Production of nanoscale crystalline materials (Si, SiC) by a highly efficient hyperbaric method

To cite this article: B S Ezdin et al 2018 J. Phys.: Conf. Ser. 1128 012100

View the article online for updates and enhancements.
Production of nanoscale crystalline materials (Si, SiC) by a highly efficient hyperbaric method

B S Ezdin¹, V V Kalyada¹, A V Ischenko¹,², A E Zarvin¹, A A Nikiforov¹ and D A Yatsenko¹,²

¹Novosibirsk State University, 1 Pirogova Street, Novosibirsk, 630090, Russia
²Boreskov Institute of Catalysis SB RAS, 5 Lavrentiev Avenue, Novosibirsk, 630090, Russia

E-mail: bse@nsu.ru

Abstract. The method of producing nanopowders of Si and SiC by pyrolysis of a silicon-hydrocarbon mixture by compression in a cyclic process in a flow reactor is proposed and implemented. The obtained powders are characterized by X-ray diffraction and transmission electron microscopy. The new design solutions and use of ceramic coatings obtained by applying microarc oxidation for the piston-cylinder assembly – a compression unit of the reactor - allowed avoiding the use of compression rings and lubricants, achieving a high compression ratio and pressure and temperature in the reactor needed for monosilane pyrolysis. Pyrolysis in the flow reactor is convenient, technological and efficient in terms of its use in the production of high purity nanopowders.

Silicon in various forms (crystalline, polycrystalline, amorphous) is the basis of modern microelectronics and photosensitive optoelectronics. The unique properties of silicon carbide (electrical, thermal conductivity, temperature, radiation resistance, etc.) cause its wide use in power electronics - ultrafast high-voltage Schottky diodes, n-MOS transistors and high-temperature thyristors. The use of nano-sized Si and SiC in solving material science problems allows greatly varying the electronic and optical properties of semiconductor materials.

Plasma-chemical synthesis, anodic electrochemical etching and chemical-thermal method are the techniques to obtain nano-sized silicon powders [1]. Monosilane thermal decomposition into silicon and hydrogen is another widely used method to produce nano-sized silicon. There are several ways to implement it: passing monosilane-argon mixture through a hot-wall tube reactor [2], laser-induced methods [3], gas-discharge plasma [4], monosilane thermal decomposition when heated by compression in an adiabatic process [5].

There are a number of methods of obtaining a nanoscale silicon carbide powder, such as adiabatic compression [10], plasma-chemical method [9], sol-gel [6], laser pyrolysis from organic precursors [7], and self-propagating high-temperature synthesis [8]. The common drawbacks of these methods are their low productivity, difficult scaling of technological facilities, and expensive unique equipment (making the cost of powders rather high). As a rule, these methods are multistage, and chemical impurities contaminating the final product are added at each subsequent technological stage. Technologies to produce high-purity Si, SiC are still being developed. Today there are about 900 patents relating to the synthesis of SiC (according to the data of PatScape.ru).
This paper describes a cyclic method of compressing starting material in the gas phase in a flow reactor. The hyperbaric compression reactor is a cyclic thermal engine in which the reaction mixture is adiabatically compressed by a piston-cylinder assembly to the temperature and pressure necessary for a rapid chemical reaction. Then, at the expansion stage, the reaction products are cooled, and then they are quenched. Thus, the reactor combines the heater, the reactor itself and the quenching device, which prevents reverse reactions [11].

The new design solutions and use of ceramic coatings obtained by applying microarc oxidation for the compression element’s surfaces of the hyperbaric compression reactor allowed avoiding the use of compression rings and lubricants and achieving high compression in the reaction area in the absence of impurities, which contaminate a final product. These characteristics of the hyperbaric compression reactor allowed using it to develop and implement a method of producing silicon and silicon-organic nano-powders.

The method ensures homogeneity of the reaction conditions in the reactor, which leads to the high nano-powder monodispersity. The possibility to change the duration of cycles and greatly vary the dosage of initial components allows selecting and maintaining optimal conditions for the production of the desired product with the highest possible efficiency.

The use of hyperbaric compression reactor to initiate and ensure passing of chemical reactions at high impulse pressures, for example, for the binding of air nitrogen, synthesis gas production, partial oxidation of hydrocarbons and many other industrial technologies seems to be a promising direction in the development of the chemical industry.

In the experiment, the mixture of monosilane, argon and one of the light hydrocarbons was used as a chemical reagent. Gases were fed to the cylinder through two pipelines. The monosilane and argon mixture (10% - SiH₄, 90% - Ar) was fed into the cylinder through one pipeline, and another light hydrocarbon (acetylene, ethylene, propane, butane or a mixture thereof) was fed through another pipeline. The mixture was compressed at a frequency close to 10 Hz, and the obtained product came out of the reactor and accumulated in the additional capacity of the collection system. The accumulated product was then studied by high-resolution transmission electron microscopy and X-ray diffractometry.

If the monosilane and argon mixture without hydrocarbons was fed into the reactor, pyrolysis SiH₄ -> Si + 2H₂ led to the formation of a nano-sized silicon powder.

Experiments for the production of silicon carbide were carried out both for concentrations corresponding to the stoichiometric ratios for the monosilane and propane mixture, as well as monosilane and acetylene mixture, and for concentrations with carbon excess or deficiency, according to the stoichiometric ratios:

\[
3\text{SiH}_4 + \text{C}_2\text{H}_4 \rightarrow 3\text{SiC} + 10\text{H}_2, \\
2\text{SiH}_4 + \text{C}_2\text{H}_2 \rightarrow 2\text{SiC} + 5\text{H}_2.
\]

As further analysis showed, in the case of carbon-deficient mixtures compression, Si and SiC crystallites are observed in the final product; in the case of mixtures rich in carbon, SiC crystallites are formed, coated with several layers of graphene - the so-called Core-shell structures are formed.

The reactions of SiH₄ pyrolysis and SiC synthesis were monitored online using a UGA-200 universal gas analyzer. The detection of hydrogen in the mass spectrum was an indicator of the appearance of a conversion reaction, while the reduction or complete disappearance of the initial reagents (SiH₄, C₂H₂) was an indicator of the completeness of the conversion process.

A D8 Advance powder X-ray diffractometer (vertical goniometer with 0/2θ-geometry) manufactured by Bruker (Germany) was applied for X-ray diffraction analysis. The device was equipped with a Lynx-Eye linear semiconductor energy-dispersive detector. The X-ray tube with a copper anode was the radiation source. The average radiation wavelength was CuKα = 0.154184 nm (CuKα₁ = 0.15406 nm, CuKα₂ = 0.154439 nm), the generator current was 35 mA, and the voltage was 35 V. The shooting range was 10-70° to 20 with the 0.075° step; and the time per point was 4 sec.
Figure 1 shows the diffraction patterns of the products obtained. The bar charts show the positions of the peaks for the silicon and silicon carbide phase from the Powder Diffraction File (PDF) database, cards 00-027-1402 and 00-029-1129, respectively.

Figure 1. Diffraction data for samples obtained without hydrocarbons (curve I) and for mixture (2), curve II. Bar-charts: solid - Si (PDF 00-027-1402) and dashed - SiC (PDF 00-029-1129).

It is seen that the sample is single-phase for pyrolysis without hydrocarbon, (curve I), only crystalline silicon peaks are observed (PDF 00-027-1402). There are no other phases corresponding to the material of the chamber or the piston coating. For the sample obtained using the concentrations of the carbon-deficient mixture (2), the diffraction data show the silicon (PDF 00-027-1402) and silicon carbide (PDF 00-029-1129) phases. The peaks’ broadening corresponds to an average crystallite size of not more than 10 nm.

The obtained samples were studied by HRTEM using a JEM-2010 electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a resolution capacity of 0.14 nm. Particles were put onto a copper substrate by dispersing a sample slurry in the alcohol with an ultrasonic disperser. A local analysis of the sample’s elemental composition was carried out using a QUANTAX 200-TEM energy-dispersive spectrometer (Bruker, Germany) with a XFLASH detector and the energy resolution of 130 eV. Digital processing of the obtained electron microscopic images with calculated interplanar spacings by Fourier analysis was carried out in GatanDigitalMicrograph. Figure 2 shows the obtained results.

Figure 2. Electron-microscopic images of the nano-Si sample particles.
The Figure 2 shows that the sample consists of particles of 30-50 nm in size, composed of disordered nano-crystallites of the size from 5 to 15 nm, which form micron dendritic aggregates. The chemical composition due to EDS and the interplanar distances 3.16, 3.12 and 3.09 Å correspond to the 3.1355 Å of [111] direction for the silicon structure (PDF 00-027-1402).

Figure 3 shows typical electron microscopic images of the obtained silicon carbide samples’ morphology and structure for the mixture (1).

![Figure 3](image)

**Figure 3.** Electron-microscopic images of particles for the mixture (1). Nano-sized crystallites of SiC - (b), covered with 2-5 graphene layers. and Si - (c). The sample is represented by two morphologically different types of particles: rounded well-crystallized silicon carbide particles (more contrasting in the image) and less contrasting nano-sized particles forming extended dendrite aggregates. Dimensions of silicon carbide particles vary in the range of 10-40 nm. The observed interplanar distances of 2.49 and 2.52 Å correspond to the distance of 2.52 Å in the [111] direction for silicon carbide SiC (PDF 00-029-1129). The composition of the initial gas mixture was close to the stoichiometric ratio (1).

Figure 3c shows crystalline silicon particles (the interplanar distance 3.1355 Å corresponds to the (111) plane of 20-30 nm with an amorphous surface layer obtained from the reaction carbon-deficient mixture. Figures 3a and 3b show core-shell structures. The nucleus is formed with crystallites of 3-7 nm, covered with several layers of graphene.

**Conclusions**

It is shown that the monosilane pyrolysis in the presence of argon by cyclic compression in a flow reactor allows obtaining nano-sized silicon and silicon carbide powders of high purity. The high repeatability in chemical composition and physical characteristics (crystallites, amorphous state) of the synthesized product is achieved depending on the main initial parameters - chemical composition, pressure in the reactor, etc. It is shown that the proposed method provides a high degree of the initial reagents processing.

The products obtained during nano-powders synthesis in a cyclic compression reactor are chemically pure and determined only by the initial reagents purification. No impurities, which contaminate a final product, are added during the technological processes. The final products do not require further processing, as in most of the proposed methods, such as chemical etching, etc. and is ready to be applied in technologies and tasks of materials science with the aim to produce materials with pre-defined functional characteristics, including modified metals and alloys structure [2, 13].

The proposed method of producing nano-sized silicon and silicon carbide powders is technologically convenient. The process is cyclical and can be fully automated. It requires feeding the gaseous reagent and collecting the resulting products for continuous production. Time for continuous
operation of the reactor depends on the reliability of its mechanisms, the amount of starting materials and need for the product - nano-sized silicon carbide crystallites.

Acknowledgement
The work was performed using equipment provided for collective use by the center of "Applied Physics" of NSU with the financial support of the Ministry of Education and Science of the Russian Federation 3.5918.2017/ITR and 3.5920.2017/ITR. The sample was characterized within the frames of the budget project No. AAAA-A17-11704170079-8 for Boreskov Institute of Catalysis.

References
[1] Weitzel C E, Palmour J W, Carter C H, Moore Jr, Nordquist K J, Allen S, Thero C and Bhatnager M 1996 IEEE Trans. Electron Devices 43 1732-5
[2] Li G, Burggraf L W, Shoemaker J R, Eastwood D and Stiege J A E 2000 Appl. Phys. Lett. 76 3373-5
[3] Liu X, Zhang J, Yan Z, Ma S and Wang Y 2001 Mater. Phys. Mech. 4 85-8
[4] Nychyporuk T, Marty O, Bluet J M, Lysenko V, Guillot G, Barbier D and Perrin R 2006 Mater. Sci. Forum 763 527–9
[5] Pozdnyakov G A, Yakovlev V N and Saprykin A I 2014 Dokl. Phys. Chem. 456 61-3
[6] Seog I S and Kim C H 1993 J. Mater. Sci. 28 3277-82
[7] Tougne P, Hommel H, Legrand A, Nerlin N, Luce M and Cauchetié 1993 Diamond Related Mater. 2 486-90
[8] Narayan J, Raghunathan R, Chowdhury R and Jagannadham K 1994 J. Appl. Phys. 75 7252-7
[9] Anshakov A S, Urbach E K, Urbach A E, Faleev VA and Cherednichenko V S 2017 Thermophysics and Aeromechanics 24 473–82
[10] Pozdnyakov G A, Yakovlev V N, and Saprykin A I 2017 Dokl. Phys. Chemistry. 476 301-4
[11] Ezdin B S, Zarvin A E, Kalyada V V and Yaskin A S 2016 Chem.Petr.Eng. 52 26-28
[12] Nikiforov A A 2010 Method of microarc oxidation (RF patent No. 2389839)
[13] Cherepanov A N, Ovcharenko V E, Liu G and Cao L 2015 Thermophysics and Aeromechanics. 22 131-6