SINGLE & MULTIWALL NANOTUBES AS TEMPLATES FOR SIC NANOSTRUCTURES

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Introduction

The mechanical, chemical, thermal and electronic properties (wide band gap) of SiC make it an attractive material to include in the family of nanotubes. Potential applications for SiC nanostructures include nanosensors and nanodevices operable at high temperature, high frequency and high power [1, 2] and as a support material in the catalysis field[3]. SiC nanotubes have been obtained through various techniques [3-7].
In these studies, a thermally induced templated synthesis in which a reaction of SWCNT at high temperature in the presence of gaseous Si in a reduced carrier gas atmosphere leads to a variety of SiC nanostructures depending on the conditions. The results show a variety of SiC based nanostructures, such as nanorods and nanotubes. In addition, the results help elucidate what formation processes take place during the reaction and highlight the distinctive role of H.

Experimental

The starting material was a black powder containing 70% of SWCNT with a mean diameter of 1.25 nm produced by a laser ablation process optimized for high SWCNT yield. The carrier gas was ammonia gas (or nitrogen), and the source of silicon was commercial silicon powder (Goodfellows, 99.99%). The SWCNT and Si were placed in an Al_2O_3 crucible to a ratio of 1:1. The crucible plus contents was then placed at the centre of a horizontal tube furnace (Carbolite STF 16/180). A schematic view of the experimental setup is described elsewhere[8]. A highly sensitive needle valve then controls the carrier gas entry that in this instance was at a base pressure of $5*10^{-5}$ mbar. A reaction temperature of 1450^oC was used throughout. Dwell times of 30 min., 4, 8 and 20 h were used with a heat up period of 30 min. and a cool down time of several hours. After the thermally induced templated synthesis the resultant material was removed from the crucible. The product consisted of a portion that was light grey, and the remainder was black unreacted SWCNT. The light grey material was then carefully separated (manually) for analysis.
The morphology of the reacted nanostructures were studied using scanning electron microscopy (SEM, Hitachi S4500) and transmission electron microscopy (TEM, FEI

Tecnai F30) which also allowed EELS mapping of the nanostructures. In addition, electron diffraction measurements were performed in a purpose built high-resolution EELS spectrometer described elsewhere[9]. The energy loss was set to zero. These EELS measurements probe an area of about 1 mm^2 and thus present information for a bulk average of the produced nanostructures. Raman measurements were conducted on a Bruker FTRaman spectrometer with a resolution of 2 cm^{-1}.

For the measurements tiny quantities of the product were pressed onto standard platinised microscopy grids were upon they were annealed at 450 ^{o}C for 12 h in vacuum prior to measurement so as to remove contaminants.

Results and Discussion

Reaction times ranging from 0.5 – 20 h were used. The produced samples were a soot comprised of two species; a grey material in the center and the remainder was black concomitant with the starting SWCNT.

These discussions are based only on the grey product (unless otherwise stated). The amount of grey material increased with reaction time and many changes are observed in the produced nanostructures depending on the reaction time. Some of these changes are observable from their surface morphology whilst others not. The shortest reaction time of 0.5 h yielded SiC nanorods with a C coating. With increasing reaction time one obtains pure SiC nanorods that then transform into SiC nanotubes, then SiC nanocrystals, which, with yet longer reaction times disappear altogether. This rather striking observation is indicative of some decomposition process. These various nanostructures were only observed when using NH_3 as the carrier gas. When using N_2 as the carrier gas only SiC nanorods were obtained which were narrower in diameter suggesting H plays a key role in the formation of the transformed nanostructures.

Bulk studies on the stochiometry of the samples began with electron diffraction studies that showed all samples to be a mix of SiC α and β phases with random orientation and Raman studies showed the α phase consists of many polytypes.

High-resolution EELS studies confirmed the samples altered bonding environment (from SWCNT to that of SiC). In addition the Si edges show no superposition of spectral features from SiC and Si [10].

Studies on a local scale of the produced samples were conducted using Transmission electron microscopy (TEM), including cross-sectional EELS. These studies not only revealed the structural nature of the SiC nanostructures but also the role of H in the reaction process, which begins with SWCNT bundles and Si powder (fig. 1. 1). Analysis of the black material showed it consisted primarily of SWCNT with small localized regions where SiC crystallization has begun and illustrates the earliest stages of the reaction process are localized (fig. 1. 2). These local crystallization sites can then grow laterally and also outward due to excess C that diffuses out from crystallized regions forming a C outer layer. This stage (0.5 h) is observed as SiC nanorods with a carbon cladding with diameters ranging from 19 – 60 nm (fig. 1. 3). Eventually the C source is used up from the C coating and the lateral SWCNT bundle, yielding a SiC nanorod (fig. 1. 4). One might then expect that at this stage the reaction ceases and this is indeed the case for samples prepared in N_2. However, when NH_3 is used, a remarkable

transformation process begins. At the reaction temperature used NH_3 decomposes to N and H indicating that H is responsible for the transformation process.

The sample prepared with a 5 h reaction time contained a small fraction of nanocrystals (< 5%), and an even quantity of SiC nanorods and porous nanorods (fig. 1. 4 & 5 respectively). In addition, the diameters of the porous nanorods (d = 40 – 100 nm) tended to be larger than those of the nanorods (d = 20 – 60 nm) and both nanorod species were on the whole larger than the C cladded nanorods. Increasing the reaction time to 8 h yielded 3 types of species (aside from a small fraction of SiC nanocrystals); nanorods (d = 40 – 80 nm) and porous nanorods (d = 70 – 150 nm) as with the 5 h sample and now, additionally, hollow nanorods or SiC nanotubes (diameter range 100 – 250 nm) which where closed ended (fig. 1 4, 5 & 6 respectively). The transformation of the SiC nanorods to porous nanorods and then onto nanotubes has not previously been reported and raises the interesting question as to what exactly is the role of H in this process? It is well known that amorphous SiC can be hydrogenated (a-SiC:h) and it has been shown that H substitutes Si[11]. That H substitutes Si atoms in this reaction is highly probable, and it may also substitute C atoms, although, H preferentially bonds to C as opposed to Si [11]. Furthermore at 1450°C C-H bonds can easily break[12]. This substitution process then in essence leads to the decomposition of SiC, which will occur at a higher rate in the center of the nanorods as this is where the concentration of H is greatest. It follows then that the decomposition process will provide a source of Si and C atoms that can diffuse outward.
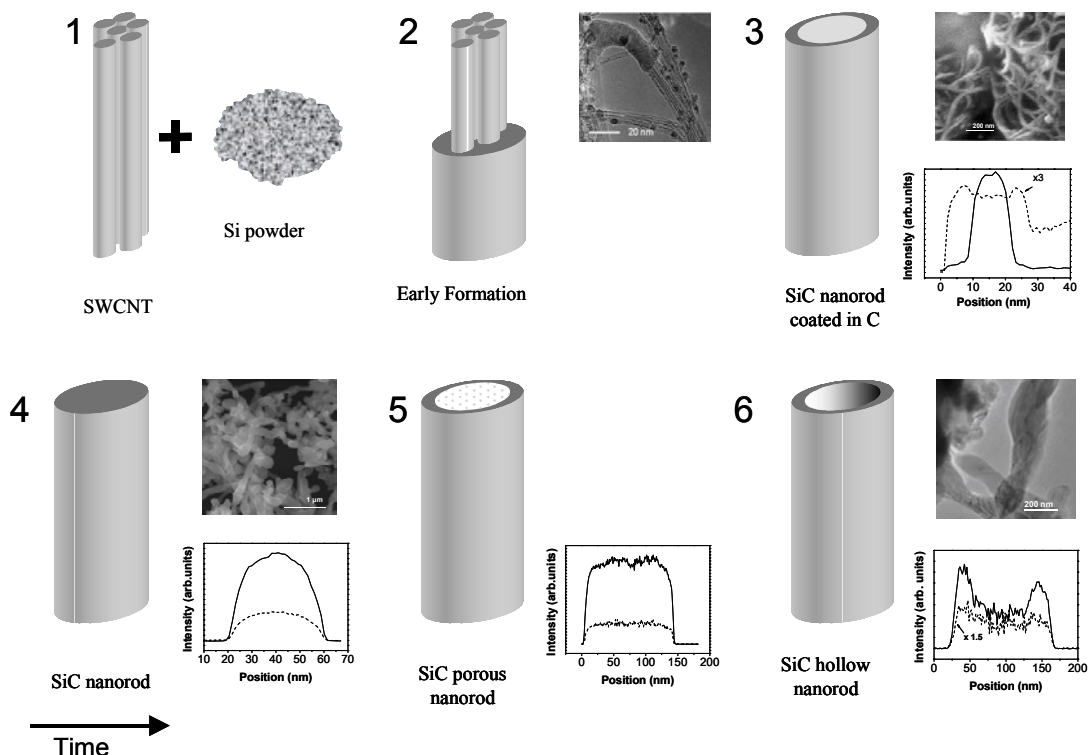

Figure 1. The various stages of the reaction. 1. Starting materials. 2. Initial SiC formation with TEM image of the nanostructure. 3. SiC nanorod coated in C 4. SiC nanorod 5. SiC porous nanorod. 6. SiC nanotube. 3 & 4 include an SEM micrograph of the structures, 2 & 6 include a TEM image and 3 to 6 include an EELS map across the nanorod/nanotube. Reaction time increases from 1 through 6.

This we observe as the outer diameters of the SiC nanorods increase with reaction time whilst at the same time becoming porous and then closed ended nanotubes.

Not all the outwardly diffused Si and C will reform on the surface of the SiC nanorods/nanotubes such that eventually the nanotubes disintegrate leaving only SiC crystals which we observed with the sample from a 12h reaction and, with a sufficiently long reaction time, one obtains the total decomposition of the SiC species, which we observed with a 20 h reaction sample where virtually no material remained. Thus, the formation order when H is present in the reaction, is from SWCNT to SiC nanorods cladded in C, to SiC nanorods, to porous SiC nanorods, to SiC nanotubes to eventual total decomposition. This process is illustrated in Fig. 1

In addition, the process could be used as a means to convert SiC nanorods into SiC nanotubes and early experiments show this to be the case. The use of Multiwall CNT as templates can also yield SiC nanotubes.

Conclusions

To conclude, this is the first report of a reaction process that combines the substitutional ability of H on SiC which leads to the novel transformation of SiC nanorods to nanotubes. It is also the first report of SiC nanostructure formation via gaseous Si in the presence of SWCNT.

The reaction will not only help in our knowledge of hydrogenated SiC were currently very little is understood, it may also open the path, through a modification of this process, for the controlled etching of SiC films in micro/nano electronic applications.

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