflections of (111), (200), (220) and (311). Ding (Ding *et al*, 2014) also reported similar observation that SiC nanowires have diffraction peaks of β-SiC which show (111), (220) and (311) cubic reflections with 2θ values of 35.0°, 60.1° and 71° respectively. It can also be observed that no peaks corresponded to carbon and silicon dioxide were detected in X-ray diffraction pattern in Figure-4 b). This indicated complete conversion of MWCNTs to SiCNTs occurred in this study.

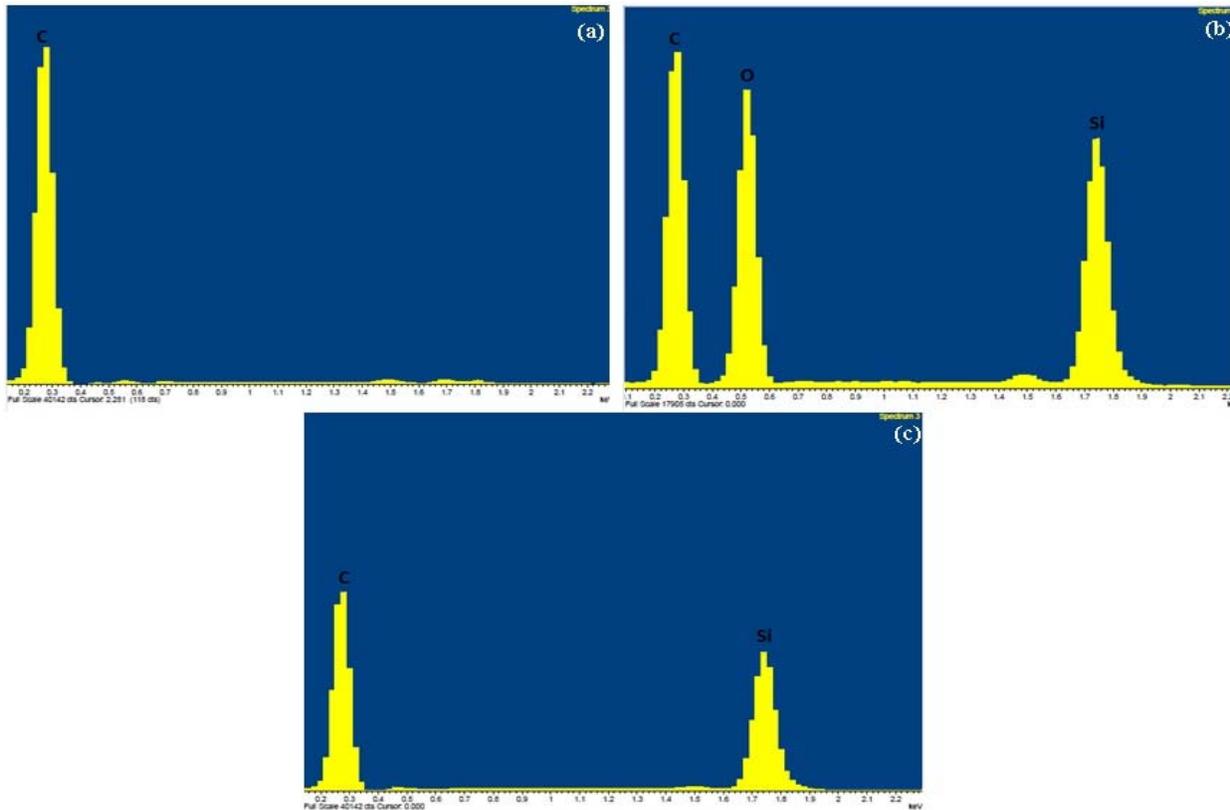


Figure-3. Energy-dispersive X-Ray spectroscopy (EDX) analysis for a) MWCNTs, b) Mixture of MWCNTs and SiO₂ and c) SiCNTs.

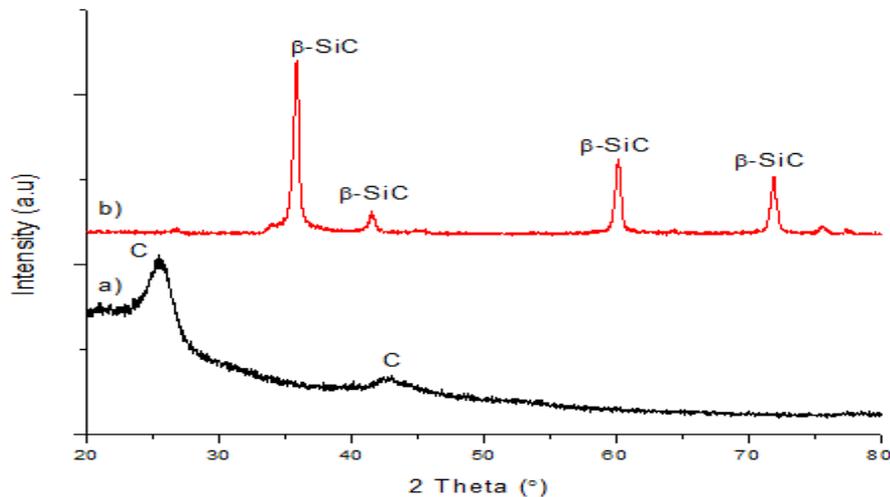


Figure-4. X-ray diffraction patterns of a) MWCNTs and b) SiCNTs.

Photoluminescence spectroscopy (PL)

Figure-5 shows the photoluminescence spectra of MWCNTs, mixture of MWCNTs and SiO₂ and SiCNTs. Figure-5 a) and b) shows that MWCNTs and mixture of MWCNTs and SiO₂ have emission at 620 nm which corresponded to the band gap of 2.0 eV (MWCNTs).

Figure-5 b) shows emission at 674 nm corresponded to band gap of 1.84 eV (SiO₂) while SiCNTs spectrum shows the emission at 465 nm and corresponded to band gap of 2.67 eV as seen in Figure-5 c). Compared to bandgap of bulk 3C-SiC of 2.39 eV (Lee *et al.*, 2015), the PL



spectrum of silicon carbide nanotube is considerably blueshifted.

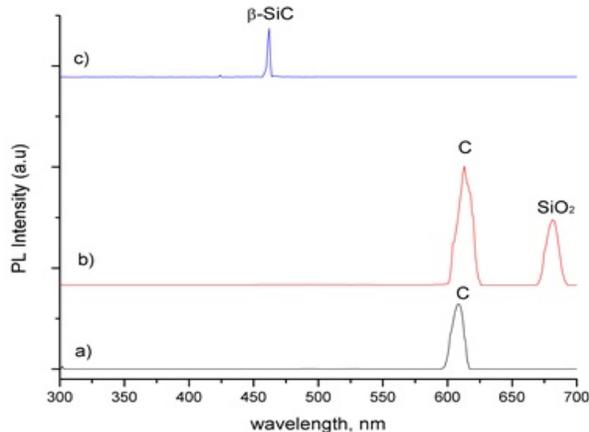


Figure-5. Photoluminescence spectra of a) MWCNTs, b) Mixture of MWCNTs and SiO₂ and c) SiCNTs.

Fourier transform infrared (FTIR)

FTIR transmission spectra of MWCNTs, mixture of MWCNTs and SiO₂ and SiCNTs are shown in Figure-6. All FTIR spectra shown absorption bands at 3400cm⁻¹ to 3500cm⁻¹. These absorption bands indicated the presence of water molecule in MWCNTs, mixture of MWCNTs and SiO₂ and SiCNTs. Similar absorption band was reported by Derradji *et al.* (Derradji *et al.*, 2015). These may due to the exposure of specimens to surrounding which caused the absorption of water molecule into the specimen especially during handling of the specimen. Water molecule content was higher in carbon nanotube spectra while silicon carbide nanotube was lower in the content of water molecule. Similar observation also can be made for absorption bands of C=C bonds at 1630cm⁻¹ to 1640cm⁻¹ (John, 2000) in which the presence of C=C bonds was high for MWCNTs but significantly reduced after the MWCNTs and SiO₂ were converted to SiCNTs after exposing the mixture to microwave irradiation. This is in good consistence with the XRD patterns in Figure-4 in

which the peak corresponded to carbon diminished in the XRD pattern of SiCNTs, indicating the complete conversion of MWCNTs to SiCNTs.

The result were in good agreement with the reported value (Chen *et al.*, 2011). It is well known that luminescence arises from the transitions of electrons trapped at surface states to valence band of nanotube. Besides that, there are numerous surface defects in SiC depends on the surface area which can affect the luminescence properties of SiC (Li *et al.*, 2013). Nur Fatin (Fatin *et al.*, 2015) also concluded that the PL spectrum of the SiC nanocrystalizes are strongly depend on quantum confinement effects attributed to size of the nanocrystallites embedded in the nanowires.

From Figure-6 b) the absorption band at 1100cm⁻¹ to 1000cm⁻¹ can be seen in the spectrum for mixture of MWCNTs and SiO₂. This absorption band represents the presence of SiO₂ bonds that was available in spectrum of mixture of MWCNTs and SiO₂. The presence of this absorption band is in good consistence with the absorption bands reported previously for silicon dioxide (Lisovskyy *et al.*, 2005). Absorbance bands of 516cm⁻¹ and 694cm⁻¹ in Figure-6 b) indicated the absorption bands for the Si-O stretching vibration and these absorption bands only present in spectra of mixture of MWCNTs and SiO₂ since SiO₂ are abundant in the mixture. Ye (Ye, Zhang and Lee, 2012) also reported the similar absorbance band of the Si-O stretching bands at 520cm⁻¹ was present in the SiO₂ xerogel.

Spectrum for SiCNTs in Figure-6 c) shows the absorption band from 1000cm⁻¹ to 700cm⁻¹ and this absorbance band are represent the Si-C stretching bond of SiCNTs. Absorbance band of Si-C stretching band only shown in FTIR spectra of SiCNTs which indicates the successful conversion of MWCNTs and SiO₂ to SiCNTs. Li (Li *et al.*, 2011) also reported similar absorbance bands of the Si-C stretching bonds lies from 700cm⁻¹ to 1000cm⁻¹ in the spectra of SiC particles and whiskers synthesized from rice husk using microwave heating.

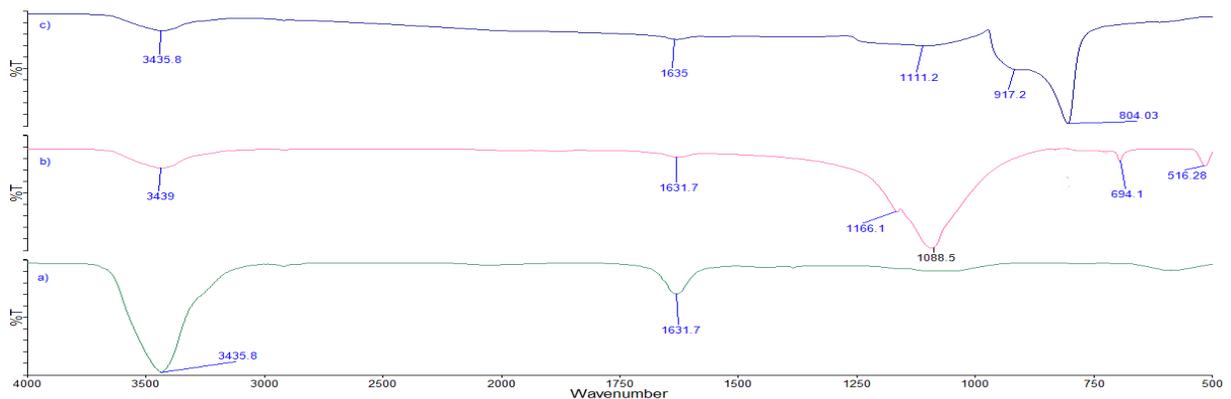


Figure-6. Fourier transform infrared (FTIR) spectra of a) MWCNTs, b) Mixture of MWCNTs and SiO₂ and c) SiCNTs.



CONCLUSIONS

Silicon carbide nanotube was successfully synthesized by microwave irradiation of mixture of silicon dioxide and carbon nanotube in the ratio 1:3 to 1400 °C for 40 minutes. The tubular structure of the carbon nanotube was retained after the synthesis by the formation of SiC nanotubes. XRD pattern confirmed the SiCNTs consist of single β -SiC phase. Band gap characterization and photoluminescence properties of SiCNTs were investigated. A sharp photoluminescence emission at 465 nm was observed and the band gap for SiCNTs was 2.67 eV. Absorbance bands of Si-C stretching band present in the FTIR spectra and thus indicated that the silicon carbide nanotube was successfully synthesized by exposing mixture of silicon dioxide and carbon nanotube to microwave irradiation.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Higher Education, Ministry of Higher Education (KPT) for funding this research through the Fundamental Research Grant Scheme (FRGS) with the grant number 9003-00441. The author also would like to acknowledge all the team members in Institute of Nano Electronic Engineering (INEE), University Malaysia Perlis (UniMAP) for their guidance and help.

REFERENCES

- [1] Alfano, D. (2011). Spectroscopic properties of carbon fibre reinforced silicon carbide composites for aerospace application. Properties and Application of silicon carbide, In Tech Open, pp.231--250.
- [2] Cao, L.Z., Jiang, H., Song, H., Li, Z.M., Miao, G.Q. (2010). Thermal CVD synthesis and photoluminescence of SiC/SiO₂ core-shell structure nanoparticles, Journal of Alloys and Compounds, 489(2), pp.562--565.
- [3] Chaira, D., Mishra, B.K. and Sangal, S. (2007). Synthesis and characterization of silicon carbide by reaction milling in a dual-drive planetary mill, Materials Science and Engineering A, Structural Materials Properties Microstructure Processing, 460, pp.111--120.
- [4] Chen, J., Tang, W., Xin, L., Shi, Q. (2011). Band gap characterization and photoluminescence properties of SiC nanowires. Applied Physics A, 102, pp.213--217.
- [5] Cho, S and Lee, K-H. (2010). Synthesis of crystalline TiO₂ nanostructure arrays by direct microwave irradiation on a metal substrate, Journal of Crystal Growth, 312, pp.1785--1788.
- [6] Derradji, M., Ramdani, N., Zhang, T., Wang, J., Feng, T-T, Wang, H., Liu, W-B. (2015). Mechanical and thermal properties of phthalonitrile resin reinforced with silicon carbide particle. Materials and Design, 71, pp.48--55.
- [7] Ding, J., Deng, C., Yuan, W., Zhu, H., Zhang, X. (2014). Novel synthesis and characterization of silicon carbide nanowires on graphite flakes. Ceramics International, 40, pp.4001--4007.
- [8] Ding, J., Zhu, H., Li, G., Deng, C., Li, J. (2014). Growth of SiC nanowires on wooden templates surface using molten salt media. Applied Surface Science, 320, pp.620--626.
- [9] Fatin, N.F.N., Jannah, N.M.N., Saadah, A.R., Goh, B.T. (2015). Photoluminescence and structural properties of Si/SiC core-shell nanowires growth by HWCVD. Journal of luminescence, 157, pp.149--157.
- [10] John, C. (2000). Interpretation of infrared spectra, A practical approach, R.A. Meyers (Ed). Encyclopedia of Analytical Chemistry, pp.10815--10837.
- [11] Karoly, Z., Mohai, I., Klebert, Sz., Keszler, A., Sajo, I.E., Szepvolgyi, J. (2011). Synthesis of SiC powder by RF plasma technique. Powder technology, 214, pp.300--305.
- [12] Keller, N., Pham-Huu, C., Ehret, G., Keller, V., Ledoux, M.J. (2003). Synthesis and characterization of medium surface area silicon carbide nanotubes. Carbon, 41, pp.2131--2139.
- [13] Lee, K.M., Hwang, J.Y., Urban, B., Singh, A., Neogi, A., Lee, S.K., Choi, T.Y. (2015). Origin of broad band emissions of 3C-silicon carbide nanowire by temperature and time resolved photoluminescence study. Solid State Communications, 204, pp.16--18.
- [14] Li, J., Shirai, T and Fuji, M. (2013). Rapid carbothermal synthesis of nanostructured silicon carbide particle and whiskers from rice husk by microwave heating method. Journal of Advanced Powder Technology, 24, pp.838--843.
- [15] Li, Y., Chen, C., Li, J-T., Yang, Y., Lin, Z-M. (2011). Surface charges and optical characteristics of colloidal cubic SiC nanocrystals. Nanoscale Research Letters, 6, pp.454--461.
- [16] Li, H., He, Z., Chu, Y., Qi, L., Fu, Q. (2013). Large-scale synthesis, growth mechanism and photoluminescence of 3C-SiC nanobelts. Materials Letters, 109, pp.275--278.
- [17] Lisovskyy, I.P., Litovchenko, V.G., Mazonov, D.U., Kaschieva, S., Koprinarova, J., Dmitriev, S.N. (2005). Infrared spectroscopy study of Si-SiO₂ structures irradiated with high energy electrons. Journal



www.arpnjournals.com

Optoelectronic & Advanced Material, 7(1), pp.325--328.

- [18] Méndez, U.O., Kharissova, O.V and Rodríguez, M. (2003). Synthesis and morphology of nanostructures via microwave heating, Revised Advanced Material Science, 5, pp.398--402.
- [19] Pan, S., Zhang, J., Yang, Y., Song, G. (2008). Effect of process parameters on the production of nanocrystalline silicon carbide from water glass, Ceramics International, 34(2), pp.391--395.
- [20] Pham-Huu, C., Keller, N., Ehret, G., Ledoux, M.J. (2001). Research Note The First preparation of silicon carbide nanotubes by shape memory synthesis and their catalytic potential. Journal of Catalysis, 200, pp.400--410.
- [21] Senthil, K and Yong, K. (2008). Enhanced field emission from density controlled SiC nanowires. Journal of Material Chemical and Physical, 112, pp.88--93.
- [22] Wu, Y.J., Wu, J.S., Qin, W., Xu, D., Yang, Z.X., Zhang, Y.F. (2004). Synthesis of h-SiC nanowhiskers by high temperature evaporation of solid reactants, Material Letters, 58, pp.2295--2298.
- [23] Xin, L.P., Shi, Q., Chen, J.J., Tang, W.H., Wang, N.Y., Liu, Y., Lin, Y.H. (2012). Morphological evolution of one-dimensional SiC nanomaterials controlled by sol-gel carbothermal reduction, Material Characterization, 65, pp.55--61.
- [24] Ye, J.K., Zhang, S.W and Lee, W.E., (2012). Novel low temperature synthesis and characterization of hollow silicon carbide spheres. Microporous Mesoporous Material, 152, pp.25--30.
- [25] Zheng, Y, Zheng, Y., Wang, R., Wei, K. (2008). Direct determination of carbothermal reduction temperature for preparing silicon carbide from the vacuum furnace thermobarogram. Vacuum, 82, pp.336--339.