5th Wide Bandgap Materials – progress in synthesis and applications

and

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jointly with

2nd International Workshop on Science and Applications of Nanoscale Diamond Materials

Integration and functionalisation of wide bandgap materials: fundamentals, device technology and applications for energy saving, environment friendly electronics and medical systems

ABSTRACT PROCEEDINGS

28 June – 2 July 2010, Zakopane, Poland

Combustion Synthesis of One-Dimensional Silicon Carbide

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Summary: Silicon carbide nanowires were efficiently produced via a combustion synthesis route using Si/PTFE and ferrocene-doped Si/PTFE starting mixtures. The products were characterized using various techniques (SEM, TEM, etc.). The SiC nanowires were chemically purified and the mass balance of the process was performed. Optical emission spectroscopy (OES) was used to estimate the mean combustion temperature.

Keywords: combustion synthesis, nanowires, silicon carbide, emission spectroscopy.

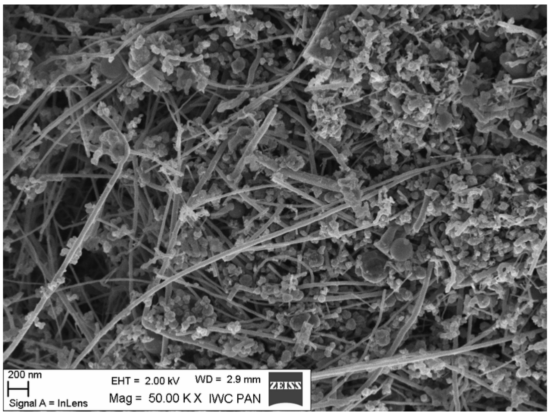
Introduction

The combustion synthesis is a versatile and efficient route to produce high-melting nanomaterials. It has been successfully used to produce semi-conducting silicon carbide nanowires (SiCNWs) [1]. The metallic properties of N-doped wires were also shown [2] and their cathodoluminescence was studied [3]. Here, we present the study on optimization of SiCNWs synthesis from Si/PTFE (teflon) and Si/PTFE/ferrocene mixtures. The study has been carried out in the modified calorimetric bomb shown in Fig. 1.

Fig. 1: Modified calorimetric bomb as a high-pressure reactor used for combustion synthesis.

Results

Several tests with stoichiometric Si/PTFE mixtures were carried out under air atmosphere (10 atm). After the reaction the product were chemically purified. Fig. 2 presents respective SEM images.



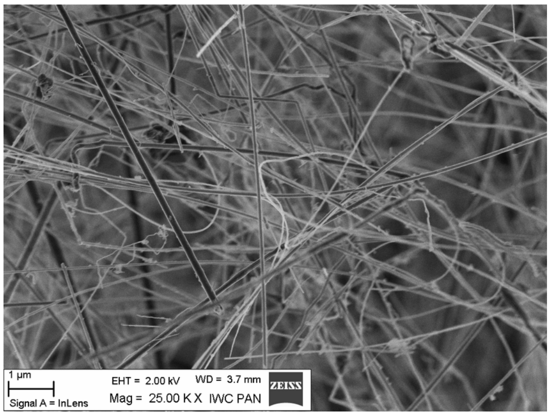


Fig. 2: SEM images of SiC nanowires grown from a powder mixture Si/PTFE (left – raw product, Right – purified product).

Purification process was carried out for the three various fractions of products separately, significantly, which were different in physical characteristics: (i) spongy material filling the bomb (main product), (ii) crucible residue and (iii) fine powder from the bottom of the reactor. The material balance of the whole process was performed, including both the synthesis and purification protocol. The overall degree of conversion of starting silicon was found equal to approximately 93% for the spongy material, 95% for the crucible residue and 88% for a fine powder from the bottom of the reactor. The total conversion of silicon into SiCNWs was ca. 20%. A total of approximately 7.6 g of pure SiC nanofibres were produced, which is the amount sufficient for further study of various exploratory applications.

The runs were also carried out with the addition (20 wt%) of ferrocene to the starting reactants (Si/PTFE). The aim was twofold: (i) iron encapsulation in silica and/or (ii) iron promotion of carbon nanotube growth. The combustion atmosphere was O_2-N_2 mixture, with oxygen content within 0-100 vol. %. With the increased oxygen content both the content of unreacted silicon and formed carbon decreased monotonically. The total conversion of starting silicon close to 100% was achieved. SEM images of the products showed mostly the presence of SiCNWs and silica nanoparticles, with the content of the latter ones dominating for oxygen content above 50 vol. %. Thus, the combustion process definitly involves participation of gaseous intermediates.

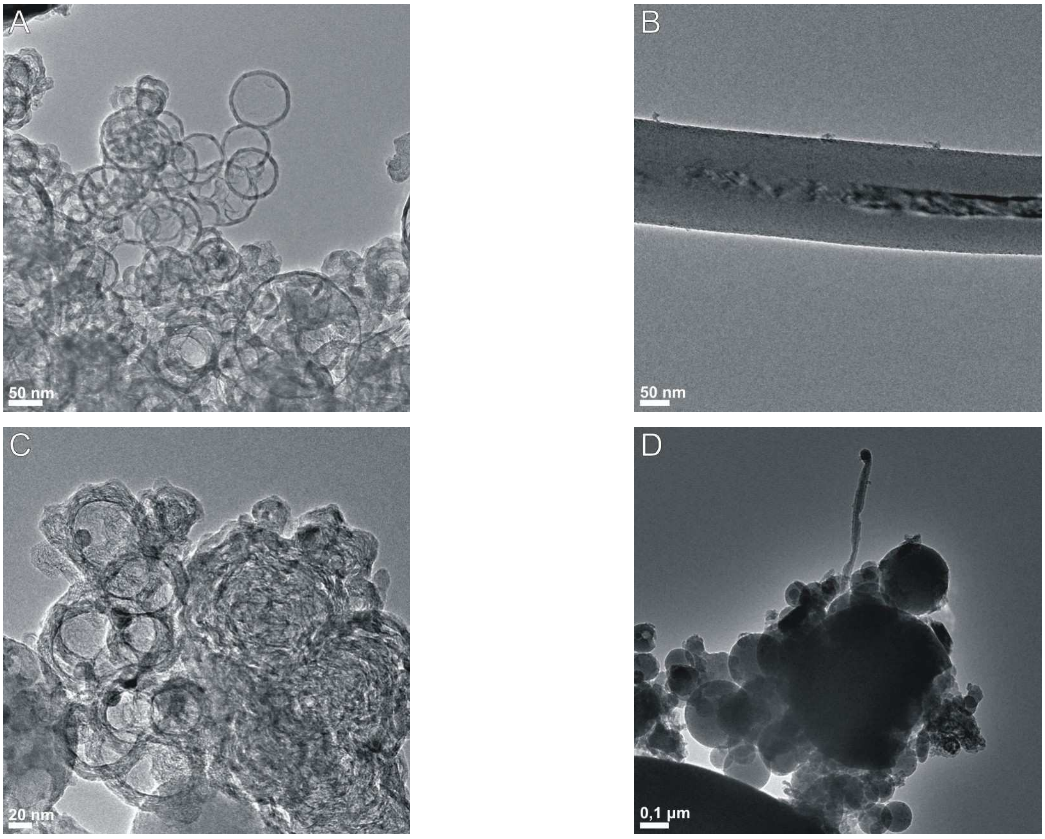


Fig. 3: TEM images of product obtained at 50% O_2 (A, B) and in pure O_2 (C, D).

The inclusion of oxygen to the buffer gas in the reaction system Si/PTFE/ferrocene drastically changes the product morphology (TEM observations – Fig. 3). The product synthesized at 50% oxygen content (Fig. 3 A,B) contains primarily well crystallized onion-like hollow carbon nanoparticles with the diameters between 20 nm and 150 nm. SiC nanowires with relatively with thin amorphous coating, amorphous carbon particles and spherical Fe micropartilces (1-5 um in diameter) are also present in this sample. The product obtained under pure oxygen atmosphere has totally different morphology (Fig. 3. C,D). The SiC nanowires are coated with very thick amorphous coating (10-30 nm). Carbon phase exists mainly as disordered hollow nanoparticles. Moreover this sample contains a plenty of silica particles having very uniform spherical shape. This preliminary results suggest that oxygen participates in the course of reaction. The oxygen partially oxidizes Si-based products and etches the as-formed carbon particles.

The preliminary measurements were performed to carry out the spectral diagnostics of the reaction zone. Using the registered light signal emitted during the process, its average temperature was estimated. Calculations were based on a well-known Planck equation and the Hartmann formula. Qualitative effects as emission or absorption band in the system depend on the reaction atmosphere. Some of results, for five similiar experiments in air, are presented in Figure 4. Data obtained for a process carried out under an argon atmosphere are presented as a reference.

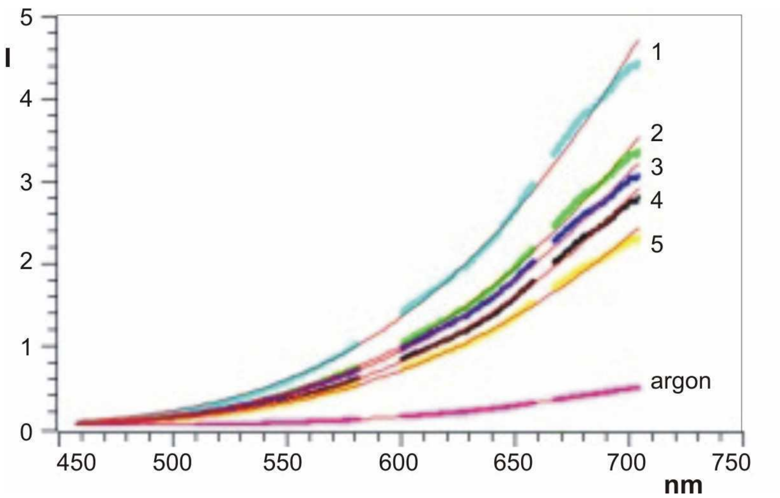


Fig. 4: Estimated process temperatures for fixed (10 atm) initial pressures of air (1700-1734 K; set of five experiments) and argon (1694 K); Planck curves fitted to experimental data.

Acknowledgement

This research was co-financed by the European Regional Development Fund within the Innovative Economy Operational Programme 2007-2013 (title of the project "Development of technology for a new generation of the hydrogen and hydrogen compounds sensor for applications in above normative conditions" No UDA-POIG.01.03.01-14-071/08-00). M.B. thanks the DFG RU-1540/9-1 for financial support.

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