

Silicon Carbide Nanowires Synthesis and Preliminary Investigations

J. PATYK^{a,*}, R. RICH^b, M. WIELIGÓR^b AND T.W. ŻERDA^b

^aNicolaus Copernicus University, Institute of Physics, Grudziądzka 5, 87-100 Toruń, Poland

^bTexas Christian University, Department of Physics and Astronomy, Fort Worth, TX 76129, USA

As the field of biotechnology expands and the semiconductor industry approaches the limit of size reduction with conventional materials, these and other fields will increasingly rely on nanomaterials with novel properties. Silicon carbide (SiC) possesses many properties that make it appealing to research and industry: a large band gap, high hardness, high strength, low thermal expansion, chemical inertness, etc. It is known that silicon carbide nanowires can be synthesized through a reaction between silicon vapor and multiwalled carbon nanotubes. This process was refined to produce smaller, straighter nanowires. This was done by analyzing the dependence of the reaction rate on the partial vapor pressure of silicon. The reaction rate was studied by comparison of SiC and multiwalled carbon nanotubes peak intensities in X-ray diffractograms, which produced an estimate of the respective reactions' SiC yields. The particle morphologies were then analyzed with transmission electron microscopy. Finally, Fourier transform infrared spectroscopy was utilized to study the intensities and frequencies of the SiC infrared absorption bands. This data was analyzed with respect to the previously determined yield and particle sizes of the respective SiC nanowire samples.

PACS numbers: 81.05.Je, 81.07.Gf, 81.10.St, 81.20.Ka

1. Introduction

Silicon carbide (SiC) is playing a key role in many fields. Synthesis of silicon carbide wires of nanometer diameters is of interest because of the unique mechanical, optical, electronic, and other properties of these nanowires. There are three main growth mechanisms of SiC nanowires: (A) vapor–liquid–solid (VLS) [1, 2], (B) template-assisted growth from carbon nanotubes (CNTs) [3–6] and silicon nanowires [7], and (C) vapor–solid mechanism from nanostructured carbon particles [8, 9], silica [10], silicon [11], and silicon carbide [12]. The mechanism of formation of SiC nanowires (SiC NW) from carbon nanotubes has not been fully characterized.

In this paper we are presenting a new method of synthesis of such material — synthesis from multiwalled carbon nanotubes (MWCNTs) and silicon vapor at high temperature. The advantages of the method is lack or very thin silicon oxide outer shell and potential possibility to synthesize SiC nanowires from the ordered, grass-like MWCNTs. It seems that the presented method should allow to synthesize SiC nanotube filled with carbon. Such a composite nanomaterial may have a unique properties. Presented article reports results of preliminary investigations of SiC NW synthesized from MWCNTs and silicon vapor.

2. Experimental setup

MWCNTs were placed in a small, quartz vial and this vial was sealed, under vacuum (about 3×10^{-4} Pa), inside a larger quartz tube. The tube was then heated in a larger, evacuated alumina tube to prevent the collapse of the quartz tube inside. After sintering, the Si powder was sealed off from the MWCNT to prevent contamination, and the quartz tube was opened. After measuring the SiC yield the sample was burned in air to remove excess carbon that had not reacted with Si and is exposed to air.

The vapor pressure of Si varies exponentially with the temperature and depends on the temperature of the coldest point of the container. Therefore we could utilize the temperature control of the quartz tube to vary the pressure of Si vapor exposed to MWCNTs.

The MWCNT were kept separate from the Si, so the temperature at which the reaction between solid MWCNT and gaseous Si occurs can be controlled independently if only it is higher than the temperature of the coldest point of the tube.

3. Measurements

Mixtures of commercially produced SiC and MWCNT were analyzed by X-ray diffraction using Philips PW2773 diffractometer with a Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$). Ratio of the intensity of the SiC (111) reflection to the sum

* corresponding author; e-mail: jkp@fizyka.umk.pl

of that intensity and intensity of MWCNT (111) reflection from the mixtures were compared to their known SiC mass concentration (from mixtures' substrates weighting) to form a calibration curve (Fig. 1).

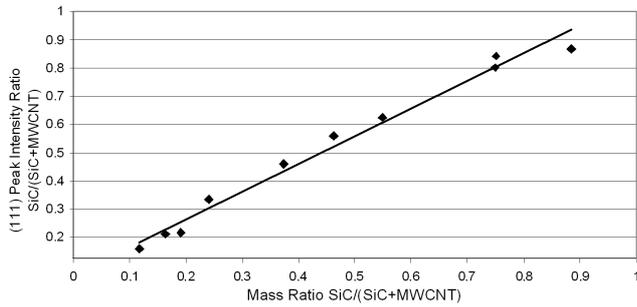


Fig. 1. XRD calibration curve for SiC content determination. Prepared using commercially produced SiC powder and MWCNT.

X-ray diffractograms were collected from subsequent SiC nanowire samples. The aforementioned calibration curve was used to measure the SiC concentration, and therefore the reaction progress, in the mentioned samples.

With sintering temperature held constant (1200 °C), a very large increase in yield for Si temperature between 1100 °C and 1125 °C was found.

It is believed that if Si vapor pressure is kept below that at 1125 °C, thin wires will form in larger numbers than large clumps.

TEM images (Fig. 3, Fig. 4) show that short sintering times seem to be most conducive to the production of thin nanowires. Material synthesized at lower temperature (1200 °C at Fig. 4 vs. 1250 °C at Fig. 3) and with lower Si vapor pressure (1000 °C at Fig. 4 vs. 1200 °C at Fig. 3) but for much longer time (25 h at Fig. 4 vs. 1 h at Fig. 3) consists of thicker wires.

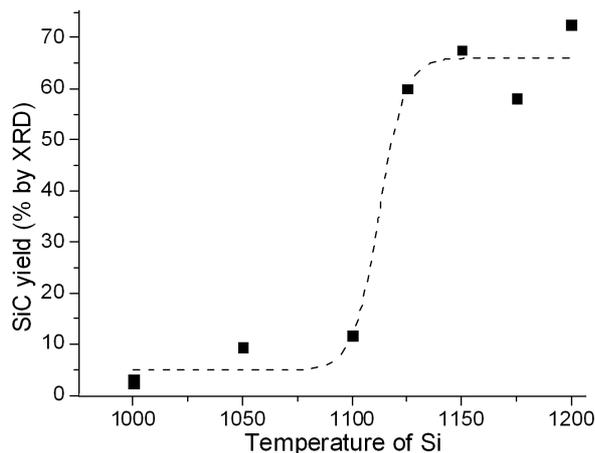


Fig. 2. SiC synthesis yield versus temperature controlling Si vapor pressure.

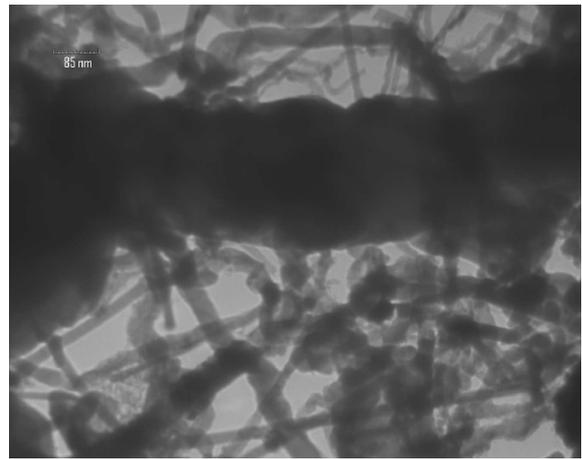


Fig. 3. SiC nanowires synthesized after 1 h sintering with Si temperature 1200 °C and reaction temperature of 1250 °C.

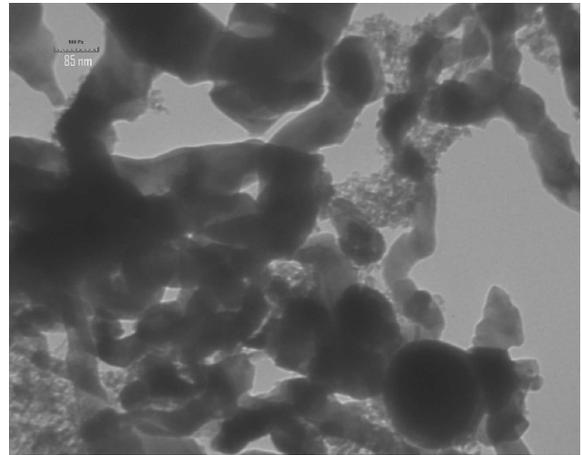


Fig. 4. SiC nanowires synthesized after 25 h sintering with Si temperature 1000 °C and reaction temperature of 1200 °C.

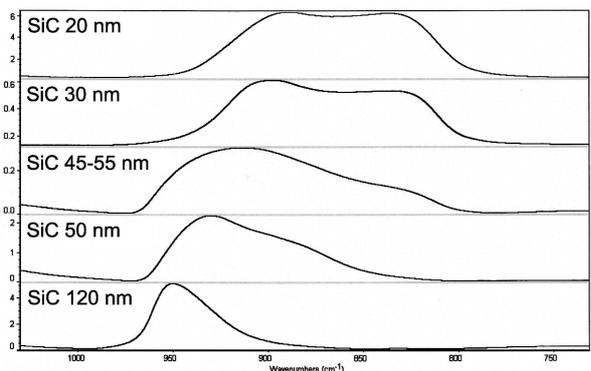


Fig. 5. FTIR spectra of different average grain size commercial SiC powders.

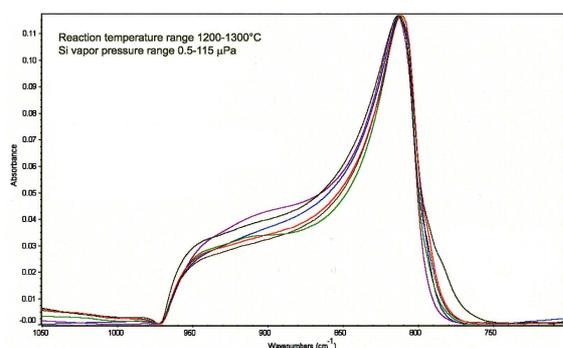


Fig. 6. FTIR spectra of SiC nanowires synthesized at different conditions from MWCNT and Si vapor.

To get a better idea of what happens to the infrared absorption spectrum of SiC with increasing particle size, data was first collected on commercially produced, spherically-shaped SiC nanosized powder.

It is seen that the transverse optical mode (TO) located around 835 cm^{-1} (20 nm) reduces in intensity and shifts towards higher frequencies with increasing grains size. The longitudinal optical mode (LO) located around 900 cm^{-1} (20 nm) shifts towards higher frequencies with increasing grains size as well.

A striking difference is noticed when comparing the commercially produced nanoparticles to our SiC nanowires. There is very little difference in the intensities of the LO and TO band between samples, possibly indicating that the size distribution of the grains in our samples remains constant.

4. Conclusions

It was shown that there is possibility to produce SiC nanostructures from MWCNTs and Si vapor. Infrared spectroscopy suggests that the mechanism of the synthesis leads to the formation of nanostructures built from grains of similar size, independently of the rate of Si delivery and rate of synthesis. Comparison of the yield of the synthesis for different Si delivery and for different time of the reaction allows us to believe that the large

increase of the yield is connected with the formation of SiC on the surface of MWCNT, increase of the intrinsic strain and consequently crushing of the SiC surface. This process allows Si vapor to penetrate inner carbon walls of the nanotube.

The presented method of the preparation should possibly allow us to produce SiC nanotubes filled with unreacted carbon. There is a question of the structure of the core carbon and SiC shell. Further investigation should answer that and some other questions connected either to the method of synthesis or properties of the synthesized materials.

References

- [1] X.T. Zhou, H.L. Lai, H.Y. Peng, F.C.K. Au, L.S. Liao, N. Wang, I. Bello, C.S. Lee, S.T. Lee, *Chem. Phys. Lett.* **318**, 58 (2000).
- [2] H.F. Zhang, C.M. Wang, L.S. Wang, *Nano Lett.* **2**, 941 (2002).
- [3] H. Dai, E.W. Wong, Y.Z. Lu, S. Fan, C.M. Lieber, *Nature* **375**, 769 (1995).
- [4] Y. Zhang, T. Ichihashi, E. Landree, F. Nihey, S. Iijima, *Science* **285**, 1719 (1999).
- [5] K.L. Wallis, M. Wieligór, T.W. Żerda, S. Stelmakh, S. Gierlotka, B. Palosz, *J. Nanosci. Nanotechnol.* **8**, 3504 (2007).
- [6] Y. Wang, T.W. Żerda, *J. Phys., Condens. Matter* **18**, 2995 (2006).
- [7] Y.F. Zhang, Y.H. Tang, Y. Zhang, C.S. Lee, I. Bello, S.T. Lee, *Chem. Phys. Lett.* **330**, 48 (2000).
- [8] G.W. Meng, Z. Cui, L.D. Zhang, F. Philipp, *J. Cryst. Growth* **209**, 801 (2000).
- [9] M. Bechelany, A. Brioude, P. Stadelmann, G. Ferro, D. Cornu, P. Miele, *Adv. Funct. Mater.* **17**, 3251 (2007).
- [10] X.C. Wu, W.H. Song, B. Zhao, W.D. Huang, M.H. Pu, Y.P. Sun, J.J. Du, *Solid State Commun.* **115**, 683 (2000).
- [11] K. Saulig-Wenger, D. Cornu, F. Chassagneux, G. Ferro, T. Epicier, P. Miele, *Solid State Commun.* **124**, 157 (2002).
- [12] W. Yang, H. Araki, Q. Hu, N. Ishikawa, H. Suzuki, T. Noda, *J. Cryst. Growth* **264**, 278 (2004).