Fabricating SiC Nanowire by Vacuum Heating Multilayer Graphene in Silicate Refractory Tube

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Abstract. One dimension silicon carbide (SiC) was synthesized by vacuum heating multilayer graphene sheets in silicate refractory tube. Scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and Raman spectroscopy were used to study the microstructures and components of the vacuum heated materials. SEM images show the morphology of the synthesized SiC nanowires. XRD patterns and Raman spectra verified that graphene sheets remained and the wire like material was SiC nanowire. Therefore, vacuum sintering technology can be used to synthesize SiC nanowires.

1. Introduction
Silicon carbide has been used as grinding material, abrasive tools and refractory material for its excellent high temperature resistance, wear resistance and corrosion resistance, high strength and high thermal conductivity. Recently, one dimensional silicon carbide nanowires has attracted the interest of many researchers. It was proved by theoretical calculation and experiment results that SiC nanowires and SiC nanorods have much better mechanical properties and thermal and electrical properties than those of bulk SiC. Therefore, one dimensional silicon carbide nanowire has the potential to be widely applied in electronics, optics and composites fields. The promising applications make the synthesis of SiC nanowire a favorite subject for researchers. Up to now, several synthesis methods have been reported to synthesize SiC nanowire, such as carbon nanotubes template-assisted growth[1], laser ablation synthesis[2], chemical vapor deposition (CVD)[3], molten salt synthesis[4, 5] and, especially recently reported growth SiC nanowires on graphene sheets[6], etc.

Graphene, which owns many excellent properties [7-9], have attracted tremendous attention of researchers, is expected to be the potential material for synthesizing SiC nanowires due to its huge specific surface area. In this report, SiC nanowires were synthesized by vacuum heating multilayer graphene sheets in a tube furnace.

2. Experiments
The multilayered graphene platelets (< 5 layers, Nanjing Kefu Nanotech Inc.), as shown in Figure 1a and b, were used for vacuum heating experiments.
Figure 1. Multilayer graphene (a) graphene powder and (b) SEM images of graphene.

Figure 2. Vacuum heating treatment curve.

The multilayer graphene sheets were vacuum heated in a silicate refractory tube vacuum furnace (GSL-1700X-S, Dachun, Hefei, China). First, put the 2g graphene into a Al₂O₃ square crucible in one thin layer, then put the square crucible into tube vacuum furnace, evacuate the tube to 50 mTorr (the max vacuum degree of the equipment), after that fill the tube with argon gas to 1 stand atmospheric pressure, then evacuate the tube to 50 mTorr again, repeat it 3 times to make sure no more oxygen remain in the tube. The temperature evolution during vacuum sintering was shown in Figure 2. A Rigaku Ultima IV Multipurpose X-Ray diffraction system was used to detect the material composite with Cu-Kα source. A Hitachi S-4700 Field emission SEM and Hitachi SU5000 were used to study the morphology of the materials after vacuum heating. The Raman spectra were obtained by a HORIBA LabRAM HR800 Raman spectrometer (HORIBA Jobin Yvon, NJ, USA). A 632.8nm He-Ne laser was focused by an Olympus 50x objective (MPLN50x, Olympus America) as an excitation source, at the center of the sample placed in an open air environment at room temperature.
3. Results and discussion

3.1. Results
Figure 3 is SEM images of vacuum synthesized SiC nanowires. It can be observed on the images that after vacuum heating graphene sheets still exist and wire like materials were synthesized, which were proved to be the SiC nanowires. The nanowires were located at the edge of graphene sheets, and with the averaged length of about 40μm and diameter of about 40 nm. It should be noted from Figure 3a that the SiC nanowires were not distributed homogeneously, this means SiC nanowires were not growth with a same state on the graphene sheets. Figure 3b and c are magnified images of Figure 3a. It can be observed from Figure 3b that the outside shape of the nanowires was different. Some of the nanowires with a rather smooth surface, but some of them were twisted and have a coarse surface with microsteps, as it can be further observed on Figure 3c.

![Figure 3. SEM images of synthesized SiC nanowires.](image)

Figure 4 is the XRD test results of SiC nanowires and the remained graphene sheets. It can be seen from the XRD pattern that a peak located at ~26.5°, and this is C (002) peak of multilayer graphene sheets[10]. The others are typical characteristic peaks of SiC. This means after vacuum heating, graphene was still there and SiC nanowires were synthesized. And EDS test further proved that the nanowires were SiC. As it can be seen on the Figure 5b, the square area on Figure 5a contains mainly wire like material, and the elements showed on Figure 5b were Si, C, O, Al and other elements. It was due to the Al₂O₃ square crucible used in this experiment, from which come Al and O elements.

![Figure 4. The XRD patterns of graphene and SiC nanowires.](image)
Figure 5. (a) SEM image of SiC nanowires and, (b) EDS spectra of the marked area on image (a).

Figure 6 is the Raman spectra of vacuum heated graphene sheets with synthesized SiC nanowires. It can be found on Raman spectra the outstanding peaks at 1333.1, 1571.7 and 2660.4 cm\(^{-1}\), which corresponding to D, G and 2D peaks of multilayer graphene\[11\]. Comparing these Raman spectra with typical Raman spectra of multilayer graphene without vacuum heating, it can be noticed that the location of these characteristic peaks were shifted and the intensity of D and G peaks (ID and IG) were also changed. The increased ID means the defects of graphene sheets increased after vacuum heating and partially reacted with SiO\(_2\) and SiO. The typical peaks of SiC was not found, this maybe because the density of SiC was much high than that of graphene sheets, so when Raman samples were prepared, it was got much graphene sheets from the top of the vacuum treated materials.

3.2. Discussion
The growth mechanism of SiC nanowires in this report should be the vapor-solid mechanism. In this experiment, just vacuum heated graphene sheet on Al\(_2\)O\(_3\) square crucible in a tube furnace, and the tube was made of silicate refractory, which consist of SiO\(_2\). It was reported that the critical reaction temperature of SiO\(_2\) was 1330-1427K. So during the vacuum heating process the following reactions could take place\[12\]:

\[
\text{SiO}_2(s)+3\text{C}(s)=\text{SiC}(s)+2\text{CO}(g) \\
\text{SiO}_2(s)+\text{C}(s)=\text{SiO}(g)+\text{CO}(g) \\
\text{SiO}(g)+2\text{C}(s)=\text{SiC}(s)+\text{CO}(g)
\]
The growth process might be like this, firstly, the carbon atoms located at the edge of graphene sheets reacted with solid SiO$_2$ (which is contained in the silicate refractory), to form nucleus of SiC crystal and then gas state SiO and C reacted on the SiC crystal, thus SiC growth in one dimension to form SiC nanowires.

4. Conclusion
(1) Vacuum heating was used to synthesize SiC nanowires; XRD, EDS and Raman spectra proved that after vacuum heating treatment, graphene sheets kept the basic structure and SiO$_2$ reacted with graphene from the edge and defects area, SiC nanowires were synthesized.

(2) In this vacuum heating experiment the synthesized SiC nanowires have an average length of about 40 μm and diameter of about 40 nm.

(3) The growth mechanisms of SiC nanowires can be explained by vapor-solid mechanism.

5. References
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