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Usage of Transformer Plasma System for Si Nanopowder Synthesis

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This article describes the new method for silicon production; such silicon is suitable for use in solar cell manufacturing. Transformer plasma system is described as a source of nanopowders, for example, Si. Some thermodynamic results for chemical reactions in plasma jet and some experimental results are given in the text. The aim of this work is to prove the efficiency of using the transformer plasma system for nanopowder production, including silicon.

Keywords: Transformer plasma system, Silicon nanopowder, Spectrum of FTIR diffuse reflectance.

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1. INTRODUCTION

Crisis in the market of solar power engineering because of the prevalence of old technologies and their high cost price is observed at present. There is a great demand for a new method of SoG-Si production. We propose a new method which uses the plasma-chemical synthesis of Si nanopowder from the powder blend of micron SiO_2 and carbon source powder using the transformer plasma system. Powder with the particle size of about 20 nm is obtained after plasma-chemical synthesis. Then this powder should be agglomerated and tableted using fluorine based binder. Such tablets can be used in the usual Czochralski process for the growing of silicon ingots. Plasma-chemical synthesis is suitable for the production of other types of nanopowders. Transformer plasma system does not make pollution in contrast to usual arc systems, but, at the same time, such system is less cost than microwave plasma generators.

Plasma synthesis of nanopowders attracts more attention during the last years. There were developed many new processes for the production of nanopowders of metals, alloys and ceramics. To this end, one uses a wide spectrum of technologies, plasma discharge, arc discharge, electrical blasting, self-maintaining high-temperature synthesis, burning synthesis, spray pyrolysis, sol-gel method and mechanical attrition. Plasma systems can achieve a temperature of 10000 K; such high temperature is sufficient for the implementation of almost any chemical reaction.

“Induction” plasma systems developed by Canadian company Tekna Plasma Systems Inc. are the best ones for such purposes [1]. They are very efficient, if low impurity level is needed. Other plasma systems give additional impurities because of destruction of an electrode during operation. “Transformer” system as well as the “induction” one does not have electrodes, and therefore it does not introduce additional impurities. Moreover, it operates at the much lower frequency (about 3 MHz for the “induction” and 10-100 kHz for the “transformer”) that allows to use considerably cheaper power sources.

In the given work we present the results of the theoretical and experimental works as well as the results of the analysis of the product obtained during synthesis in plasma reactor with the transformer system of plasma production.

2. EXPERIMENTAL TECHNIQUE

Two experiments have been performed. The first one is the reaction of monosilane decomposition. The second experiment has used the mixture of SiO_2 and carbon as the initial reagents. Before blending these materials were grinded to the size of 1 μm using a resonance jet mill. They were mixed in certain proportions. This mixture was fed to the “transformer” plasma reactor. Si, C, and O were the dominant components of this mixture.

Scheme of the carbothermal reduction reaction for SiO_2 with the formation of silicon is the following:

$$SiO_2 + 2C = Si + 2CO\uparrow. \quad (1)$$

Thermodynamic calculations (isobar potential $\Delta G < 0$) give the minimum temperature of this chemical reaction which is about 1700 °C (Fig. 1).

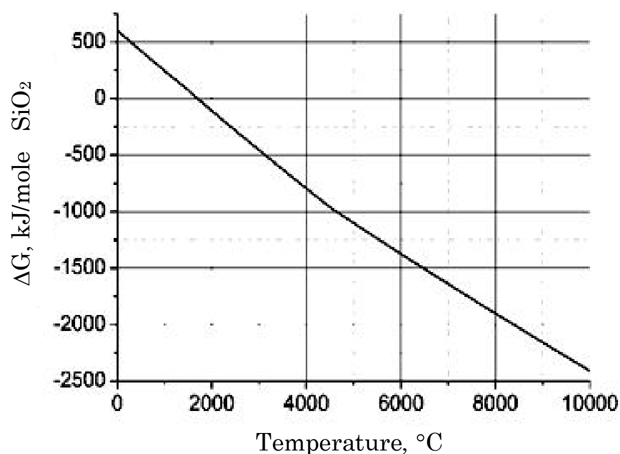

Fig. 1 – Isobar potential of the reaction (1)

As it is seen from Fig. 2, there are two explicit temperature ranges in which fast quenching gives maximum amount of the desired product (silicon): the first one – in the range of 3400-3500 °C and the second one – about 8000 °C. It is clear that in order to obtain pure silicon in the first case quenching should be sufficient to avoid residual SiO in the product (about 1600 °C).

Material can be heated up to 4000-5000 °C in the plasma jet. Such temperature is enough for a total decomposition of the initial mixture to separate elements.

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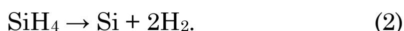
Use of fast quenching at the output of plasma torch allows to obtain elementary Si and gas CxOy which is easily separated from the base product. This whole process takes place in the inert argon atmosphere. Product is caught using the bag filter which is located after cyclone in the path of the reaction products. Product was obtained in the form of a powder.

Collected material in hermetic vessel is transported to the bag box. Bag box was under the argon atmosphere. Nanosized silicon powder was tableted in inert atmosphere using fluorine containing binder. Such tablets are not afraid oxidation, in contrast to silicon nanopowder which acquires immediately brown color in the air. Then, tablets were used as a raw material for the Czochralski oven. Quartz crucible was used for melting. Obtained silicon ingot had metallic grey color and did not have visible pollutions.

Further work in this direction will be focused on the preparation of monocrystalline ingot and determination of the electrophysical parameters of plates of this ingot.

Experimental work on thermal decomposition of monosilane SiH_4 in "transformer" plasma system was also performed. Argon was used as the orifice gas. Reaction took place at the atmospheric pressure, quenching was not used. Cyclone and bag filter were applied for the collection of powder. Reaction occurred according to the following scheme:



$$SiH_4 \rightarrow Si + 2H_2. \quad (2)$$

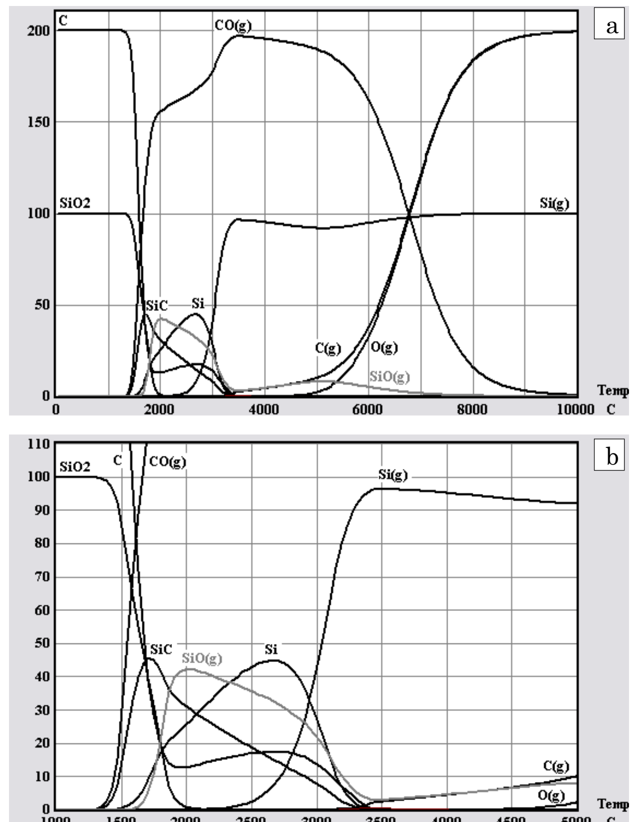


Fig. 2 – Equilibrium composition of the Si-O-C system (molar ratio Si : O : C = 1 : 2 : 2) (a); expanded scale of the temperature range 1000 °C-5000 °C (b)

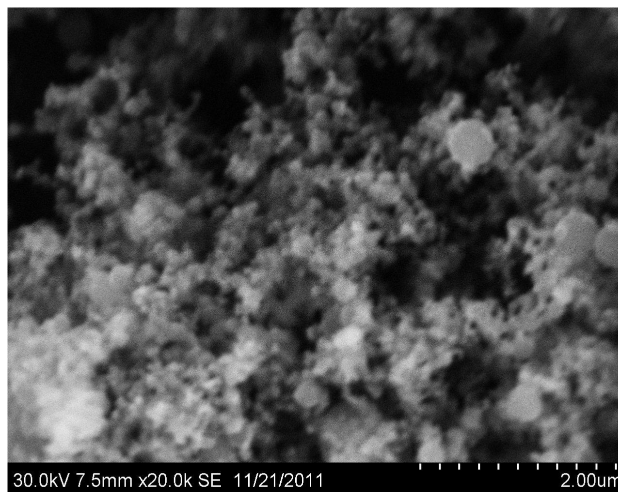


Fig. 3 – Micrograph of the obtained powder

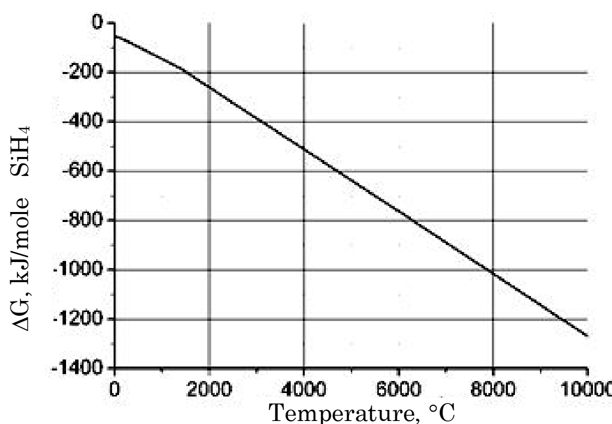


Fig. 4 – Isobar potential of the reaction (2)

The initial purity of monosilane was enough to prevent the additional reactions. Decomposition reaction of monosilane is thermodynamically favorable (isobar potential $\Delta G < 0$) in the whole temperature range from room temperature to 10000 °C (see Fig. 4). Nevertheless, some amount of energy is necessary for the Si-H bonds rupture. Decomposition of SiH_4 starts at 450 °C. Less than 5.4 kJ of energy is necessary for heating of 10 g of SiH_4 up to this temperature; it is a rather small amount. In Fig. 5 we present the equilibrium composition of the Si-H system at the molar ratio of Si : H = 1 : 4 (for monosilane). Calculations show that from the point of view of the purity of the final silicon, minimum temperature should be not less than 8000 °C, since silicon hybrids, which will pollute the product, will remain at a lower temperature.

The obtained material was collected, and it participated in the operations as well as in the previous case (see Fig. 3).

Moreover, fluorine based binder which is used for silicon tableting promotes additional cleaning of silicon in melting. Fluorine is a very active element which reacts with many impurities; and products of such reactions in the form of gases are removed by vacuum system of an oven.

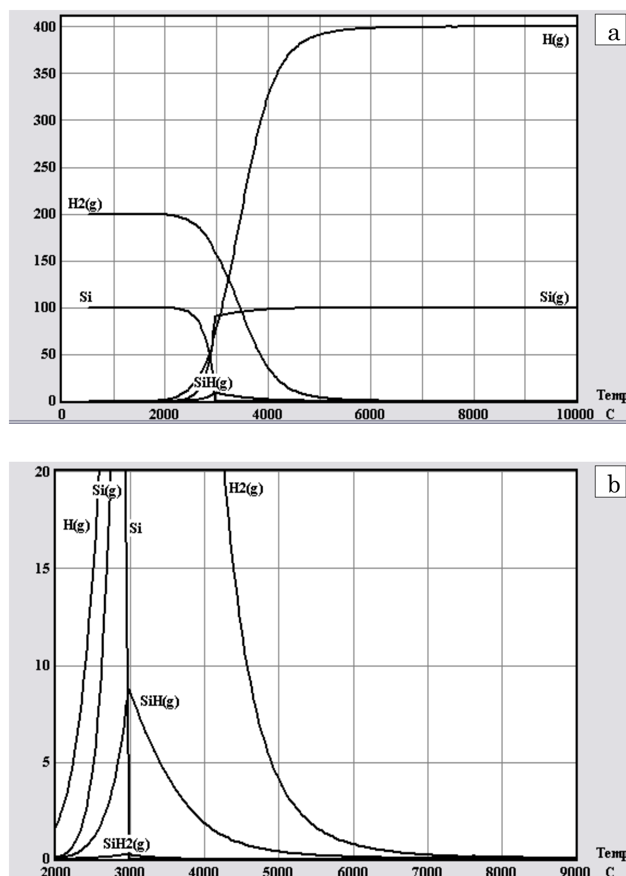


Fig. 5 – Equilibrium composition of the Si-H system (molar ratio Si : H = 1 : 4) (a); expanded scale of the temperature range 2000 °C-9000 °C (b)

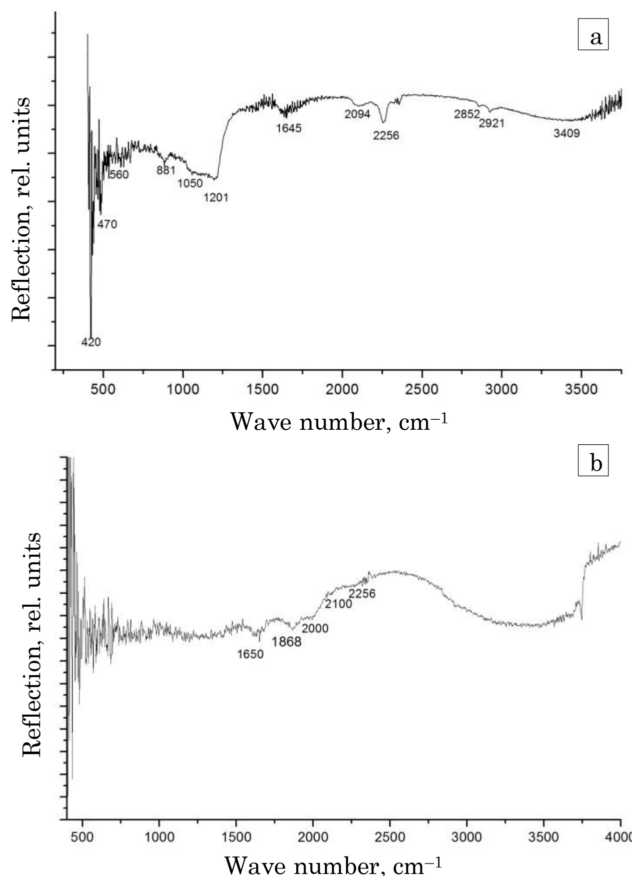


Fig. 6 – Infrared spectrum of the diffusion reflection for powder obtained at monosilane decomposition in plasma (a) and powder obtained in the reaction of silicon oxide with carbon (b)

3. ANALYSIS OF THE RESULTS

We have performed the analysis of the infrared spectra of the obtained powders (Fig. 6).

In Fig. 6a reflection at the wave numbers of 470 cm^{-1} and 1050 cm^{-1} corresponds to the Si-O-Si bonds, 881 cm^{-1} most probably corresponds to the vibrations of Si-OH or Si-O bonds [1-3]. Vibrations in the region of 560 cm^{-1} correspond to the Si-O bonds. Broad peak in the region of 3000-3600 cm^{-1} and peak in the region of 1600-1645 cm^{-1} are connected with the longitudinal and transverse vibrations of O-H bonds, respectively [4]. Peak in the region of 2256 cm^{-1} corresponds to the deformation vibrations of Si-O-Si bonds [5], and wave number 2094 cm^{-1} corresponds to the vibrations of Si-H$_x$ bonds [6]. Weak peaks in the regions of 2852 cm^{-1} and 2921 cm^{-1} correspond to the vibrations of C-CH$_x$ bonds.

Broad bands in the regions of 3000-3600 cm^{-1} and 1650 cm^{-1}, corresponding to the longitudinal and transverse vibrations of O-H bands, respectively, are present in Fig. 6b; they are similar to those shown in Fig. 6a. Low-grade vibrations in the region of 2256 cm^{-1} correspond to the stretching vibrations of Si-O-Si bonds, 2100-2200 cm^{-1} – stretching vibrations of Si-H$_2$ bonds. In the region of 500-1250 cm^{-1} spectrum is rather distorted; O-Si-O, Si-O-Si, O-Si-H vibrations can be present in this region [6]. Unfortunately, some values were not explicitly determined, in particular, for the wave number 1868 cm^{-1}.

4. CONCLUSIONS

We have performed the experimental works on the production of silicon nanopowder using the transformer plasma system. The developed device can be successfully used for the production of other nanopowder materials. The obtained powder after the appropriate preparation is applicable for the production of ingots by the technique similar to the DSS method for multicrystalline silicon ingots. Spectra of the infrared diffusion reflection have shown the presence of bonds with water molecules and oxygen typical for silicon. Under the storage conditions of the obtained powder not in an isolated inert atmosphere, its reaction with substances present in air occurs because of its high reaction capacity.

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