Production of nano-dimensional crystalline silicon on fast cyclic compression setup

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

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

E-mail: bse@nsu.ru

Abstract. The method of producing nano-dimensional silicon powders from monosilane pyrolysis by compressing in a cyclic process in the flow reactor has been proposed and implemented. The resulting powder has been examined by X-ray diffraction and electron microscopy. The new design solutions and ceramic coatings obtained by using microarc oxidation for the piston-cylinder assembly – a compression unit of the reactor, allowed avoiding the use of compression rings and lubricants and achieving high compression ratio, pressure and temperature in the reactor needed for monosilane pyrolysis. Pyrolysis in the flow reactor is convenient, technological and efficient to be used in the production of high purity silicon nanopowders.

Application of nano-dimensional powders in various production technologies for new functional materials with predefined characteristics and modification of the existing materials' surfaces with the purpose to improve their performance characteristics cause a great interest in studying the nano-powders characteristics and methods of their production.

Nano-dimensional silicon powders are interesting by their photoluminescence characteristics [1], i.e. the possibility of using them as luminophores for converting ultraviolet radiation into visible light; as well as by electroluminescence characteristics [2] - the possibility of emitting light of the visible range with the transmission of electric current. These characteristics can be used to miniaturize data transmission devices - light emitting diodes, photodetectors, light guides, as well as in signal processing devices - integrated circuits. Nano-dimensional silicon powders have been widely used in the production of sensor elements for chemical and biological sensors, the physical characteristics of which change when a marker occurs in the controlled environment [3].

Plasma-chemical synthesis, anodic electrochemical etching and chemical-thermal method are used to obtain nano-dimensional silicon powders [4-6]. Silicon monoxide and dioxide are applied as starting materials. These methods are low in yield and are not scalable. In addition, they require unique and costly equipment. These disadvantages are the cause of high production costs of the powders. A wide size distribution (from one to hundreds of nanometers) and high impurity content in the resulting product are observed. The control and influence of the initial parameters upon the dispersion and morphology of the powders constitute a significant obstacle for these methods.

Monosilane thermal decomposition into silicon and hydrogen is another widely used method to produce nano-dimensional silicon. There are several ways to implement it: passing monosilane-argon
mixture through a hot-wall (1000°C) tube reactor [7], gas-discharge plasma [4, 5] and laser-induced methods [8]. High energy intensity, high polydispersity of the powders obtained due to heterogeneity of conditions in the reactor, and as it has been mentioned above, high production cost, are among the disadvantages of these methods. The method of producing nano-dimensional silicon by monosilane thermal decomposition when heated by compression in an adiabatic process was proposed in [9]. This method is not continuous and flowing, and therefore, it cannot be applied for industrial production of nanopowders.

This paper describes a cyclic method of compressing starting materials in the gas phase in the flow reactor. Pyrolysis and then synthesis of starting materials take place during the compression-rarefaction cycles in the piston-cylinder assembly of the reactor. The method ensures homogeneity of the reaction conditions in the reactor, which leads to high nanopowder monodispersity. When the working cycle of compression-rarefaction finishes, we get a product which does not require further technological processing.

The compression reactor is well-described in [10]. Reagents are compressed inside the cylinder by a piston, the surfaces of which are covered with a protective ceramic layer made of aluminium oxide by thermo-electrochemical oxidation [11]. The coating withstands repeated thermal cycling while ensuring high sliding. The surface friction coefficient is close to 0.01. This allows minimizing the gap between sliding surfaces. Therefore, no lubrication is required to run the piston-cylinder assembly, i.e. the reagents are not contaminated by additional chemical substances.

The monosilane-argon mixture was used as a chemical reagent in the experiment. Argon was used to increase the adiabatic index of the mixture. The gases were fed into the cylinder through a pipeline. The mixture was compressed at a frequency close to 10 Hz. The product was accumulated in an additional tank of the collection system and was examined by X-ray diffractometry and high-resolution transmission electron microscopy (HRTEM).

The reaction of monosilane SiH$_4$ → Si + 2H$_2$ pyrolysis was monitored online using a UGA-200 Stanford Research Systems universal gas analyzer. The greater amount of hydrogen indicated a pyrolysis reaction and disappearance or a small amount of initial reagents (SiH$_4$) showed that the raw materials were fully processed.

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 is 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 (CuKα$_1$ = 0.15406 nm, CuKα$_2$ = 0.154439 nm), the generator current was 35 mA, and the voltage was 35 kV. The shooting range was 10-70° to 2θ with the 0.075° step; the time per point was 4 sec.

Figure 1 shows the diffraction pattern for the obtained product sample. The bar chart shows peaks positions of silicon from the Powder Diffraction File database (PDF card 00-027-1402). Figure 1 shows that the sample is single-phase, and only the peaks of crystalline silicon are observed. There are no other phases corresponding to the material of the chamber or the coating of the piston. Diffraction peaks have a specific shape: a narrow top and a wide base (most pronounced for reflex 111). Such a peak shape may indicate the presence of bimodal distribution of crystallites in size. The size distribution was evaluated by modeling the diffraction profile. The resulting diffraction pattern was obtained as a superposition of scattering (1: 1) from spherical crystallites with dimensions of 4 and 15 nm, which best describe the broadening of the peaks.

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 by dispersing the sample slurry in alcohol onto a copper substrate using an ultrasonic disperser. Digital processing of the obtained electron microscopic images with calculated interplanar distances by Fourier analysis was carried out in GatanDigitalMicrograph. Figure 2 shows the results obtained.

Figure 2 shows that the sample consists of 30-50 nm particles, which are composed of disordered nanocrystallites in the size range from 5 to 15 nm and form micron dendritic aggregates. The interplanar distances 3.09, 3.14, 3.17 and 3.26 Å correspond to the 111 direction for the structure of silicon.
Figure 1. Diffraction pattern, bar chart – silicone phase (PDF 00-027-1402). Model calculations for spherical crystallites with dimensions 4-15 nm is shown in the inset.

Figure 2. Electron-microscopic images of the silicon nanopowder sample’s particles.

Conclusions
The paper shows that monosilane pyrolysis in argon by using the cyclic compression in the flow reactor allows obtaining high purity silicone nanopowders. The product obtained is chemically pure and is determined only by the level of purification of the starting reagents. Technological processes do not lead to additional contamination. The resulting product does not require further processing, as in most methods, such as chemical etching, etc. It is ready to be applied in technologies and tasks of material science with the purpose to obtain materials with predefined functional characteristics, including modification of the metals and alloys’ structure and characteristics [5, 12].

The reactor’s optimal modes needed for the monosilane pyrolysis to produce nano-dimensional silicone with crystallite sizes of 5-15 nm were determined. A high repeatability in composition and size of the synthesized product was achieved, depending on the main input parameters - chemical composition of the mixture, the pressure in the reactor etc. It has been shown that the proposed method provides a high degree of the starting reagents processing.
The proposed method for obtaining nano-dimensional silicon is suitable for the industrial production of high purity silicon nanopowders. The process can be fully automated. Time for continuous operation of the reactor depends on the reliability of its mechanisms, the amount of starting materials and demand for the product.

Acknowledgement
The work was performed using the equipment of the "Applied physics" NSU center for collective use with the grants of the Ministry of Education and Science of the Russian Federation 3.5918.2017/ITR and 3.5920.2017/ITR. The diffraction model calculations were carried out with the financial support of the Foundation for Assistance to Small Innovative Enterprises in Science and Technology (“UMNIK” program, project No. 12349GU2/2016).

References
[1] Efremov M D et al 2004 JETP Letters 80 619–22
[2] Vandyshev E N, Gilinskii A M, Shamirzaev T S and Zhuravlev K S 2005 Semiconductors 39 1319–22
[3] Morales-Sánchez A, Barreto J, Domínguez C, Aceves M, Leyva K M, Luna-López J A, Carrillo J and Pedraza J 2010 Materials Science and Engineering 174 123–6
[4] Ishchenko A A, Fetisov G V and Aslanov L A 2011 Nano-Silicon: Properties, Production, Application, Methods of Research and Control (Moscow: Fizmatlit) 648
[5] Gusev A I 2005 Nanomaterials, Nanostructures, Nanotechnologies (Moscow. Fizmatlit) 416
[6] Anshakov A S, Urbach E K, Urbach A E, Faleev V A and Cherednichenko V S 2017 Thermophysics and Aeromechanics 24 473–82
[7] Wiggers H, Starke R and Roth 2001 Chem. Eng. Technol. 24 261–4
[8] Vladimirov A, Korovin S, Surkov A, Kelm E and Pustovoy V 2011 Las. Phys. 21 830–5
[9] Pozdnyakov G A, Yakovlev V N and Saprykin A I 2014 Dokl. Phys. Chem. 456 61–3
[10] Ezdin B S, Zarvin A E, Kalyada V V and Yaskin A S 2016 Chem. Petr. Eng. 52 26–8
[11] Nikiforov A A 2010 Method of Microarc Oxidation (RF patent No. 2389839)
[12] Cherepanov A N, Ovcharenko V E, Liu G and Cao L 2015 Thermophysics and Aeromechanics 22 131–6