

# Large Scale Synthesis of SiC Nanofibers from Various Carbon Precursors

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## ABSTRACT

Submicron and micron sized graphitic particles were compared with multiwalled carbon nanotubes (MWNTs) as precursors for producing several grams of SiC nanofibers in a 3'' diameter hotwalled chemical vapor deposition reactor. Nickel nitrate and the carbon precursor were dispersed in tetrahydro furan and dried to disperse the nickel used as a catalyst. Samples were characterized by SEM, TEM, EDS, and XRD. Carbon precursor size and shape, and nickel catalyst concentration are compared. While all carbon precursors produced single crystalline SiC nanofibers, large sized carbon precursors also produced large sized SiC particles by direct conversion. Small amounts of SiC fibers with low aspect ratios and wide ranging diameters and lengths were produced when little or no catalyst was used with carbon precursors. Surface area and volume of the carbon precursor is believed to have a large effect on the quality and quantity of SiC nanofibers produced.

**Keywords:** chemical vapor deposition, vapor-liquid-solid mechanism, and SiC nanofibers

## 1 INTRODUCTION

Nanotubes and nanofibers have great promise as reinforcing material in composites due to their outstanding mechanical, thermal, and electrical properties.[1] There is increased interest in hetero-atomic nanomaterials due to their unique electronic properties which can be controlled by changing their chemistry.[2] SiC fibers and whiskers have been widely used and studied as a reinforcing material for composites for their extraordinary properties, such as high thermal conductivity, high thermal stability, excellent mechanical strength, and chemical inertness.[3] However, most industrial applications use micron sized whiskers with low aspect ratios, which have much lower strength compared to their nanosized counterparts. Single crystalline SiC nanofibers also have great promise in producing high toughness and strength composite materials.

Many methods are currently used to produce SiC nanofibers including chemical vapor deposition, thermal plasma synthesis, carbon nanotube confined reactions, and template catalyst free methods; however it is a challenge to economically produce bulk amounts of high quality SiC nanofibers. Processes which produce high quality SiC nanofibers often limit the quantity of fibers synthesized by limiting the growth to two dimensions on a wafer.[4] Other

processes use carbon nanotubes confined reactions to fabricate SiC nanofibers which can limit them as fillers in composite materials due to their high cost. For many methods it is difficult to consistently grow large quantities of high quality SiC nanofibers. Despite the various growth methods, only three known mechanisms can fabricate SiC nanofibers: vapor-liquid-solid (VLS), vapor-solid (VS), and direct conversion (DC) of carbon nanotubes. Our previous work used graphite particles as an inexpensive carbon precursor to make SiC nanofibers in bundles along with SiC particles with similar sizes to their graphitic precursor. In this proceeding submicron and micron sized graphitic particles were compared with MWNTs as precursors for producing several grams of SiC nanofibers.

## 2 EXPERIMENTAL

A horizontal hot-walled chemical vapor deposition reactor was assembled from an MTI GSL1600-80X Bench-top High Temperature Tube Furnace and MKS mass flow controllers. Silica, with 0.5-10 mm particle size and 99% purity (Sigma Aldrich, WI) and silicon with 325 mesh (less than 44 microns) and 99% purity (Sigma Aldrich), were mixed with a 2:1 molar ratio and then put into high purity alumina crucible and leveled, as previously described.[5] Then carbon precursors were added to the crucible and leveled. The crucible was put inside a hot wall CVD chamber with 100 sccm Ar/H<sub>2</sub> (5%H<sub>2</sub>) gas. Certain trials utilized 10 sccm of methane, hydrocarbons, or CO<sub>2g</sub>. The temperature was raised to 1500 °C at 150 °C/hour and held for 15 hours.

Various carbon precursors shown in table 1 were used such as such as MWNT, submicron graphite (SMG), micron sized graphite (MG), and large graphite (LG). Nickel (II) nitrate hexahydrate (Sigma Aldrich) was used to prepare nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>) solutions. Catalyst quantities chosen were 10 μmol, 25 μmol, 50 μmol, or 200 μmol moles of Ni<sup>+2</sup> per gram of carbon precursor. When catalysts are used, carbon source materials were soaked and mixed in nickel nitrate tetrahydro furan solutions at room temperature, then dried over night. The dried carbon source was placed on top of the Si/SiO<sub>2</sub> mixture for ease of separation after the reaction. When nickel nitrate was used, the H<sub>2</sub> in Ar/H<sub>2</sub> gas was used to reduce the nickel nitrate to nickel nanoparticles. The as-prepared samples were characterized with SEM (Scanning Electron Microscopy), EDS (Energy Dispersive Spectrometer), TEM (Transmission electron spectroscopy) and XRD (X-Ray Diffraction).

**Table 1.** Carbon precursor size, purity, and volume to surface area ratio

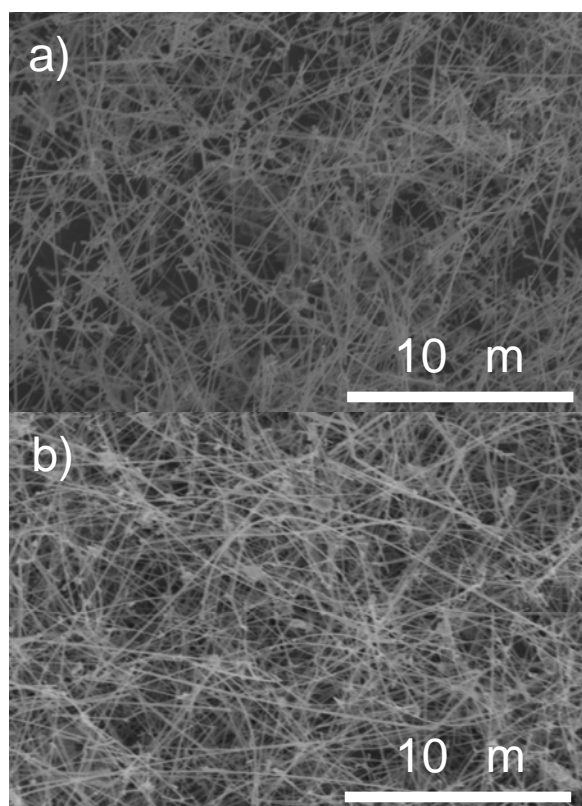
Name	Company	Purity	Size	Volume/Surface Area
MWNT	Helix Material Solutions	95%	10-30 nm diameter; 0.5-20 $\mu\text{m}$ length	2.48-7.49 nm
SMG	Nanostructured and Amorphous Materials	99.9%	450 nm diameter	150 nm
MG	Alfa Aesar	99.995%	1-15 $\mu\text{m}$ diameter	333-5000 nm
LG	Sigma Aldrich	99.99%	44 $\mu\text{m}$ diameter	14700 nm

### 3 RESULTS AND DISCUSSION

Several grams of  $\beta$ -SiC were produced from graphitic precursors and compared to SiC nanofiber samples produced from MWNTs. Various factors impacted the size and quantity of the SiC nanofibers produced.

#### 3.1 SiC Nanofibers From Graphite

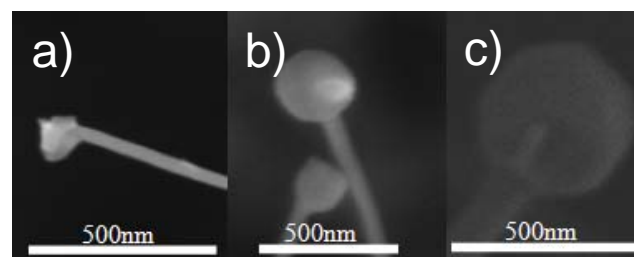
Previously our process was unable to synthesize high quality nanofibers using MG[5]; however a new catalyst mixing method has produced similar SiC nanofibers from MG as from LG, seen in figure 1, using 25  $\mu\text{mol}$  of  $\text{Ni}^{+2}$  per



**Figure 1.** SEM images of SiC nanofibers from LG (a) and MG (b) with Ni catalyst

gram of carbon. The believed primary growth mechanism for SiC nanofibers in all graphitic samples is VLS due to the presence of nickel nanoparticles found and characterized by EDS. Also, when little or no Ni catalyst was present few nanofibers were formed. If excess Ni catalyst was provided for the synthesis of SiC nanofibers, large Ni particles were found on the ends of the nanofibers as seen in figure 2. The size of the Ni particle depends directly on the concentration of catalyst provided for the reaction; however the nanofiber diameter tended to be less than 100nm despite the larger size of the Ni particle, excluding the 200 $\mu\text{mol}$  sample. This is believed to be due to the increased rate of reaction of the crystal growth in the liquid Ni particle in the  $\langle 111 \rangle$  direction. TEM images indicate that the growth direction of the VLS formed SiC nanofibers are in the  $\langle 111 \rangle$  direction. The limited quantities of  $\text{CO}_g$  and  $\text{SiO}_g$  in the liquid Ni are also believed to affect the diameters of the SiC nanofibers synthesized. Dispersion of catalyst into the carbon precursor is essential for consistent fabrication of high quality SiC nanofibers. If the samples do not evenly disperse the Ni catalyst throughout the carbon source, bundles of nanofibers will be produced similar to our previous work.[5] Poorly dispersed Ni produces various yields of SiC nanofibers with wide ranging Ni particle sizes under similar CVD conditions.

Direct conversion of the graphite to SiC particles decreases the potential yield of SiC nanofibers in the sample. However, previous studies have shown  $\text{CO}_{2g}$  is produced during the nanofiber growth process, which then reacts with more carbon source to produce more carbon monoxide.[6,7] This increases the theoretical yield over 50%; however losses



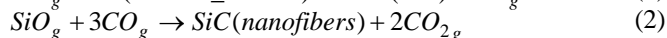
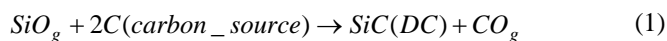
**Figure 2.** SEM images of nickel catalyst on SiC nanofibers synthesized from MWNT with 25  $\mu\text{mol}$  (a), 50  $\mu\text{mol}$  (b), and 200  $\mu\text{mol}$  (c) of  $\text{Ni}^{+2}$  catalyst

of  $\text{CO}_g$  diffusion from the crucible can lower the yield significantly.

### 3.2 SiC nanofiber Reaction Kinetics and Diffusion

Reaction kinetics and diffusion affect the SiC nanofiber synthesis in every process; however either kinetics or diffusion can be the rate determining step of the process at different times of the fabrication. The duration of the kinetically limited step is believed to be controlled by the size and shape of the carbon precursor.

Initially the silica and silicon react bringing forth  $\text{SiO}_g$  which diffuses and comes into contact with the surface of the carbon source as seen in equation 1. This produces the  $\text{CO}_g$  which is required to produce the high quality SiC nanofibers by either VS or VLS mechanism as seen in equation 2. Equation 1 also directly converts the surface of the carbon source into SiC. This is believed to be a kinetically limited step which should produce a spike in localized  $\text{CO}_g$  concentration. This spike should increase in magnitude and duration as the volume to surface area ratio decreases.

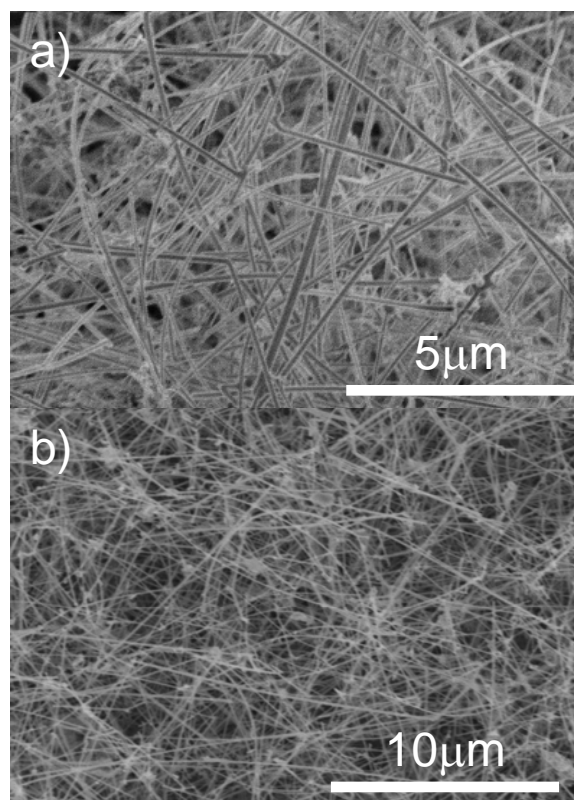


After the surface of the carbon source has been completely converted to SiC the  $\text{SiO}_g$  must diffuse through the SiC shell to produce the  $\text{CO}_g$  essential for the continuation of the SiC nanofiber growth process. Previously reported results show a time-length effect believed to occur in part from the increased time necessary for the gases to diffuse through the SiC layer of the carbon precursor.[5] When the volume to surface area ratio is large, more time is spent in the diffusion limiting step. This produces a relatively constant source of  $\text{CO}_g$  increasing the yield of SiC nanofibers. Le Chatelier's principle dictates that lower localized concentrations of  $\text{CO}_g$  and  $\text{CO}_{2g}$  will limit the diffusion of the gases from the crucible, in turn increasing the yield.

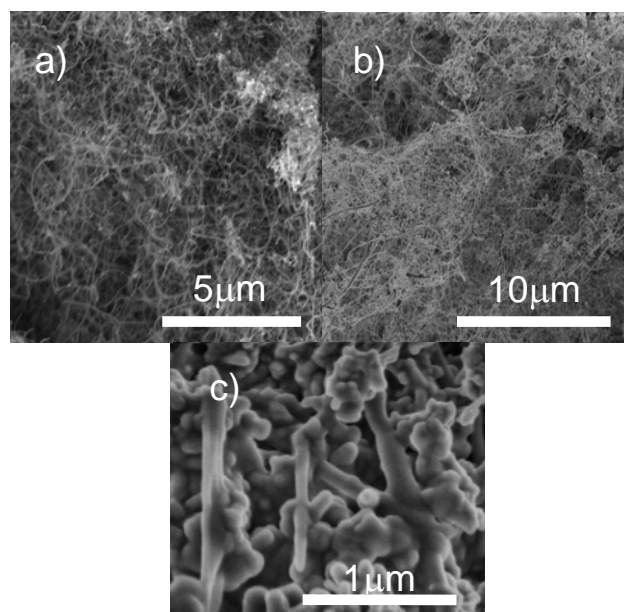
### 3.3 MWNT and Graphite For SiC Nanofiber Growth

Different shaped carbon precursors such as MG and MWNT can produce very similar SiC nanofibers as seen in figure 3, however the yields and by-products of each process varies. The shape of directly converted SiC from MWNTs is very similar to their MWNT precursors as seen in figure 4. After the lower quality, anfractuons, directly converted SiC nanofibers are sonicated some fibers fracture into whiskers or particles as seen in figure 4c, while the fibers believed to be from VLS have similar high aspect ratios after sonication. The anfractuons nanofibers act more like whiskers or particles and have less promise in nanocomposites that require enhanced bending and tensile strengths. This renders the SiC formed by direct synthesis an unwanted by-product regardless of the carbon source.

High quality SiC nanofiber yields are highest, with sufficient time, from graphitic precursors with large particles

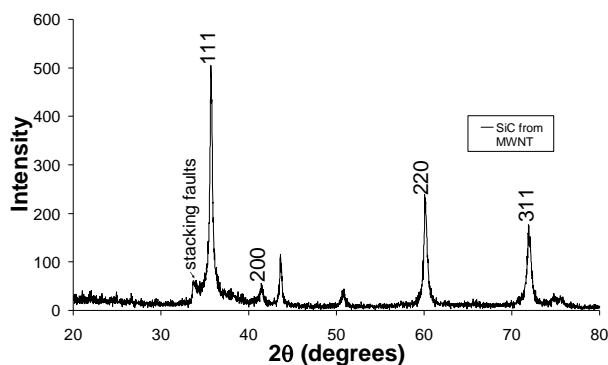


**Figure 3.** SEM images of SiC nanofibers synthesized from MWNT (a) and MG (b) with Ni catalyst



**Figure 4.** SEM image comparison of MWNT (a), SiC nanofibers created from DC of MWNTs (b), and SiC nanowhiskers and nanoparticles observed after sonication (c)

providing the system with a steady source of  $\text{CO}_g$ . Yields of 50-70% were achieved with ~2.0 g of MG per trial, resulting in ~3.5 g of SiC. Higher yields can be produced by modifying the growth process. SMG does not provide as high of yields



**Figure 5.** XRD of SiC nanofibers formed from MWNT

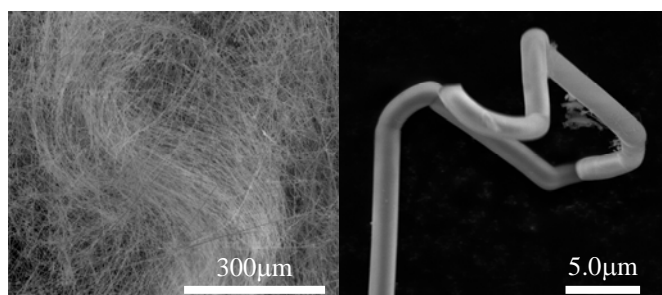
believed to be caused by the small volume to surface area ratio.

The quality of SiC nanofiber powders from MWNT and MG was confirmed using XRD. Figure 5 shows a typical XRD spectrum taken from a SiC nanofiber powder fabricated from MWNTs. Previous TEM investigations show SiC nanofibers synthesized are single crystalline and have thin  $\text{SiO}_x$  and/or amorphous carbon coatings. These coatings can be tailored by changing the  $\text{SiO}_2/\text{Si}$  molar ratio and  $\text{CO}_g$  concentration respectively. When the nanofibers are used in composite materials the thin coatings can provide a better interface and dispersion in the matrix material.

### 3.4 Reactive Gases

Reactive gases can also be used to help increase yield of the SiC nanofibers. When  $\text{CO}_{2g}$  was introduced into the system the yield of SiC nanofibers increased. The average production of SiC powder from 1.0 g of carbon source is 1.6-1.7 g. The highest yield of SiC nanofibers from that powder is between 50-70% from MG. With  $\text{CO}_{2g}$  introduced with the 1.0g of carbon the average production of SiC increases to 2.0g. When  $\text{CO}_{2g}$  is introduced into the system there are limited ways for it to incorporate into the SiC process. First the  $\text{CO}_{2g}$  can react with the carbon source producing  $\text{CO}_g$ . This removes impurities from the SiC and helps to increase the yield. The  $\text{CO}_g$  produced can then incorporate itself into the SiC nanofiber through VLS or VS mechanisms. The  $\text{CO}_{2g}$  can also incorporate itself into the wall of the SiC nanofiber producing an amorphous coating which increases the diameter of the fiber; however this is unlikely and unsubstantiated from SEM images. An added theoretical benefit is the  $\text{CO}_{2g}$  limits the diffusion of the  $\text{CO}_{2g}$  produced from SiC nanofiber by Le Chatelier's principle. This helps to make the SiC nanofiber production yields more consistent, allowing the process to become one step closer to large scale industrial manufacturing.

Methane additions did little to enhance the yield and quality of SiC nanofibers; however some unique larger submicron/micron nanofibers were produced when certain hydrocarbons were added to the system. These large white



**Figure 6.** SiC fibers synthesized with hydrocarbon addition

fibers were located on the outside of the powder and were easily distinguished from the grey, green, blue, and tan colors normally produced and can be seen in figure 6. Colors of the SiC produced depended on the type of precursor and catalyst used.

### 4 CONCLUSIONS

Currently MG produces the highest yields of SiC nanofibers under scale up conditions. By tailoring other experimental conditions, such as reactive gases, higher yields can be achieved. All carbon sources produce unwanted by-products by DC; however limiting the size of the by-product can limit the effect seen by those by-products. This provides great promise for using relatively low cost SiC nanofibers as fillers for composite materials. Future work will investigate the mechanisms and tailor experimental conditions to produce higher yields of bulk SiC nanofibers in an economic manner.

### ACKNOWLEDGEMENT

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