Particles of porous silicon formed from silica powders of plant origin and their structural properties

I Kashko¹, K Girel¹, K Yanushkevich² and H Bandarenka¹

¹ Department of Micro- and Nanoelectronics, Belarusian State University of Informatics and Radioelectronics, Minsk, 220013, Belarus
² Scientific and Practical Materials Research Center of Belarusian Academy of Sciences, Minsk, 220072, Belarus

Abstract. In this paper, we present the results on study of formation regularities, morphology, composition and photoluminescence of porous silicon particles fabricated by the magnesiothermal reduction of different samples of biogenic silicon dioxide based on rice husk, bamboo husk and bamboo joints at 650 °C at argon atmosphere.

1. Introduction
Porous silicon has been one of the most actively studied nanomaterials since the very beginning of its discovery [1]. PS presents the bulk silicon permeated with pores of micro- or nanometer diameters. However, the properties of PS differ a lot from those of the bulk silicon. In particular, it can behave like a direct-gap semiconductor, showing intense luminescence [2], which is due to quantum effects in nanoscale silicon structures [3]. Using PS can solve the problem of creating light-emitting diodes integrated with other electronic devices on a silicon substrate [4]. PS presents a favourable template for deposition of other semiconductors [5] and metals [6, 7] to fabricate nanomaterials with novel properties. The other outstanding feature of PS is its biocompatibility, which is not typical for the single crystal silicon [8, 9]. This combined with PS high adsorption and biodegradation has been widely used in biomedicine to deliver nutrients and drugs into living tissue [10, 11].

Biomedical application of PS requires producing large volumes of this porous material. At the same time, the production process has to be cost-effective and simple [12]. Despite the traditional fabrication of PS by an electrochemical anodization is easily realized, it does not allow meeting these requirements because the price of silicon wafers is high enough to ensure the profitability of the production. To solve this problem, some researches have turned their attention to formation of PS by thermal reduction of silicon oxide, released from plants [12–14]. Many plants have a high silicon content, due to absorption of liquids from the soil containing silicic acids. The prospective plants for the PS mass production have to be fast-growing variety, which are adapted to the conditions of acid soils. Some agricultural wastes (rice, bamboo husks) and weeds (horsetail) can be used for this purpose.

At present, thermal reduction of SiO₂ is predominantly carried out in the furnaces filled with carbonaceous medium [15]. However, such a method requires high temperatures (> 2000 °C), which cause silicon sintering and pore closing. In addition, the side product of the reactions is carbon dioxide that leads to undesirable “greenhouse” effect. From the point of view of ecology, the two-step method using solar energy is very attractive [16]. The first step is a thermal treatment of SiO₂ in the presence of nitrogen to form Si₃N₄ while the second one is the solar dissociation of the nitride resulting in silicon...
fabrication. Nevertheless, this technique requires long processing time and thus is not effective. Alternative method is reduction of silicon dioxide in the presence of active metals such as aluminium and magnesium. The temperature in this case is much lower than at carbonaceous thermal reduction. It should be noted that using aluminium results in formation of the chemically stable aluminium oxide, which then is hardly removed from the final product. That is why more attention has been paid to the thermal reduction of SiO$_2$ in magnesium vapour [12 – 14]. The temperature of magnesiothermal treatment is varied in the range from 630 to 650 °C. The family of morphological types of PS particles formed by this method is very rich. Such PS has been actively studied for application in the oral delivery of drugs and nutrients, cosmetics, orthopaedics, tissue engineering, etc. Paper [17] reported development of coating which contains PS particles filled with medicines to disinfect and cure open wounds. It is very important to manage the concentration of medicines and to control pH of the covered area, which is different for injured and healthy living tissue. The PS particles can play a role of both drug carriers and sensors due to their specific optical properties [18]. However, papers on spectral sensitivity of the biogenic PS have not been published yet. It has been found that biogenic PS is a prospective candidate for use in biomedicine and cosmetics as a body powder [1]. In this case, an important requirement to the PS powder is photoluminescence in the visible range but by nowadays it has not been studied yet.

In this paper, we studied the regularities of the magnesiothermal reduction of SiO$_2$ based on bamboo and rice grass, as well as morphology, elemental and phase composition of the resulting PS.

2. Experimental details

Powders of SiO$_2$ based on rice husk, bamboo husk and joints were used to form PS. Silica powders were mixed with magnesium (Mg) powder and salt (NaCl) in the molar ratio 1:2.5:10. The salt was added to the reagents to prevent silicon sintering and thus pore closing. The mass of the mixture components was measured using balance Sartorius-CP225D with the 0.01 mg accuracy. The mixtures were poured to ceramic boat for the following thermal treatment. After that, ceramic boats were fixed in the quartz tube, which then was placed in the furnace Carbolite HST 1200/600 and filled with the inert gas (argon). Thermal treatment was performed at 650 °C for 6 h. The final powder samples cooled to the room temperature were mixed with the distilled water to the formation of suspension to which concentrated hydrochloric acid (HCl) was slowly added. The distilled water allowed to dissolve NaCl in the reaction product while HCl was used to remove magnesium oxide (MgO). The samples were kept in such a solution during 4 h. To provide complete interaction of the reagents and removal of the gas bubbles we used magnetic stirrer. Finally, we rinsed samples with the distilled water 3 times, filtered them and dried in the air at room temperature.

Morphology of the experimental samples was studied with scanning electron microscope (SEM) Hitachi S-4800 that provided resolution of 1 nm. Energy-dispersive X-ray analyser (EDX) Link Analytical AN 10000 built in electron microscope Cambridge Instruments Stereoscan-360 was used to reveal elemental composition of the samples. The phase analysis was performed with X-ray diffractometer DRON-3 equipped with copper cathode (Kα-radiation) at wavelength $\lambda = 0.5406$ nm. Voltage and anode current were 30 kV and 20 A respectively. Photoluminescence spectra of the PS were registered using complex included Xe Newport 6271 (excitation at 375 nm), focusing optical system, monochromators SOLAR DM 160 and MS 7504i. Pore size and porosity of PS was estimated with adsorption analyser of porosity and specific surface area ASAP 2020.

3. Results and discussion

Thermal reduction of silica to silicon in presence of magnesium occurs according to the following reaction:

$$\text{SiO}_2 + 2\text{Mg} \rightarrow \text{Si} + 2\text{MgO}.$$ 

In this work to form PS we mixed powders of biogenic silica, magnesium and salt and annealed them in the argon atmosphere at 650 oC during 6 h. It led to the formation of the composite PS/MgO, which
was released from the magnesium oxide by the treatment in HCl. As a result, we obtained the powder composed of the PS particles.

The study of the structural properties of the PS powders we performed comprehensive analysis using various methods, which allowed revealing phase and elemental composition as well as morphology of the samples.

Figure 1 shows the results of the XRD-analysis of the powders formed by magnesiothermal reduction of the SiO2 powders made of rice husk, bamboo husk and bamboo joints. It is well seen, that the whole powders consist of silicon polycrystals as the spectra have the characteristic silicon peaks. There are the silicon crystallites with the hexagonal and cubic cells in the powder based on the rice husk (Figure 1, a). At the same time, we observe just the cubic cell crystallites in the powders based on the bamboo (Figure 1, b, c). The wide band of the weak intensity in the range of 2Θ = 20 – 25 degree typical for all the spectra evidences about minor oxidation of the silicon crystallites.

XRD-analysis gave us the information on the crystalline parts of the samples while the elemental composition of the components, which atoms are not organized in the crystalline lattice were still hidden. To solve the problem, we used EDX-analysis that allows identifying all the atoms in the sample. Electron beam of the 1 µm in diameter at the energy of 20 keV was able to penetrate to 1.3 – 1.5 µm depth of the samples. Figure 3 shows EDX-spectra of the PS powder samples based both on the rice and bamboo plants. Prevalent content of silicon and oxygen atoms is typical for all the samples. Low peaks of magnesium, natrium and chorine are also observed on the spectra. The Mg presence can be caused by the two reasons. Firstly, magnesium did not fully react with silica and was partially left in the samples. Secondly, magnesium oxide was nor completely removed from the samples during the HCl rinsing. High oxygen content can be explained by the oxidation of the silicon nanocrystals. PS is characterized by the vast specific surface area that is covered with the thin oxide film in the air. Natrium and chlorine were probably left in the samples due to poor rinsing.

It should be noticed that the greatest content of the silicon atoms (65.76 %) is typical for the PS sample based on bamboo husk while the less silicon atom percentage (38.44 %) – for the product of the bamboo joints. The initial silica powder from the bamboo joints consists of particles, which sizes are much larger than those of powders made of husks. Therefore, the specific surface area of the SiO2 particles based on bamboo joints was not enough to provide complete interaction between the reagents during the thermal treatment and the reduction of silica to silicon was not fully realized.

SEM-analysis was used to study the morphology of the samples. Figure 4 shows SEM images of the PS powders formed by the magnesiothermal reduction of the biogenic silica samples. The samples are composed of particles riddled with pores which diameter varies in the range from 10 to 1000 nm. Comparing the results of XRD and SEM analyzes allows to conclude that the powders present a large set of the PS particles. Dimensions of the PS particles alter from 1 to more than 200 µm.

The sample of PS made of rice husk silica has the morphology slightly different from the other samples. Its silicon nanocrystals look like fibers (Figure 3, b) while the samples based on bamboo are similar to the sponge (Figure 3, d, f). Such effect takes a place as the PS samples inherit the morphology of the initial biogenic silica.

Gas adsorption analysis revealed that specific surface and average pore diameter of PS based on rice husk were 9 m²/g and 14.4 nm respectively. The same parameters of the PS made of bamboo husk were 44 m²/g and 7.2 nm while for the sample based on bamboo joints – 12 m²/g and 18.5 nm. Thus, the obtained materials are of mesoporous media.

It was found that pure PS powders based on the bamboo silica (both husk and joints) demonstrated weak photoluminescence in the near-IR range. It was also possible to achieve some photoluminescence of the bamboo husk PS in the range of 400 – 550 nm by its mixing with skin sebum. The PS powder based on rice husk did not show any photoluminescence at all.
Figure 1 (a, b, c). X-ray diffractograms of the PS powder samples formed from the silica powders based on rice husk (a), bamboo husk (b) and bamboo joints (c)
3. Conclusion
In present work, the mesoporous silicon powders were fabricated by the magnesiothermal reduction of biogenic silica powders based on the rice husk, bamboo husk and bamboo joints. It was found that the silicon skeleton of PS samples has polycrystalline nature. We suppose that the surface of the silicon skeleton of PS is highly oxidized in the air. The PS powder based on bamboo joints contains the smallest amount of the silicon atoms comparing to other PS powders due to limited access of magnesium to the whole volume of the silica particles upon thermal reduction. It was shown that the morphology of the PS particles is defined by the morphology of the initial biogenic silica. This fact opens an opportunity to vary morphology of the porous material by the choosing plant type. The possibility to form PS powders based on the biogenic silica, which can demonstrate photoluminescence, was revealed. Additional research on optimization of the reduction regimes are carried out now to achieve greater specific surface area of the PS samples and increase effectiveness of their photoluminescence.
Figure 3 (a, b, c, d, e, f). SEM images of the PS powder samples formed from the silica powders based on rice husk (a, b), bamboo husk (c, d) and bamboo joints (e, f).

Acknowledgments
Authors would like to thank very much Prof. Leigh Canham for fruitful discussions on the topic. This work has been supported by the Fund for Fundamental Research and Ministry of Education of Belarus.

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