Silicon based nanoparticles synthesis in atmospheric pressure microwave plasma

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Abstract: This study focuses on the synthesis of silicon carbide (SiC) nanoparticles, based on the deposition of reaction products from the plasma phase of a microwave discharge (surfatron) at atmospheric pressure. Tetramethylsilane diluted in a controlled flow of argon was used as a feedstock. The yield was an agglomerate of SiC particles of 6–15 nm size encapsulated in a carbon shells. A centrigugation method was evaluated to remove the carbon shells. Characterization of nanoparticles involving electron microscopy and x-ray analysis were performed.

Keywords: atmospheric plasma, microwave discharge, surfatron, nanoparticles synthesis.

1. Introduction

Plasmas at atmospheric conditions are promising for a large variety of applications, from bio-medical treatments to combustion enhancement or nano-material synthesis. At low pressure, plasmas are also widely used in the semiconductor industry. They are directly involved in forming nanostructures and compounds, whether by sputtering or etching process. Silicon carbide nanoparticles (SiC NPs) have been proposed as a promising material for optoelectronic [1], biomedical imaging [2], or other diagnostic techniques [3]. However, their fabrication in efficient bottom-up processes requires more effort.

Currently, there are four main commercially available techniques of SiC NPs production: laser ablation [4], milling [5], etching [6], and thermal reduction [7]. These methods are expensive, and the most affordable options start at tens of thousands of US dollars. In 2016, the authors of [8] proposed a convenient and straightforward method for synthesizing NPs from the plasma phase using tetramethylsilane (TMS) as a feedstock. However, the work omits possible accompanying difficulties in implementing the product according to the prescribed method, such as the excessive formation of amorphous carbon in the sample due to the ratio of Si:C as 1:4, or methods of purification of the final material. The main motivation of the present study is to develop a low-cost, scalable, atmospheric pressure, plasma-based technique to produce small (less than 10 nm) NPs of silicon carbide suitable for photonic applications. This paper will attempt to cover the untouched aspects of the plasma synthesis of SiC from TMS.

2. Experimental setup and procedure

An experimental setup was designed for NPs synthesis by atmospheric pressure microwave plasma. The source of microwave radiation was a solid-state microwave generator (200 W, 2450 MHz, SAIREM), which supplied the resonant cavity, a surfatron (SAIREM), with microwave radiation via a coaxial line. A quartz tube with outer and inner diameters of 6 and 4 mm was placed inside the surfatron, through which argon (Ar) buffer gas was blown to generate plasma. Tetramethylsilane, Si(CH₃)₄, was used as a feedstock and was delivered to the plasma reactor through a bubbler with argon as a carrier gas. Ar and TMS flowrates were regulated by MKS Instruments mass-flow controllers (MFCs) with maximal ranges of 200 and 10 standard cubic centimetres per minute (sccm), respectively. An MKS Type 247D four-channel readout controlled the MFCs. The products of the plasma were deposited on a standard microscope glass slide. The setup schematic is shown in Fig. 1.



Fig. 1. Schematic of the experimental setup.

3. Results

Flowrates of 200 sccm for Ar and 0.4 sccm for TMS, and a microwave power of 30 W were chosen as optimal parameters to run a stable discharge with reproducible and predictable yield deposition. The typical synthesis time was within 15-20 minutes after which the inner walls of the discharge tube became heavily contaminated with the reaction products. Due to the amount and volume of material deposited inside the tube and its intense heating the process was then interrupted. The gap between the tip of the tube and the glass slide was within 2-3 mm. The flask with TMS was preliminary purged with Ar during 20 minutes at 14 sccm, to drastically decrease the amount of air left inside. The resulting material deposited onto the glass slide was a thin film which was removed and ground into powder for further analysis. The samples were stored under a vacuum in a desiccator since SiC NPs are capable to slowly react with ambient air to form SiO_2 on the exposed side [9].

A Bruker D8 Twin X-ray Powder Diffractometer (XRD) was used for the primary analysis of the samples deposited on the glass slide and removed from the tube. The resulting patterns are shown in Fig. 2.



Fig. 2. XRD patterns of the raw material extracted from the glass slide and quartz tube.

The samples featured broad and intense diffraction peaks. The location of the peaks of the black line representing the material obtained from the glass substrate is in relative agreement with the standard pattern of 6H-SiC. The broadening of the whole XRD pattern might be associated with the strain crystallization in the synthesised material and must be further confirmed. From the width and position of the peaks, the crystallite size can be estimated by the Cherrer equation, which was about 5 nm. The grey pattern, corresponding to the sample taken from the tube, has an additional peak at $2\theta = 26^{\circ}$ associated with graphite. Note that this peak is minimal on the sample deposited on the glass slide, which meant that a significant part of the carbon was inside the quartz tube. Thus, only the material deposited on the glass substrate was considered for further analysis.

For visual control of the resulting particles Zeiss Merlin scanning electron microscope (SEM) was used. In Fig. 3 the structure of the thin film deposited is shown at different scale. The micrographs show that initially the sample had a porous sponge-like structure. The characteristic size of the grains was estimated to be 10–20 nm.



Fig. 3. SEM micrographs of the obtained material at different magnification.

For SEM energy dispersive X-ray spectroscopy (EDS) the sample was ground with a pestle and mortar, diluted in ethanol, and ultrasonicated for 30 minutes. This SEM EDS analysis was performed to roughly estimate the ratio of elements. The EDS mapping of the elements is shown in Fig. 4.



Fig. 4. SEM EDS mapping of the NPs.

It was expected to have predominance of carbon over silicon since the Si:C ratio in TMS was 1:4. A small inclusion of oxygen due to exposure to air was also expected. To remove the carbon excess, a method based on differential centrifugation [10, 11] was applied. The sample diluted in ethanol was centrifuged at 4950 rounds per minute (rpm) for 5 minutes. After that, the ethanol was removed, and the particles were dried at 80 °C. After this treatment SEM EDS was carried out again on the processed material. As a result, the silicon-carbon ratio was changed, and the amount of silicon was increased, but the presence of oxygen remained and almost doubled (see Table 1).

 Table 1. Atomic ratio of elements in the sample before and after treatment of the NPs.

	Si, Atomic %	C, Atomic %	O, Atomic %
Before	21	66	13
After	31	45	24

Transmission electron microscopy was performed with a Titan ST (FEI). The same approach was applied for the sample preparation. Lacey carbon TEM grids were used. The nanographs of the raw material are shown in Fig. 5.



Fig. 5. TEM nanographs of the raw material in different regions.

The grain size (Fig. 5a) lay within the range of 6–15 nm and encapsulated in multi-shells. To quickly estimate the interplanar lattice parameter (d-spacing) for selected areas a method based on inverted fast Fourier transform (IFFT) was applied. For example, selected crystallite showed 0.261 nm which corresponded to $d_{101} = 0.262$ nm of

6H-SiC or can be $d_{111} = 0.261$ nm of 3C-SiC. Amorphous carbon is also present in the sample. It is noticeable that some grains formed prolonged or polygonal shapes with multi-walls (Fig. 5b). IFFT method showed 0.344 nm and 0.359 nm distance between such walls for different objects which can be considered close to graphite with $d_{002} = 0.335$ nm but more within $d_{002} = 0.341$ nm of carbon nanotubes. Authors of [12,13] observed such structures and authors of [14] described and classified them. According to their work these forms appear due to graphitization which normally occurs at temperatures > 1000 °C. In their work the spacing between such walls varied within 0.334-0.340 nm. To confirm that such structures originated from carbon-based materials the synthesis was performed with pentane, C5H12, as precursor instead of TMS under the same experimental conditions. A TEM nanograph of the obtained material is presented in Fig. 6.



Fig. 6. TEM nanograph of the raw material synthesised from pentane.

The figure shows that the structures formed were similar to those obtained from TMS, prior to centrifugation. It seems that all observed structures (ribbons, rods, onions) were derived from carbon. The spacing between the walls was 0.352 nm and in accordance with previous values.

Other TEM images (Fig. 7) were obtained after the treatment previously described.





Fig. 7. TEM nanographs of the material after treatment.

The figures show a noticeable change in particles distribution. If previously the material consisted of agglomerated grains, now a more discrete distribution of fewer NPs can be seen (Fig. 7a). Although NPs were still surrounded by amorphous carbon, the previously observed multi-shell structures were gone (Fig. 7b). The d-spacing for the chosen crystallite was 0.250 nm and in agreement with $d_{102} = 0.251$ nm of 6H-SiC, as previously.

4. Conclusion

In this work a method to produce NPs from microwave plasma at atmospheric pressure was proposed. The synthesis took part in argon discharge with tetramethylsilane as a precursor. SiC NPs with residual carbon were expected as a result due to the lack of stoichiometry of the feedstock. TEM analysis revealed formation of different carbon nanostructures, which was additionally demonstrated by a change of precursor. SiC NPs appeared to be encapsulated in carbon shells. The aftertreatment technique seemed to eliminate such multiwall structures and partially remove the excess of amorphous carbon from the sample. However, the current study requires further work and assessment. For accurate carbon and silicon mass distribution analysis, organic elemental analysis (CHNSO) and inductively coupled plasma mass spectrometry (ICP) will be applied. High resolution (S)TEM with EDS and electron energy loss spectroscopy (EELS) will help to resolve crystal and chemical structure.

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5. References

[1] S. Kamiyama, M. Iwaya, T. Takeuchi, I. Akasaki, R. Yakimova, M. Syväjärvi, **522** (2012).

[2] S. E. Saddow, Silicon Carbide Biotechnology, (2016).
[3] D. Beke, J. Valenta, G. Károlyházy, S. Lenk, Z. Czigány, B. G. Márkus, K. Kamarás, F. Simon, A. Gali, J, Phys. Chem. Lett., **11**, 1675 (2020).

[4] S. Castelletto, A. Almutairi, G. Thalassinos, A. Lohrmann, R. Buividas, D. Lau, P. Reineck, S. Juodkazis, T. Ohshima, B. Gibson, B. C. Johnson, Optics letters, **42**, 7 (2017).

[5] A. Muzha, F. Fuchs, N. V. Tarakina, D. Simin, M. Trupke, V. A. Soltamov, E. N. Mokhov, P. G. Baranov, V. Dyakonov, A. Krueger, G. V. Astakhov, Appl. Phys. Lett., **105**, 243112 (2014)

[6] B. D. László, Z. Szekrényes, I. Balogh, Z. Czigány, K. Kamarás, Á. Gali, Journal of Materials Research, 28 (2013).

[7] G. Q. Jin, X. Y. Guo, Microporous Mesoporous Mater., **60**, 207 (2003).

[8] S. Askari, A. Ul Haq, M. Macias-Montero, I. Levchenko, F. Yu, W. Zhou, K.K. Ostrikov, P. Maguire, V. Svrcek, D. Mariotti, **8**, 39 (2016).

[9] P. Soukiassian, F. Amy, 144–147 (2005)

[10] J. Robertson, L. Rizzello, M. Avila-Olias J. Gaitzsch, C. Contini, M. S. Magoń, S. A. Renshaw, G. Battaglia, Sci Rep, 6, 27494 (2016).

[11] Z. Abdullaeva, Synthesis of nanoparticles and nanomaterials, Springer (2017).

[12] G. Xi, S. Yu, R. Zhang, M. Zhang, D. Ma, Y. Qian, J. Phys. Chem. B, **109**, 27, 13200–13204 (2005).

[13] R. Joshi, J. Engstler, P. Haridoss, J. J. Schneider, Solid State Sciences, **11**, 2 (2009).

[14] S. Welz, M. J. McNallan, Y. Gogotsi, Journal of Materials Processing Technology, **179**, 1–3 (2006).