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Synthesis of Silicon Carbide Nanowhiskers by Microwave Heating: Effect of Heating Temperature

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Abstract: Silicon carbide (SiC) is an attractive material for its excellent properties such as wide band gap, high chemical stability and thermal conductivity. The conventional method for the preparation of SiC is Acheson process, a time and energy consuming process. In this article, demonstration of SiC nanowhiskers synthesis has been done by using microwave heating. Silica and graphite in the ratio 1:3 were mixed in ultrasonic bath, dried on hot plate and cold pressed uniaxially into a pellet die. The pellets were heated by using laboratory microwaves furnace at 1350ºC, 1400ºC and 1450ºC with heating rate of 20ºC/min and soaked for 40 minutes. Different characterizations and testing were done to study the effect of heating temperature on the synthesis of SiC nanowhiskers. 1400ºC is proved to be the most suitable tempearture for the synthesis of SiC nanowhiskers. β-SiC appeared as the only phase in the x-ray diffraction pattern of SiC nanowhiskers formed at 1400˚C with no traces of raw materials. Field emission scanning electron microscopy confirmed the presence of only a negligible amount of graphite or silica in SiC nanowhiskers synthesized at 1400ºC. Furthermore, energy dispersive x-ray spectroscopy analysis revealed that only elemental C and Si were present in SiC nanowhiskers synthesized at 1400ºC. Meanwhile, photoluminescence spectrum indicated the presence of single β-SiC peak at 440 nm which is associated with band gap of 2.8 eV. Single absorption bands of Si-C bond were detected at 803.5 cm^{-1} in fourier transform infrared spectrum. SiCNWs produced in this study at 1400ºC has good thermal stability with 6% of weight loss, indicates its potentiality for high temperature electronics.

Keywords: Microwave heating; Silicon carbide nanowhiskers; Synthesis; Graphite; Silica

Sinteza nanodlačic iz silicijevega karbida z mikrovalovnim segrevanjem: Vpliv temperature gretja

Izvleček: Silicijev karbid (SiC) je zelo zanimiv material zaradi svojih odličnih lastnosti, kot je široka energijska reža, kemijska stabilnost in termična prevodnost. Konvencionalen je SiC pridobiva z Acheson-ovim procesom, ki p aje energijsko in časovno izredno potraten. V članku predstavljamo sintezo nanodlačic SiC s pomočjo gretja z mikovalovi. V ultrasonični kopeli je bil apripravljena mešanica silicija in grafita v razmerju 1:3, nato posušena na vroči plošči in hladno stisnjena matrico peleta. Peleti so bili nato segrevani z laboratorisko mikrovalovno pečiso pri 1350 °C, 1400 °C in 1450 °C s hitrostjo gretja 20 °C/min in trajanjem 40 min. Opravljene so bile različne karakterizacije nanidlačic. Izkazalo se je, da je temperature 1400 °C najprimernejša za izdelavo nanodlačic. V vzorcu sipanja x žarkov se izkazalo, da nanodlačice vsebujejo le β-SiC brez ostankov surovega materiala. Elektronska mikroskopija je potrdila prisotnost le zanemarljivega dela silicija in grafita. Fotoluminiscenca je nakazala le eden vrh signala pri 440 nm kar je v skladu z energijsko režo 2.8 eV. Absorpcijski pas je bil zaznan pri 803.5 cm^{-1} v fourierjevi transformaciji infrardečega spektra. Izdelane nanodlačice so pokazale dobro termično stabilnost z 6 % izgubo teže, kar pomeni, da predstavljajo zanimiv material za visokotemperaturno elektroniko.

Ključne besede: mikrovalovno gretje; nanodlačice iz silicijevega karbida; sinteza; grafit; silicij

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1 Introduction

Silicon carbide (SiC) is a very attractive semiconductor due to its excellent properties such as high hardness, good flexibility, high thermal conductivity, high thermal stability, excellent chemical stability and large band gap. Because of these attractive properties, it possesses great potential for industrial and engineering applications such as abrasives [1, 2], high power electronics [3, 4], harsh environment electronics and composite reinforcements [5, 6]. SiC nanomaterials such as SiC nanocrystals and nanowhiskers have many potential electronic applications. For example, SiC nanocrystals (NCs) exhibit photoluminescence in the near-UV to the visible blue spectral region and making them attractive candidates for the fabrication of light-emitting devices [7]. Moreover, several field emission measurements on the SiCNWs suggested that SiCNWs are potential candidates for the cold cathode field emission device (FED) because of their unique electrical, chemical, and mechanical properties [1]. SiC has been produced by several methods, however, most SiC are produced now-a-days using the Acheson process [2]. This process produces SiC by heating mixture of quartz sand and powdered coke (carbon-based material) in an iron bowl using voltages 50,000 V for 20 hours at temperatures around 2200–2400˚C. The drawbacks of this industrial production process include high energy consumption and the product has low purity. Moreover, this process is time consuming; therefore several alternative methods have been previously reported for SiC synthesis. Most commonly used methods for SiC synthesis are carbon thermal reduction [9], physical evaporation, sol-gel process [10, 11] and chemical vapor deposition [12]. However, there are still some drawbacks that limit the wide applications of these methods, such as high energy consumption, long processing time and extensive chemical usage, although these processes can successfully synthesize SiC.

Recently, researchers have applied microwave heating for the synthesis of inorganic materials [13-16]. From mid-1980s until 2007, hundreds of papers have been published regarding the applications of microwaves in chemical synthesis [16-21]. Development of new routes for the synthesis of inorganic material is an integral aspect of materials chemistry. The development of alternative synthesis methods is a continuing need for fast and energy-efficient techniques. Microwaves are electromagnetic radiation, whose wavelengths lie in the range of 1 mm to 1 m [16]. Microwave synthesis has emerged in recent years as a new method to synthesize a variety of materials that has shown significant advantages against conventional synthesis procedures. Microwaves can volumetrically heat materials and give sudden increase in the temperature of the material comparing to conventional heating processes that rely on external radiant energy to heat materials by mode of conduction, convection and radiation. Microwave heating is a process in which the materials couple with microwave, absorb the electromagnetic energy volumetrically, and transform into heat [15]. The carbonaceous materials are among the most sensitive to microwaves irradiation [23]. This is due to the fact that carbon based materials generate heat from the motion of electron through joule heating within the grain of carbon when exposed to microwave irradiation, although carbon based materials have no freely-rotatable dipoles [23]. Materials scientists have identified several advantages of microwave processing of ceramics such as economical, rapid heating, large scale production and reduced cracking and thermal stress [14]. Other than that, Mingos et al. [12] proposed that synthesis of inorganic material using microwave heating can enhance the mechanical properties of the material since the sintering time is generally shortened and thus reduced the possibility of secondary crystallization.

Silicon carbide nanowhisker (SiCNW) is a silicon carbide 1-D nanostructure in whisker/needle form. One-dimensional silicon carbide (1D SiC) nanomaterials have shown unusual properties such as extremely high strength, good flexibility and fracture toughness, lead to many potential applications such as sensors, field emitting diodes and solar cells [1, 24]. 1-D nanostructure is also expected to play an important role as both interconnect and as functional units in fabrication of electronics, optoelectronics, electrochemical and electromechanical devices at nanoscale dimensions [1, 25, 26]. In particular, β-SiC nanowhiskers, with an energy band gap of 2.39 eV and relatively high electron mobility would be a suitable material for applications in nanoelectronic devices.

In this study, microwave heating was used to synthesize SiCNWs from the mixture of graphite and silica since it is generally faster, cleaner, and more economical than the conventional methods. The effect of heating temperature was studied to determine the most suitable temperature for the synthesis of SiCNWs from silica and graphite. Previously, several researches have studied the effect of heating temperature on the synthesis of silicon carbide from silica and carbon-based starting materials. For examples, Wang et al. [27] studied the synthesis of SiC whiskers on graphitic layers using expanded graphite (EG) by silicon vapor deposition without catalyst at temperature ranged from 1000 to 1400˚C. Wang et al. [27] found that the amount of β-SiC on graphite increases with the temperature and the largest amount of β-SiC formed at 1400˚C. Other than that, Jin Li et al. [28] have synthesized nanostructured

SiC particles and whiskers from rice husk by microwave heating at temperature ranged from 1100˚C to 1500˚C. They found that 1500 ˚C is the most ideal temperature for the synthesis of β-SiC. Therefore, heating temperature is believed to have significant effect on the quality and purity of the end products during the synthesis of SiCNWs. To the best of our knowledge, no study on the effect of heating temperature on the microwave synthesis of SiCNWs from graphite and silica was reported. Thus, in this study, the effect of heating temperature on the morphology, composition, optical properties and purity was studied and presented.

2 Material and Methods

2.1 Sample preparation

Silica (particle size ≤ 50 μm) and extra pure fine graphite powder (particle size ≤ 50 μm) were used as starting material. Mixture of silica and graphite in molar ratio of 1:3 with total of 1 gram was acquired. Ethanol was used as liquid medium to mix the raw material. Ultrasonic mixing bath was used as the external mean to generate vibration in the ethanol for the homogeneous mixing of the raw materials. The mixtures were then dried using hot plate to vaporize the ethanol. Before subjecting to microwave heating, the mixture was compressed to become pellet. The process of making pellet is essential to separate the mixture of SiO_2 and graphite from the graphite powder placed around the pellet inside the crucible . The pressure that applied to the mixture during the compression process was 312.4 MPa to ensure mixtures were fully compressed.

2.2 Synthesis of SiCNWs by microwave heating

Microwave heating was performed in Synotherm microwave sintering furnace (MW-L0316V) with multi-mode cavity in which 2.45 GHz microwave radiation was bring out through a waveguide.

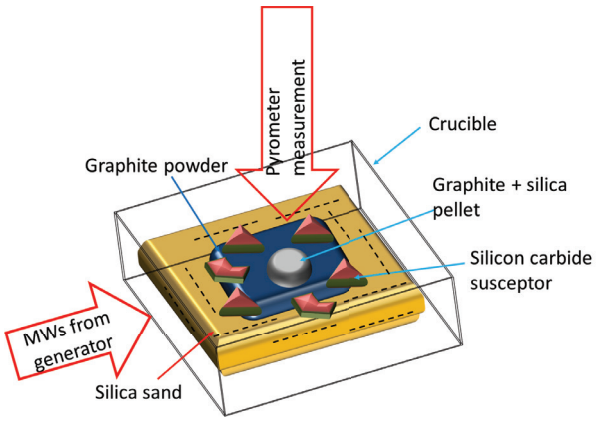

Figure 1: Setup for sample preparation inside the microwave cavity.

The pellet was placed in silica crucible and it was placed in microwave cavity as shown in Fig. 1. Silica sand was used as heat insulator to prevent heat lost. SiC susceptor functioned as microwave absorber to absorb and convert electromagnetic energy to heat because SiC susceptor is a good microwave absorbing material. The pellets were heated to different temperatures of 1350˚C, 1400˚C and 1450˚C with heating rate of 20°C/min and soaked for 40 minutes. The synthesis was performed under argon atmosphere.

2.3 Characterization of SiC nanowhiskers

After the microwave heating was conducted, samples were characterized by using x-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive x-ray spectroscopy (EDX), photoluminescence spectroscopy (PL), fourier transform infrared spectroscopy (FTIR) and thermo-gravimetric analysis (TGA).

The morphologies of samples were observed by using FESEM model Nova Nano 450 at magnification 200K and accelerating voltage of 5 kV while EDX (EDX OXFORD FM29142) was used to determine the elemental composition of the specimens. The samples in the powder form were added into ethanol and ultrasonicated for homogeneous dispersion. The dispersions were then dropped on the substrate and the substrate was heated by using hot plate to evaporate the ethanol. The samples on the substrate were then subjected to characterization using FESEM and EDX. The built in software for OXFORD FM29142 enables automatic correction and robust spectrum processing that works in non-flat sample measurement with no need for any background fitting adjustment. Meanwhile, XRD Siemens Diffractometer Model D-5000 using Cu Kα radiation source in θ/2θ mode was used to investigate the composition of specimens. Measurements were made with fast duration scan (1s) and small step size (0.02°). Optical properties of SiCNWs synthesized from the mixtures were identified by using the photoluminescence spectroscopy (PL FL3-11 J81040) with xenon lamp at 400 watt and excitation wavelength at 360 nm and recorded from wavelength of 300 nm to 650 nm while FTIR (FTIR MAGNA550 kBr) was used to scan the samples from 500 to 4000 nm^{-1} with spectrum resolution of 4 cm^{-1}. Purity of SiCNWs was evaluated indirectly by using Perkin-Elmer Pyris 6 TGA analyzer. Samples about 10 mg were heated from 30 to 1300°C with the heating rate of 10 °C/min in atmospheric air to investigate the purity of the as synthesized SiCNWs.

3 Result and Discussions

3.1 Characterization of SiCNWs using FESEM

Fig. 2 shows the FESEM images of SiO_2 and graphite subjecting to microwaves heating at different temperatures. It can be seen that the heating temperature of SiO_2 and graphite significantly influenced the synthesis of SiCNWs. Fig. 2 (a) shows the mixture SiO_2 and graphite after subjecting to microwaves heating at 1350˚C. It can be observed that only a small amount of nanowhiskers were formed around particles that is believed to be unreacted SiO_2 and graphite. Besides, the nanowhiskers that formed from the reaction between silica and graphite were not fully grown as indicated by red circles in Fig. 2 (a). It is believed that this might be due to the fact that heating temperature at 1350˚C was not sufficiently high to enable the full reaction between graphite and SiO_2 for the complete formation of SiC nanowhisker. Similar observation was reported by Wang et.al that hybridized silicon carbide (SiC) whiskers on graphitic layers in expanded graphite (EG) by silicon vapor deposition without catalyst. They reported that for the synthesis conducted at low heating temperature (1100˚C to 1300˚C), small amount of SiC was produced due to incomplete reactions [27].

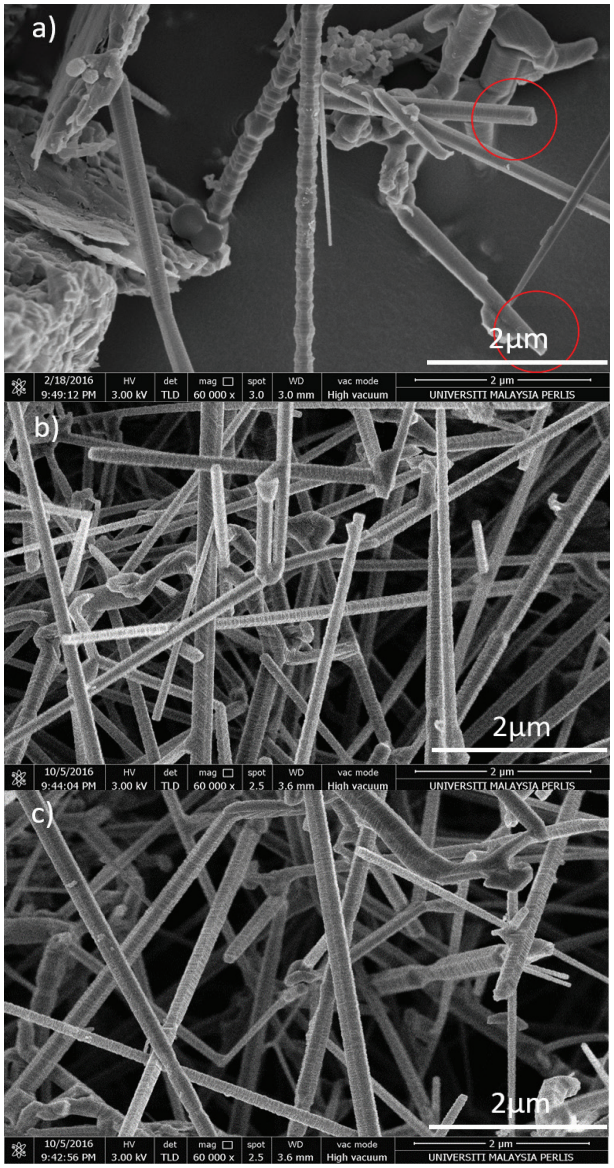

Figure 2: FESEM images of SiCNWs synthesized by microwave heating of mixture of SiO_2 and graphite at heating temperatures of a) 1350˚C b) 1400˚C and c) 1450˚C.

Fig. 2 (b) shows the FESEM image of SiCNWs formed from the mixture of SiO_2 and graphite that was subjected to microwaves heating at 1400˚C. SiC in the form of nanowhiskers can be observed clearly. The diameters of SiCNWs are uniform along the length of the nanowhiskers. Only small amount particles of graphite or silica were observed, such that almost all graphite and silica were converted to SiCNWs. Wang et.al [27] have also reported similar result in which large amount of SiC in the form of nanowhiskers were formed at 1400˚C. The diameters of the nanowhisker were measured by using ImageJ version 1.48 and they were ranged between 70 nm and 100 nm.

Fig. 2 (c) shows the SiC whiskers formed by microwaves heating mixture of SiO_2 and graphite at 1450˚C. It can be observed that the amount SiC whiskers are similar comparing to those formed at 1400˚C in Fig. 2 (b). Large amount of SiCNWs can be observed. The diameter of the SiCNWs formed were measured and are ranged from 70 nm to 120 nm which are similar to SiCNWs in Fig. 2 (b**).** The diameter for the SiCNWs formed at 1450 ˚C are slightly larger and this might due to the increase of heating temperature. Similar result were also obtained by Wang et al [27]. They reported that the diameter of β-SiC nanowhiskers in the specimen treated at 1400 ˚C were larger than those treated below 1400 ˚C [27]. With the increasing heating temperature, the rate of reaction of SiC was increased. This caused higher SiC formation rate on the intially formed SiCNWs during the heating process, and led to larger diameter of SiCNWs at higher temperature.

3.2 Characterization of SiCNWs using XRD

XRD patterns of SiCNWs synthesized from mixture of SiO_2 and graphite at different temperatures are shown in Fig. 3**.** For SiCNWs synthesized at 1350˚C as shown in Fig. 3 (a), small peaks corresponding to SiO_2 at 2θ of 22.3˚ associated with plane (100) of SiO_2 (JCPDS card 01-089-3434) was observed. A peak of carbon phase was also observed at 27˚ corresponding to plane (002) of graphite (JCPDS card 03-065-6212).

Generally, the presence of carbon and SiO_2 is due to the presence of unreacted graphite and silica. Peaks of ß-SiC (111) and (220) were also observed at 2θ of 36˚and 61˚. This indicated that reaction of SiO_2 and graphite to form SiCNWs at 1350˚C was incomplete. This observation is in good agreement with the corresponding FESEM image in Fig. 2 (a) where only small amount of SiCNWs along with graphite and silica were observed.

Fig. 3 (b) shows the XRD pattern of SiCNWs synthesized from mixture of SiO_2 and graphite at 1400˚C. Three peaks that were corresponded to (111), (220) and (311) crystal planes of cubic ß-SiC (JCPDS card 074-2307) were observed at 2θ of 36˚, 61˚ and 72.5˚. Bin li et.al. [10] also reported similar result in which diffraction peaks of β-SiC at 2θ of 35.8˚, 60˚ and 71.8˚ corresponding to (111), (220) and (311) cubic reflections were obtained. No signal of either SiO_2 or carbon was deteced in this XRD pattern. It can be concluded that mixture of SiO_2 and graphite were converted completely to SiCNWs when 1400˚C was used such that the amounts of the raw materials were too small to be detected by XRD. This result is in good agreement with the FESEM images in Fig. 2 (b) in which only SiCNWs were observed.

For SiCNWs synthesized from mixture of SiO_2 and graphite at 1450˚C, as in Fig. 3 (c), peaks corresponded to ß-SiC as major phase appeared at 2θ values of 36˚, 61˚ and 72.5˚, respectively. The relative intensities of these peaks were similar compared to Fig. 3 (b). In good agreement with FESEM image of Fig 2 (c), SiCNWs were observed with only small amount of graphite or silica particles.

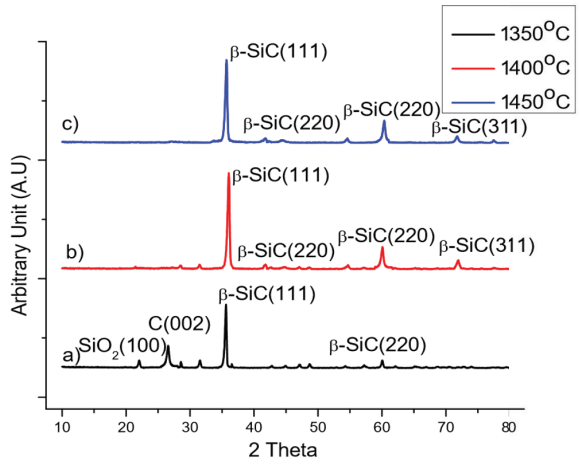

Figure 3: XRD patterns of SiCNW synthesized by microwave heating of mixture of SiO_2 and graphite at heating temperatures of a) 1350˚C, b) 1400˚C and c) 1450˚C.

3.3 Characterization of SiCNWs using EDX

Fig. 4 shows the EDX spectra of the SiCNWs synthesized by microwave heating at 1350˚C, 1400˚C and 1450˚C. Qualitative analysis was conducted to identify the elements that are present in the as synthesized SiCNWs. EDX spectra with high accuracy after subjecting to automatic correction and robust spectrum processing using the built in software were obtained. Fig. 4 (a) shows the EDX peak of SiCNWs that synthesized from mixture of silica and graphite at 1350˚C. From the peak, 3 elements were detected which are Si, C and O. O element is corresponded to the presence of silica in the end product. This indicated that silica was not fully reacted in this process, and this is in good agreement with XRD result in Fig. 3 and FESEM images in Fig. 2 (a). Similar observation was reported by Quah et al. [29] and they attributed the presence of O element in the EDX spectrum to the presence of unreacted SiO_2 in final product.

For EDX spectra of SiCNWs synthesized at 1400˚C and 1450˚C, peaks corresponded to Si and C elements were observed. This indicated that mixture of SiO_2 and graphite reacted completely to form SiCNWs at 1400˚C and 1450˚C.

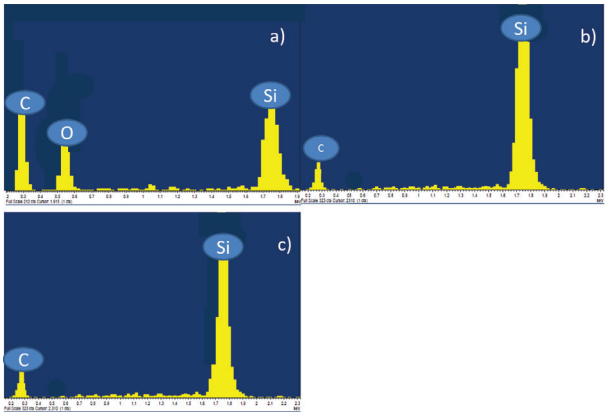

Figure 4: EDX spectra of SiCNWs synthesized by microwave heating of mixture of SiO_2 and graphite at heating temperatures of a) 1350˚C, b) 1400˚C and c) 1450˚C.

3.4 Characterization of SiCNWs using FTIR

FTIR transmission spectra of SiCNWs synthesized from mixture of graphite and SiO_2 at different heating temperatures are shown in Fig. 5. From the spectra, it can be concluded that SiCNWs were successfully synthesized at all temperatures since FTIR peaks corresponded to Si-C stretching bond were present at around 800 cm^{-1} in all FTIR spectra of SiCNWs. However, as in Fig. 5 a), it can be observed that SICNWs at heating temperature of 1350˚C has absorption band of relatively low intensity at 801.7 cm^{-1} that indicates only small amount of SiCNWs were formed. FTIR peak corresponded to

stretching bond of Si-O bonding group was also observed at 1097.28 cm^{-1}. The presence of this absorption band indicated the presence of unreacted SiO_2. Similar absorption bands were reported by Zhao et al. [30] and Rajarao et al. [31]. Zhao et al. [30] obtained such absorption peak at 1080cm^{-1} and they suggested that this peak was associated with the Si–O–Si bond of mesoporous silica. Rajarao et al. [31] also reported absorption band at 1045cm^{-1} and this peak was attributed to Si-O-Si bond. Absorption bands at 1640.2 cm^{-1} were also observed in Fig. 5 (a) due to the presence of C=C bonds of graphite [32]. The presence of absorption bands of both SiO_2 and graphite indicate that 1350˚C was insufficient to enable complete reaction between SiO_2 and graphite and thus some of the SiO_2 and graphite were left unreacted.

For FTIR spectrum of SiCNWs formed at 1400˚C, only one peak was observed at 803.5cm^{-1} corresponding to the presence of Si–C bond that indicated the successful synthesis of SiCNWs. This result is in good agreement with the XRD pattern of SiCNWs synthesized at 1400˚C in Fig. 3 (b) which indicates the presence of single phase β-SiC and thus denotes complete conversion of graphite to SiCNWs. FTIR spectrum of SiCNWs synthesized at 1450˚C as shown in Fig. 5 (c) also revealed the presence of single phase β-SiC due to the presence of absorption peak of Si-C stretching bonds centered at 804.6 cm^{-1}.

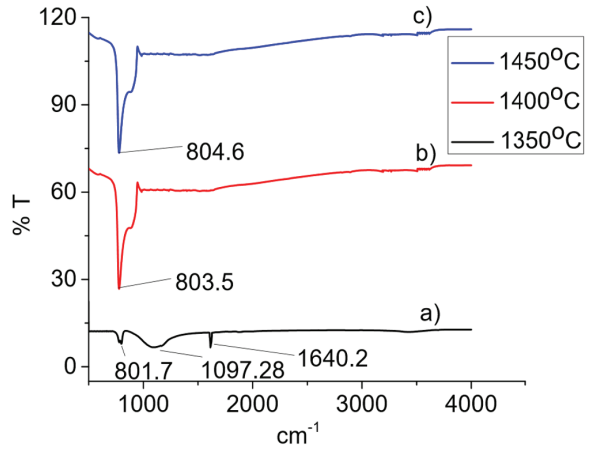

Figure 5: FTIR spectra of SiCNWs synthesized by microwave heating of mixture of SiO_2 and graphite at heating temperatures of a) 1350˚C, b) 1400˚C and c) 1450˚C.

3.5 Characterization of SiCNWs using PL

PL spectra of SiCNWs synthesized at different heating temperatures were showed in Fig. 6. Fig. 6 shows peaks of SiCNWs at 440 nm (2.8 eV) in all spectra. The peaks are obviously blue-shifted in comparison with the band gap of 3C-SiC (2.39 eV). The blue shift of the PL peak of 3C-SiC nanomaterials has been reported by several researchers [33,34,35]. For example, the peak at 418 nm for 3C-SiC nanobelts has been reported by Wu et al [36]. They proposed that the location of this peak depends on the nanostructure, morphology and size of 3C-SiC materials. The collective influence of size confinement effect and defects lead to the blue shift of the peak. Thus, the peak emission appeared around 440 nm may be due to size confinement effect and defects.

In Fig. 6 (a), PL spectrum of SICNWs synthesized from blend of SiO_2 and graphite at 1350˚C shows the presence of PL peak attributed to oxygen discrepancy in SiO_2 and carbon at wavelength about 380 and 620 nm which corresponded to band gap of 3.2 eV and 2.0 eV, respectively. This PL spectrum result is in good agreement with the XRD result of SICNWs synthesized at 1350˚C which shows the presence of XRD peak corresponded to SiO_2 and carbon. Nandanwar et al [37] reported the characterization of SiO_2 nanoparticles and also reported PL peak of pure SiO_2 at 381.8 nm.

Fig. 6 (b**)** and (c) shows that in the PL spectra of SiCNWs synthesized at 1400˚C and 1450˚C, only one peak appeared at 425nm and this peak is corresponded to β-SiC. This indicated that only SiC is present in the SiCNWs synthesized at heating temperature 1400˚C and 1450˚C. This result is in good consistent with the XRD result in Fig. 3 (b) and (c) that graphite and SiO_2 react completely to form single phase SiCNWs.

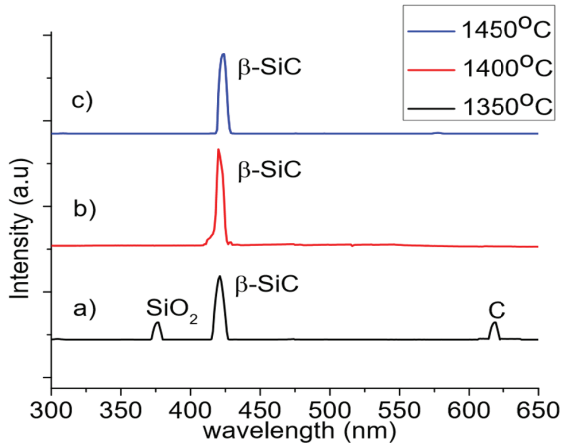

Figure 6: PL spectrum of SiCNWs synthesized by microwave heating of mixture of SiO_2 and graphite at heating temperatures of a) 1350˚C, b) 1400˚C and c) 1450˚C.

3.6 Thermal Gravimetric Analysis of SiCNWs

Thermal Gravimetric Analysis (TGA) curves of SiCNWs synthesized at different heating temperatures are presented in Fig. 7. TGA was conducted to evaluate indirectly the quantity of SiCNWs. For SiCNWs synthesized

at 1450˚C in Fig. 7 (b), the weight loss started at 700ºC with a total of 7 wt %. Similar weight loss occurred for SiCNWs synthesized at 1400˚C with 6 wt% as shown in Fig. 7 (a). These small weight losses of SiCNWs can be attributed to the oxidation of small amount of unreacted carbon and loss of moisture. The presence of moisture may happen during the handling of sample since sample is powder which can easily absorb moisture. Corriu et al. [38] proposed that the weight loss which occurred at 450 ºC to 750 ºC domain was attributed to the air oxidation of the carbon. This indicated graphite was almost fully converted to SiCNWs with only very small amount of unreacted carbon for both SiCNWs synthesized at 1400 ˚C and 1450 ˚C. This result is in good agreement with XRD result in Fig. 3 a) and b) in which carbon and silica were too little to be detected. This high resistance toward oxidation for SiCNWs synthesized at 1400˚C and 1450 ˚C is attributed to the formation of pure SiCNWs. TGA curves show no weight loss at temperature higher than 800 ºC for both SiCNWs formed at 1400 and 1450 ˚C, indicating the remaining residue were SiCNWs.

Fig. 7 c) shows that for SiCNWs synthesized at 1350˚C, a total of 45% of weight loss is observed starting at 700 to 950 ºC and this weight loss was attributed to the oxidation of unreacted carbon in SiCNWs. These results are in good agreement with the XRD result displayed in Fig. 3 which showed the presence of peak of unreacted carbon in SiCNWs synthesized at 1350˚C. This result demonstrated that SiCNWs produced at 1400˚C and above has relatively high purity and good thermal stability.

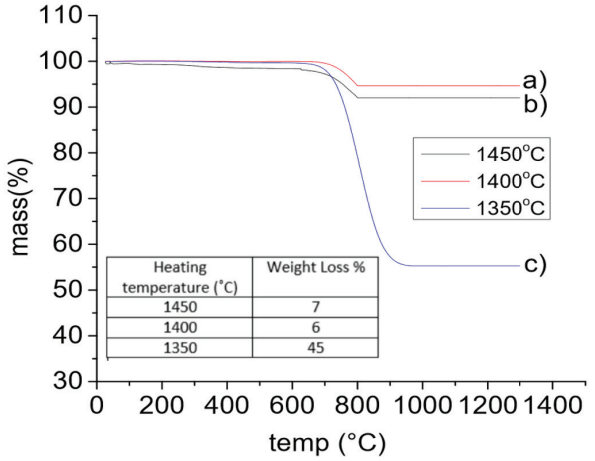

Figure 7: TGA curves of SiCNWs synthesized by microwave heating of mixture of SiO_2 and graphite at heating temperatures of a) 1400˚C, b) 1450˚C and c) 1350˚C.

3.7 Mechanism of Synthesis of SiCNWs by Microwaves Heating

For this research, the interactions between carbon-based material (graphite) and microwave irradiation are important to generate heat thus give many advantages in many aspects to synthesize SiCNWs. Since the quart materials are not sensitive to microwave, in this study we proposed that the heat from graphite (carbon based material) are transferred to silica via external means such as conduction, convection and radiation to assist the heating of silica. Lin He et al. [22] proposed that silica is an inorganic material that almost cannot react to microwave and the reaction are not as effective as carbon based material from the calorimetric study based on these materials. The homogeneous mixture between silica and graphite therefore significantly affects the uniformity of temperature increase for both materials. For this reason, ultrasonic mixing of graphite and silica using ethanol as medium provided homogeneous mixing.

The mechanism of microwave heating varies according to the interaction between the microwaves and target materials. Dielectric heating occurs when dielectric materials such as graphite interact with microwaves. Electric field component of electromagnetic interact with charged particles (electrons) of carbon causes the material to generate heat. Graphite is known as carbon-based material that contains charged particles which are free to move in a delimited region of the material [23, 39]. When electromagnetic field is subjected to the material such as graphite, current traveling in phase with the electromagnetic field is induced. The electron from the carbon material cannot couple to the changes of phase in the electric field and causes energy to dissipate in the form of heat. Fig. 8 shows the mechanism of dielectric heating that based on motion of electrons from carbon material to generate heat. Motion of electron from carbon through joule heating within the grain generates heat. This reaction is called Maxwell-Wagner effect and it is significantly different from the reaction between electromagnetic wave and

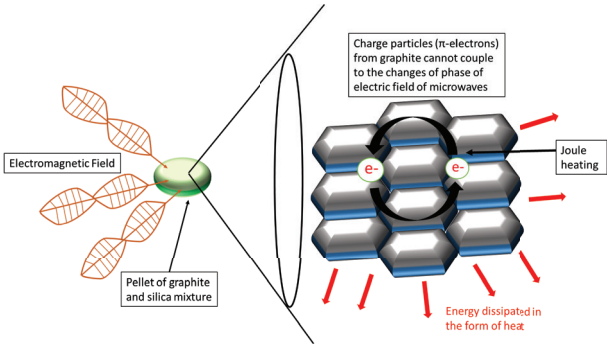

Figure 8: Interaction of microwave with graphite leads to dielectric heating of graphite.

polar liquid such as water that heat up due to vibration of molecules [40,23].

The overall reaction of formation for SiC through carbothermal reduction is generally written as [41]:

$SiO_2(s) + 3C(s) = SiC(s) + 2CO(g)$ (1)
$AG° = 598.18 - 0.3278\,T\ (kJ)$

There are multiple reactions between silica and graphite before the formation of SiCNWs. First reaction is the solid-solid reaction between silica and graphite causing the carbothermal reduction of silica by graphite to form SiO and CO gases by following reaction [41]:

$SiO_2(s) + C(s) \rightarrow SiO(g) + CO(g)$ (2)
$AG° = 668.07 - 0.3288\,T\ (kJ)$

The vapour-solid (VS) mechanism was suggested to explain the formation of SiCNWs. From reaction (3), SiO gas reacts with C to produce SiC nuclei as follow [42]:

$SiO(s) + 2C(s) \rightarrow SiC(g) + CO(g)$ (3)
$AG° = -78.89 + 0.0010\,T\ (kJ)$

Cetinkaya et.al stated for VS mechanism, Si-containing vapors such as Si gas or SiO gas are believed to react with CO gas or C solid to form SiC nuclei [43]. Thus, SiC particles from reaction (3) are believed to serve as nucleation sites for VS mechanism to occur.

$SiO(g) + 3CO(g) \rightarrow SiCNWs\ (s) + 2CO_2(g)$ (4)

From reaction (4), the VS mechanism occurred when SiO vapour and CO vapour deposited at the tip of SiC nuclei that formed from reaction (3). Fig. 9 summarizes the overall reaction between graphite and silica for the formation of SiCNWs. The nanowhisker grows along the directions of the least stable plane and forms SiCNWs, as in Fig. 10. J. Wei et al. [44] and Dehghanzadeh [45] et al. have proposed that the nanowire growth might be attributed to the reaction between SiO and carbon gases. The effect of temperature for synthesis of SiCNWs

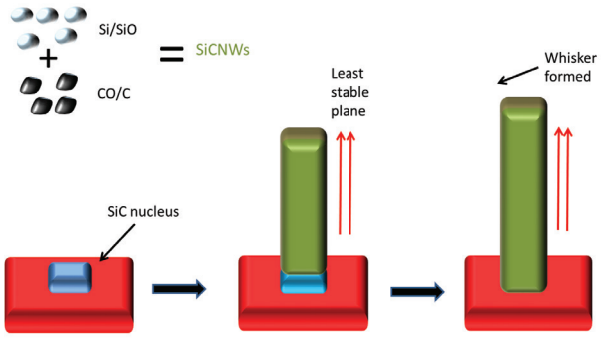

Figure 9: Schematic of SiCNWs growth from graphite and silica by microwaves heating.

has been studied by thermodynamic calculation. The Gibbs free energy for overall reaction in reaction (2) decreases with temperature thus denoted that the reaction is non-spontaneous reaction. Based on Gibbs free energy, reaction (2) is highly endothermic and the reaction is favorable to occur as the temperature increases [46]. Synthesis of SiC is basically dependent on the formation of SiO gas. Lee et al. also proposed that SiC is synthesized through the formation of intermediate SiO [47].

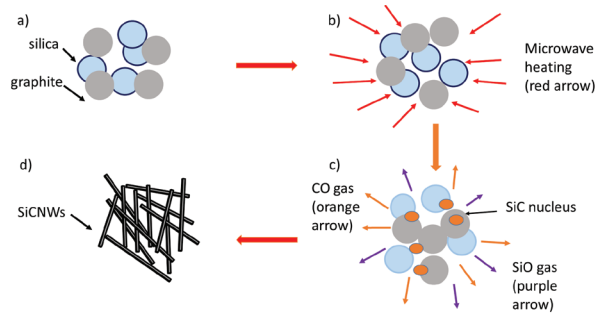

Figure 10: Schematic of SiCNWs growth from graphite and silica by microwaves heating a) Mixture of graphite and silica b) Exposing mixture of SiO_2 and graphite to microwave irradiation until 1400˚C c) Formation of SiO gas, Co gas and SiC nucleus after exposed to microwave irradiation at high temperature d) Formation of SiCNW.

The Gibbs free energy for the reaction between SiO gas and carbon as in reaction (3) is negative and thus the reaction is spontaneous, regardless of the temperature. Thus, the overall SiC formation is defined by SiO formation in reaction (2), since the Gibbs free energy decreases significantly on temperature. Furthermore, formation of SiO gas is the rate determining step for the overall reaction of SiC formation [48, 49]. Some researchers have studied the rate of reaction to synthesis SiC based on Arrhenius equation [49, 50].

$k = Ae^{-Ea/RT}$ (5)

Rate constant and activation energy are calculated based on the Arrhenius equation in equation (5). Kavitha et al. [50] studied the synthesis of nano silicon carbide powder from agricultural waste and calculated the activation energy during the synthesis of SiC using the Arrhenius equation. They reported that with the increasing of heating temperature, the activation energy decreased and caused the rate of reaction for the synthesis of SiC to increase. This explained the significant effect of temperature on the rate of reaction of the synthesis of SiC. Furthermore, for temperature at 1350˚C, it is believed that the partial pressure of SiO gases produced was lower than those produced at temperature above 1400 ˚C. Y. Li et al. [51] reported that the partial

pressure of SiO as predominant gas increased with temperature which was originated from the oxidation of silica. Thus, the amount of nucleation sites produced from reaction of SiO gas and carbon (solid) at 1350˚C was expected to be lower comparing to those formed at 1400 ˚C and 1450 ˚C. SiO and CO gases as the product from reaction at (3) and (4), respectively, react to form SiCNWs but the reaction was incomplete due to the lack of reactant (SiO) at low temperature. This explained the incomplete formation of SiCNWs at 1350˚C when the heating duration was set to 40 minutes. For temperature above 1400 ˚C, as shown by the results, heating duration of 40 minutes was sufficient for complete synthesis.

4Conclusions

SiC nanowhiskers have been successfully synthesized by microwaves heating of mixture of SiO_2 and graphite in the ratio of 1:3. The effect of heating temperature during microwave heating was studied. SiCNWs were characterized by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive x-ray spectroscopy (EDX), photoluminescence spectroscopy (PL), fourier transform infrared (FTIR) and thermo-gravimetric analysis (TGA). 1400˚C is the most suitable temperature for the synthesis of SiCNWs because of complete reaction between silicon dioxide and graphite resulted in the formation of single phase β-SiC nanowhiskers in nanoscales as proven by the results obtained from characterization and testing. By using 1350 ˚C for the synthesis of SiCNWs, traces of unreacted graphite and SiO_2 were detected that indicated incomplete conversions of graphite and silica to SiCNWs while synthesis of SiCNWs at 1450 ˚C resulted in SiCNWs with diameter higher than 100 nm.

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