

Article

Preparation of Polycrystalline Silicon by Metal-Induced Crystallization of Silicon–Carbon Powder

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Abstract: In this study, we successfully obtained crystalline silicon from silica powder using a metal-induced crystallization method. For this purpose, powders were first prepared from organosilicon compounds and finely dispersed aluminum particles, then their metal-induced crystallization was carried out by annealing at the temperature of 570 °C. Powders of organosilicon compounds (tetraethoxysilane and polyethylhydrosiloxane) were prepared by different technological operations in order to determine precisely the presence of carbon in the product. The results showed that the presence of carbon in silica powder affects the production of crystalline silicon. In silica powders containing no carbon, the formation of crystalline substances does not occur at the annealing temperature of 570 °C. The results of this study are of great importance for the production of polycrystalline silicon powders obtained at reduced temperatures.

Keywords: metal-induced crystallization; polycrystalline silicon; silica; aluminum; amorphous structure; carbon; X-ray phase analysis



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1. Introduction

Polycrystalline silicon has been widely used in microelectronics, sensor production, powder metallurgy, and as catalysts for the chemical industry. To obtain polycrystalline silicon, the methods of solid-phase crystallization [1], laser-induced crystallization [2], and chemical precipitation are used. However, in most cases the formation of Si polycrystals occurs at a high temperature. Therefore, studies aimed at reducing the temperature of the formation of crystalline silicon grains remain relevant.

The method of metal-induced crystallization (MIC), based on the formation of successive layers of metal (Au, Al, Ni, etc.) and amorphous silicon or silicon suboxide (a non-stoichiometric compound of silicon and oxygen SiO_x , in which $0 < x < 2$), appears to be promising [3,4]. The layer exchange during annealing contributes to the preparation of polycrystalline Si at relatively low temperatures. Table 1 lists the crystallization methods, operating temperatures, advantages, and disadvantages of each method.

In papers [5–7], the authors investigated the processes occurring during the gold-induced crystallization of silicon. For this purpose, successive layers of amorphous silicon suboxide and Au were deposited on substrates and then annealed. It is noted that with a gold layer thickness of 30 nm and annealing in the temperature range of 600–700 °C for 10 h, the $\alpha\text{-SiO}_x$ layer completely transforms into polycrystalline silicon. It is also noted in the articles that the thickness of the sputtered Au layer and the layer sequence play a crucial role, e.g., crystallization does not occur when a thinner gold layer is deposited.

Table 1. Comparative table of silicon crystallization methods.

Crystallization Methods	Working Temperature Range, °C	Advantages	Disadvantages
Czochralski method	1400–1600	It allows the obtainment of ultra-pure single crystals. The ability to control the structure of the crystal lattice.	High temperatures. Low crystal growth rate.
Metal-induced crystallization (MIC)	400–1000	The possibility of crystallization at relatively low temperatures. The ability to regulate crystal growth conditions, grain size, and crystal orientation.	The presence of impurities. The process proceeds in several stages.
Solid-phase crystallization (SPC)	800–1200	Allows you to obtain ultra-pure crystals. Simple technology.	High temperatures. Long processing time.
Laser crystallization (LC)	400–1000	The ability to control the structure of the crystal lattice. Fast local heating. Minimizes thermal stress by localizing heating.	Limited areas of the laser beam effect.
Rapid thermal annealing (RTA)	700–1100	Short processing time.	High power consumption. The risk of deformation of the substrate due to extreme temperature fluctuations
Zone-melting crystallization (ZMC)	>1400	It allows the obtainment of ultra-pure single crystals. The ability to control the structure of the crystal lattice.	High temperatures. Low crystal growth rate.
Chemical vapor deposition (CVD)	500–1000	The possibility of crystallization at relatively low temperatures. The ability to regulate crystal growth conditions, grain size, and crystal orientation.	It requires high temperatures and vacuum conditions. Expensive precursor gases and equipment.

In paper [8], a study of nickel-induced crystallization of amorphous silicon (*a*-Si) nanorods was performed. For this purpose, a multilayer system containing *a*-Si and Ni layers was fabricated and the effect of annealing time on the formation of crystalline silicon phase was investigated. The author states that partial crystallization of amorphous silicon nanorods occurred.

In paper [9], a method for obtaining polycrystalline silicon by aluminum-induced crystallization is described. First, a layer of Al and then a layer of hydrogenated amorphous silicon were deposited on glass substrates by sputtering. Then the samples were annealed at temperatures below the eutectic point of the Al-Si system. As a result, the structure of the silicon was changed from amorphous to crystalline.

The temperature of metal-induced crystallization depends on many factors: the composition and nature of the starting components, the order of the layers, and their thickness [10]. It is possible to obtain polycrystalline silicon with almost all metals, under certain conditions, up to the eutectic temperature [10–12]. At the same time, Si compounds with Al are characterized by the lowest eutectic temperature compared to the other considered (Au, Ni) metals.

In addition to the crystallization of silicon in thin films, methods of crystallization in powder systems are being developed. In the studies [13,14], aluminum was used to obtain polycrystalline silicon from amorphous silicon oxide. For this purpose, tablets of crushed silica glass and aluminum powder were prepared and annealed in two stages. The first stage was conducted in the temperature range of 700–900 °C, while the second stage was conducted in the temperature range of 1100–1200 °C. The reduced crystalline silicon diffused onto the surface of the tablets.

The analysis of the sources [15–19] devoted to MIC showed that in most papers their purpose and result are to obtain *poly*-Si from amorphous silicon (*a*-Si) or silicon suboxide *poly*-Si deposited on crystalline substrates. However, the epitaxial mechanism for the formation of polycrystalline structures is not possible on non-crystalline substrates. In powdered systems, crystallization processes differ significantly from metal-induced thin

film epitaxy due to the multi-step nature of chemical, physical, and physicochemical processes. Therefore, the approaches widely used in metal-induced crystallization of thin films on crystalline substrates do not work under the conditions of solid-phase exposure of powder particles. In order to realize phase transformations in powdered systems, it is necessary to take into account the thermodynamic possibility of reactions and their kinetic features.

Despite the thermodynamic possibility ($\Delta G_{298} \approx -659$ kJ/mol [20]), the reduction of silicon oxide (SiO_2) by aluminum almost does not occur (or is extremely slow) under normal conditions. Therefore, polycrystalline silicon is obtained by the reduction of silicon oxide by aluminum at higher temperatures (above 1100 °C) [9,13,14]. Kinetic restrictions on the reaction behavior at relatively low temperatures (up to 600 °C) are imposed, among other things, by the specific features of the solid-phase interaction of substances. In a powdered mixture, the reaction behavior is much more complicated, since it is often accompanied by not only chemical, but also physical and physicochemical processes and takes place in several stages. At the very beginning, the reaction occurs on the surface of the grains of the components. The reaction then occurs due to both external (movement of the component to the contact boundary) and internal (movement of the substance through the areas of direct contact of the grains) diffusion [21].

To improve the interaction in powder systems, various processing methods are used; for example, the action of mechanical vibrations [22]. Another important factor affecting the kinetic characteristics of the reaction is the presence of impurities. In particular, the formation of crystalline materials is influenced by carbon impurities [23]. At the same time, the mechanism of carbon's influence on the formation of crystalline silicon requires more detailed study.

In our previous studies, we obtained and characterized pure silica [24] and silicon-carbon powder systems [25]. In this paper, the effect of carbon in the composition of silica powder, obtained from organosilicon liquid and fine aluminum particles, on aluminum-induced crystallization of silicon is investigated. The kinetic processes of crystalline silicon formation were analyzed.

2. Materials and Methods

2.1. Materials

There are various methods for producing silica: plasma-chemical, using pulsed electron beam evaporation, sol-gel method, etc. [26–28]. Silica-containing powders were prepared from organosilicon compounds (tetraethoxysilane and polyethylhydrosiloxane) in the presence of finely dispersed aluminum particles. In order to obtain a carbon-free powder, the hydrolysis of tetraethoxysilane (TEOS) ($\text{C}_2\text{H}_5\text{O})_4\text{Si}$ of high purity (PJSC Khimprom, Novocheboksarsk, Russia) was carried out in base conditions [24]. To carry out the hydrolysis reaction, TEOS (65 mL), distilled water (12 mL), aluminum powder (5%—the percentage is calculated from the mass of the dry SiO_2 output), and a catalyst (NH_4OH , pH ~11) were added to the weighing bottle. For better mixing and to accelerate the reaction, the samples were subjected to ultrasound for an additional 2 h at a temperature of 60 °C. The experiment was conducted under stable atmospheric conditions.

The silicon-carbon powder was prepared by the pyrolysis (300 °C) of polyethylhydrosiloxane (PEGS) liquid (Point LLC, Saint Petersburg, Russia) [25] in the presence of fine Al particles.

Fine aluminum in the form of PAP-2 powder (LLC “Novosverdlovsk Metallurgical Company”, Novosibirsk, Russia) was introduced into the initial organosilicon liquids (5%—the percentage is calculated based on the mass of the dry product organosilicon liquids). The average particle Al size was 30 μm . After obtaining silica powders, their metal-induced crystallization was carried out by annealing in a muffle furnace at a temperature of 570 °C over 5, 12, 19, 35, 54, 70, or 81 h. The experiment was conducted under stable atmospheric conditions.

2.2. Research Method

The elemental composition of the obtained powders was investigated using an energy dispersive spectrometer (EDS) X-MAX 50 Oxford Instruments NanoAnalysis—scanning electron microscope accessory TESCAN MIRA 3 LMU (Tescan, Brno, Czech Republic). The active area of the crystals was 50 mm², and the resolution on the Mn K α line was 124 eV at a counting rate of 130,000 pulses/s. For better contrast during the SEM-EDS analysis, the samples were placed on a metallized chrome substrate. Chromium atoms were excluded from the results.

An X-ray diffraction method was used to identify the crystalline phases in the obtained powders. The device ARL X'TRA (ThermoTechno LLC, Ecublens, Switzerland) was used. The survey was carried out using the CuK α X-ray source in the range of measurement angles $2\theta = 4^\circ$ – 64° ; the survey was asymmetric coplanar, and the angle of incidence was sliding $\alpha = 3^\circ$ (θ -scan). X-ray spectra were identified according to the ICDD (International Center for Diffraction Data) JCPDF database "<https://www.icdd.com/pdf-2/> (accessed on 17 April 2024)". The content of crystalline phases in the obtained powders was calculated as the ratio of the area of diffraction peaks on the X-ray of each crystalline phase to the sum of the areas of all sections. To determine the values of the peak areas using the OriginPro 2021 V9.8.0.200 X64 mathematical package, an integral peak analysis was performed with the construction of a baseline according to user-defined parameters, using the 2nd derivative (zeroes) method, using automatically placed points (8 pcs). The top of the peaks of each crystalline phase were marked manually. The program also displayed the area of all sections of the X-ray. The area value was reflected minus the baseline.

Differential thermal analysis was carried out on the "NETZSCH STA 449F1" (NETZSCH-Gerätebau GmbH, Selb, Germany) apparatus. The studies were carried out in an Al₂O₃ crucible with a lid, in an atmosphere of argon and oxygen, in the temperature range of 25–1200 °C. The rate of temperature increase was 10 °C/min.

3. Results and Discussion

Figure 1 shows powder X-ray diffractograms of the substances that were obtained from tetraethoxysilane and polyethylhydrosiloxane in the presence of fine Al particles. The diffractogram of the powder that was obtained by hydrolysis of tetraethoxysilane shows an amorphous halo in the region of angles $2\theta = 15$ – 30° , which corresponds to silicon dioxide (SiO₂) of amorphous structure (PDF card 01-075-3159). The X-ray diffractogram of the powder that was obtained by pyrolysis of polyethylhydrosiloxane also shows an amorphous halo in the region of angles $2\theta = 18$ – 30° , corresponding to amorphous SiO₂. However, the diffractogram of the powder from PEGS shows another amorphous halo in the region of angles $2\theta = 6.5$ – 12° , which is characteristic of the carbon-containing phase [20]. At the same time, clear peaks belonging to the crystalline Al phase (PDF card No 85-1327) are present in the X-ray radiographs of the powders that were obtained from both TEOS and PEGS. The content of the crystalline aluminum phases in the obtained powders is 5.1% for PEGS and 4.2% for TEOS.

The results of the energy-dispersive spectroscopic study of the powders that were obtained from organosilicon liquids and Al (Table 2) indicate the presence of carbon atoms in the powders from PEGS. At the same time, C atoms are absent (less than the detection limit) from the elemental composition of the powders that were obtained from TEOS. The Al content in the powders that were obtained from the EDS data agrees well with the crystalline phase content data that were calculated from the X-ray spectra.

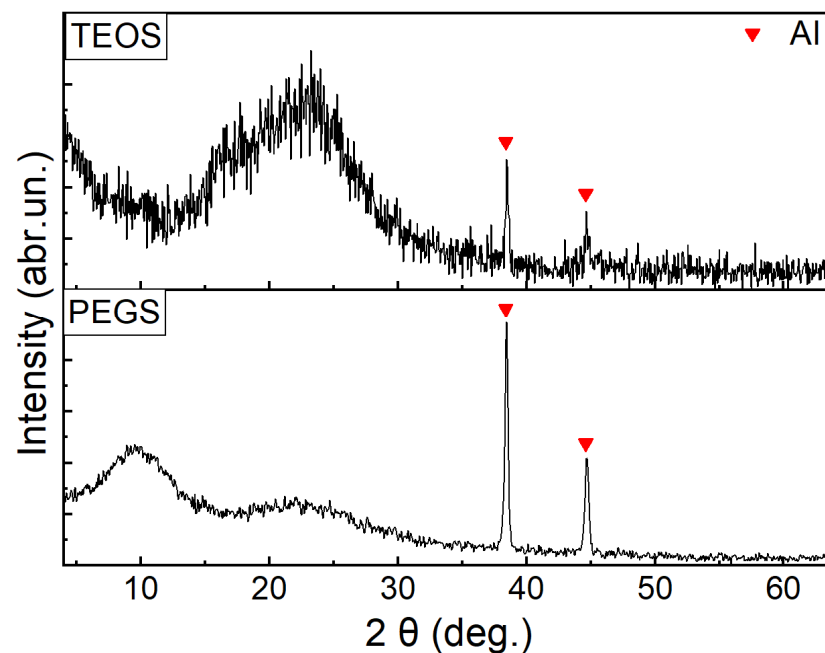


Figure 1. X-ray powder diffractograms of the materials synthesized from TEOS and PEGS in the presence of Al.

Table 2. Atomic composition of synthesized powders, wt %.

	Si	O	C	Al
Powder from TEOS	44.47 ± 0.36	51.19 ± 0.42	-	4.34 ± 0.12
Powder from PEGS	40.58 ± 0.32	39.54 ± 0.31	14.79 ± 0.21	5.18 ± 0.15

Then, the influence of the presence of carbon atoms in the composition of silica-containing powders on the preparation of crystalline silicon by aluminum-induced crystallization was investigated. For this purpose, the obtained powders were subjected to annealing in a muffle furnace at a temperature of 570 °C and various holding times.

After annealing the powders that were obtained from TEOS in the presence of Al, the amorphous silica halo in the region of angles $2\theta = 15\text{--}25^\circ$ is preserved in the X-ray diffractograms (Figure 2), but a change in shape and a displacement of the bulge is manifested compared with the data of the upper Figure 1. The change in the shape of the amorphous halo is probably associated with the formation of fine crystalline unidentified phases due to the presence of trace amounts of the carbon-containing phase in the powders prepared from TEOS. It is also worth noting that after 5 h of annealing, the intensity of the diffraction peaks corresponding to the crystalline aluminum phases decreases compared to the samples before annealing (Figure 1). After 35 h of annealing, the Al diffraction peaks disappear altogether. Other crystalline phases are not recorded. If we compare the amorphous halo on the X-ray images of the TEOS powders after 5 and 35 h of annealing, then its shape and position practically do not change. Thus, apparently, there is a chemical interaction between SiO_2 and Al at the annealing temperature of 570 °C. However, products of amorphous structure, not crystalline, are formed.

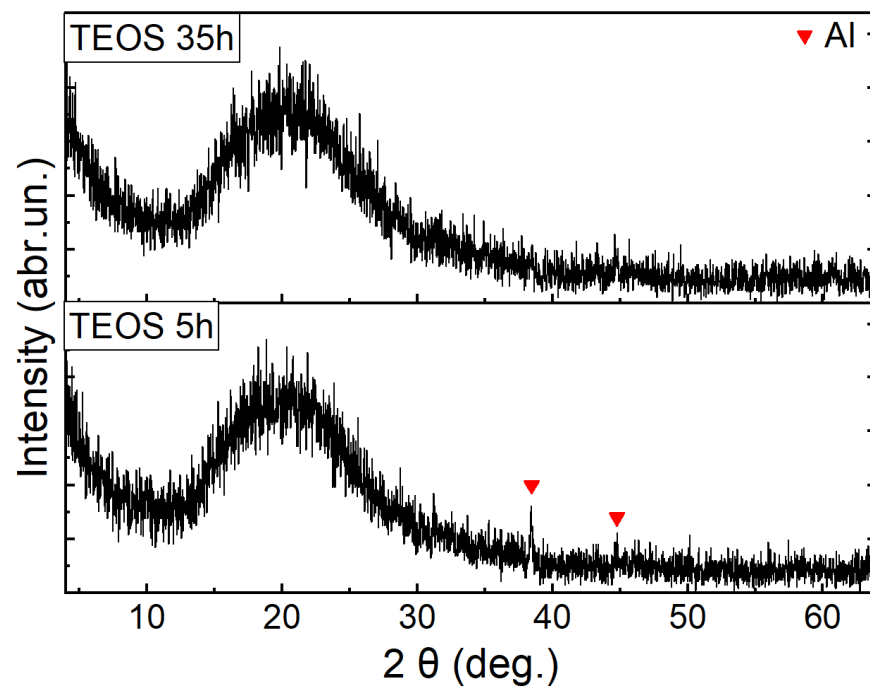


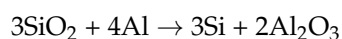
Figure 2. X-ray powder diffractograms of the samples obtained from TEOS in the presence of Al after annealing for 5 and 35 h.

In the X-ray diffractograms of the powders, in which carbon atoms were present, new peaks appear already after 5 h of annealing at 570 °C (Figure 3), referring to the crystalline phases of Si (PDF № 75-589) and Al_2O_3 (PDF №1-1303). With increasing annealing time, the ratio of the peaks changes on the diffractograms, according to the areas from which the content of the crystalline phases (Table 3) in the samples was calculated. It is also worth noting the absence of an amorphous halo in the region of angles $2\theta = 6.5\text{--}12^\circ$ on the X-ray diffractograms, which is apparently due to the combustion of carbon atoms during annealing.

Table 3. Content of crystalline phases (%) in the annealed powders obtained from PEGS and Al.

Crystalline Phase	Annealing Time, h							
	0	5	12	19	35	54	70	81
Al	5.1	4.13	2.47	1.67	0.26	0	0	0
Si	0	0.73	1.99	2.58	3.54	3.65	3.73	3.80
Al_2O_3	0	0.77	1.33	1.46	4.68	6.74	7.26	7.79

The obtained results (Figure 3, Table 3) indicate that the increase in the content of the crystalline silicon phase almost does not occur when the annealing time is longer than 35 h. The percentage content of crystalline Si is comparable to the theoretical yield (~3.5%) that was calculated from the reaction equation:



However, the amount of crystalline aluminum oxide is much less than it should be theoretically. This is probably due to the fact that part of the formed Al_2O_3 is represented by amorphous form. This is also evidenced by an increase in the intensity of the amorphous regions on the X-ray images of the annealed powders (Figure 3).

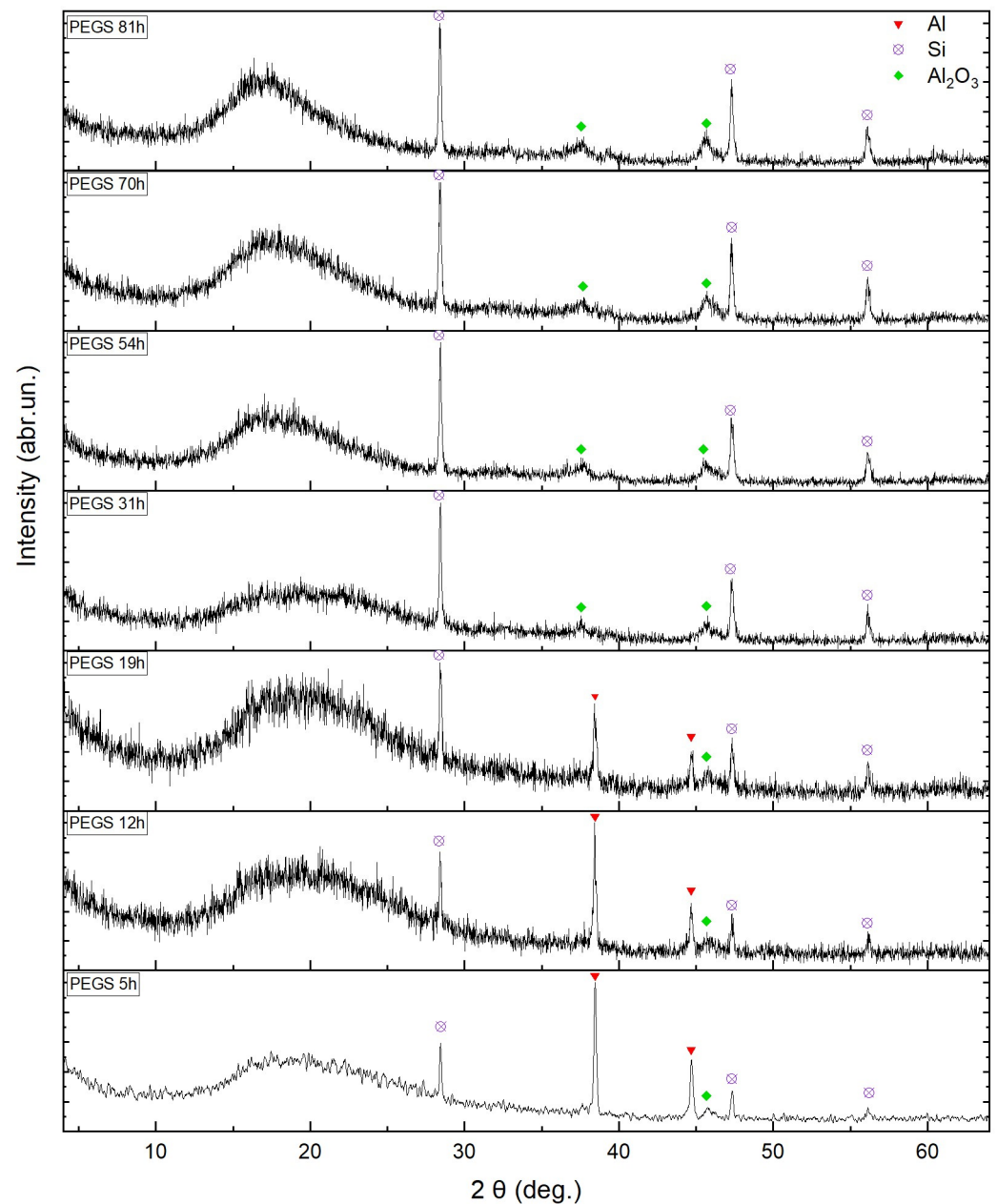


Figure 3. X-ray powder diffractograms of samples obtained from PEGS in the presence of Al after annealing for 5–81 h.

Analyzing the role of the presence of a carbon-containing phase in the processes of obtaining crystalline silicon, based on the studies conducted, it is quite difficult to establish an unambiguous mechanism of its action. The authors of [23] suggested that carbon acts as crystallization centers. However, the carbonaceous phase here is amorphous, so this is unlikely. Also, when obtaining powders from TEOS, traces of an organic carbon-containing phase are probably present in the samples, which leads, as noted above, to the formation of unidentified fine crystalline phases. Despite the presence of fine crystalline phases in the system, the reaction between SiO_2 and Al proceeds with the formation of amorphous products. In the case of powders obtained from PEGS, the carbon-containing phase is sufficient not only to begin the formation of fine crystalline phases, but also to begin their growth, i.e., the formation of full-fledged nuclei (centers) of crystallization. Further crystal growth (an increase in the content of the crystalline phase) during the Si reduction reaction from SiO_2 is possible without the participation of carbon. In this regard, it can be

assumed that carbon atoms activate the processes occurring at the initial stage somewhat and contribute to a more uniform distribution of thermal energy at the phase interface, which helps to overcome the energy barrier necessary for the start of crystallization.

To study the kinetic features of the formation of polycrystalline silicon, it is important to identify the limiting stage in order to determine ways to influence the rate of solid-phase interaction. Using experimental data on the dynamics of the changes in the crystalline phase of silicon in the reaction medium (Table 3), kinetic curves of the Si reduction process were constructed (Figure 4a) and an analysis of various mathematical models was performed (Table 4) [29]. The key stages of the kinetic analysis consisted of checking the linearity (by the confidence coefficient of the approximation R^2) of the graphs of the dependence of $F(\alpha)$ on time (τ) (the tangent of the slope angle is a constant of the reaction rate) and comparing the experimental points and curves that were calculated according to the corresponding equations in the coordinates “degree of transformation (α) – reaction time (τ)”. In the process of analyzing the Carter–Valensi model, taking into account the polydispersity of the system, a graph was plotted in coordinates $\lg F_{CV} = f(\lg \alpha)$. In this case, the tangent of the angle of inclination of the straight line is necessary to express the degree of transformation from the equation $F_{CV} = k' \alpha^{\lg(\varphi)}$. In accordance with the analysis of mathematical models, a model was selected that most adequately describes the experimental data (Figure 4b,c).

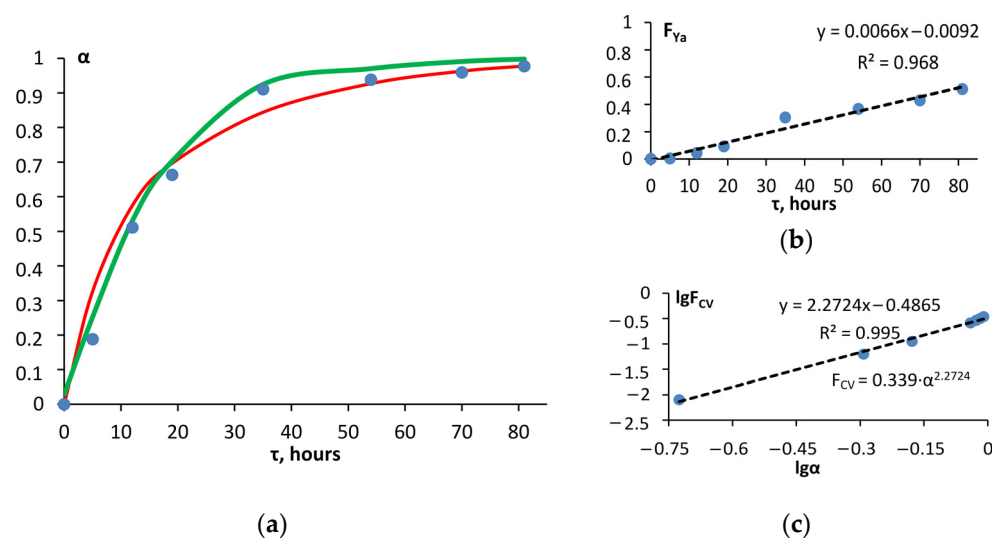


Figure 4. Graphical method for checking the applicability of kinetic equations: experimental data on the reduction of crystalline Si (dots) and curves from the equations (red—Yander, green—Carter–Valensi) (a); data processing according to the Yander (b) and Carter–Valensi (c) model.

From the results obtained (Figure 4), it follows that the recovery process occurs in the diffusion region. The kinetic curves of the thermal reduction of crystalline silicon correspond to the reactions of solid substances without self-acceleration. The calculated reaction path according to the Yander model (red curve) deviates slightly from the experimental points. The Carter–Valensi function (green curve), calculated taking into account the polydispersed distribution of particles at $z = 2$, more accurately coincides, within errors, with the experimental data for the reduction reaction of crystalline silicon. Therefore, the assumption about the action of the Carter–Valensi mechanism in the studied reaction mixture is valid, which takes into account the difference in the equivalent volumes of the coated reagent and the reaction product. Taking into account this model, acceleration of the solid-phase Si reduction reaction by increasing the process temperature is not possible, since when exposed to high temperatures, the particles sinter with the formation of large agglomerates.

Table 4. Equations of chemical kinetics models.

№ p/p	Model	Basic Kinetic Equations	Type (Features) of the Model	Approximation Coefficient R ²
1.	Yander	$F_{Ya}(\alpha) = (1 - \sqrt[3]{1 - \alpha})^2 = \frac{2kD\tau}{R_0^2} = k_{Ya}\tau$	A model of diffusion-controlled reactions. The total reaction rate is determined by the advance of the reagent or its individual components to the reaction interface or the withdrawal of products from it.	0.978
2.	Carter–Valensi	$F_{CV}(\alpha, z) = \frac{z}{z-1} - (1 - \alpha)^{2/3} - \frac{[1 + \alpha(z-1)]^{2/3}}{z-1} = k_{CV}\tau$ Taking into account the polydispersity of the system: $F_{CV}[\alpha(r, \tau)] = k\tau/r^2$	A diffusion model that takes into account the polydispersity of powders and the difference in equivalent volumes of the coated reagent and the reaction product. It takes into account the ability of defects in the crystal lattice to cause the reaction, but later their concentration and role decrease, i.e., the rate of disappearance of defects varies inversely with time.	0.995 (for z = 2)
3.	Tamman	$F(\alpha) = 1 - \sqrt[3]{1 - \alpha} = k \ln \tau$		0.979
4.	Ginstling–Braunstein	$F(\alpha) = [1 - (2\alpha/3)] - (1 - \alpha)^{2/3} = k\tau$	A decelerating diffusion mechanism with a parabolic law of product layer growth. The model is based on the assumption that the product is formed by counterdiffusion of interacting reagents through the product layer, i.e., the growth rate of the product is inversely proportional to the thickness of the formed layer.	0.935
5.	Dunwald–Wagner	$F(\alpha) = \lg(6/\pi^2 \cdot (1 - \alpha)) = k\tau$	It takes into account that the limiting stage of solid-phase interaction is the formation (or growth) of product nuclei.	0.964
6.	Avrami–Yerofeyeva	$F(\alpha) = -\lg(1 - \alpha)^{1/n} = k\tau$	A model for chain type reactions.	0.964 (for n = 1) 0.860 (for n = 2) 0.752 (for n = 3)
7.	Prout–Tompkins	$F(\alpha) = \lg[\alpha/(1 - \alpha)] = k\tau$		0.892

Note: α —is the degree of transformation ($\alpha_i = N_i/N_{i,0}$); $N_{i,0}$ and N_i —is the number of moles of the i-th component in the initial system and by the time τ elapsed from the beginning of the interaction; k —is a constant; D —is the diffusion coefficient of particles limiting the process; R_0 —is the radius of a particle of one of the components at the initial time; z —is the ratio of the equivalent volumes of the product and the reagent to be coated; r —is the average radius of particles in the volume of the reaction mixture; n —is a parameter depending on the reaction mechanism, the rate of nucleation and the geometry of the embryos ($n = \beta + \lambda$, where β —is the number of stages in the formation of the embryo (often equal to 1 or 0, the latter case corresponds to instantaneous nucleation or the case when compactly growing embryos completely cover the outer edges)); and λ —is the number of directions of effective growth embryos (equal to 3 for spheres or hemispheres, 2 for disks or cylinders, 1 for one-dimensional growth).

Methods of differential scanning calorimetry and thermogravimetric analysis were used to study the physicochemical features of temperature's effect on the synthesized silicon–carbon powder that was obtained with the addition of aluminum and without it. Figure 5 shows the thermal analysis data of the powder that was obtained from polyethyl-hydrosiloxane without additives, and Figure 6 shows the thermal analysis data of the powder that was obtained with Al addition.

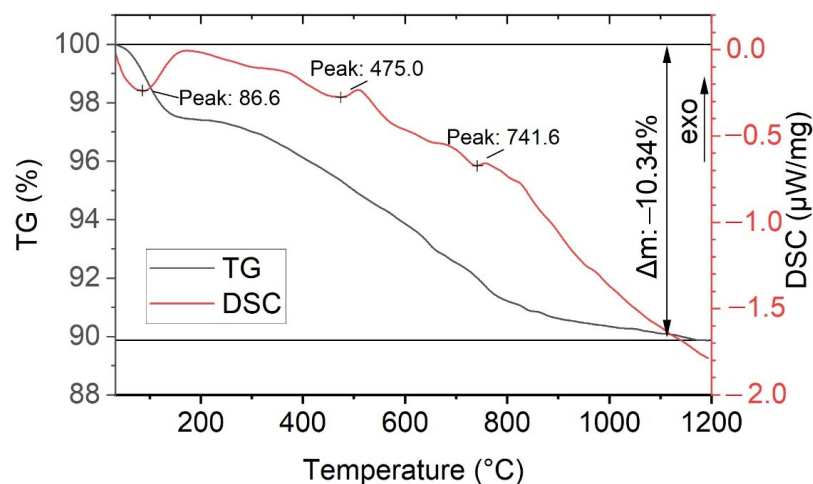


Figure 5. Thermal analysis curves for the powder obtained from polyethylhydrosiloxane without additives: 1—Thermogravimetric (TG) curve; 2—Differential Thermal Analysis (DTA) curve.

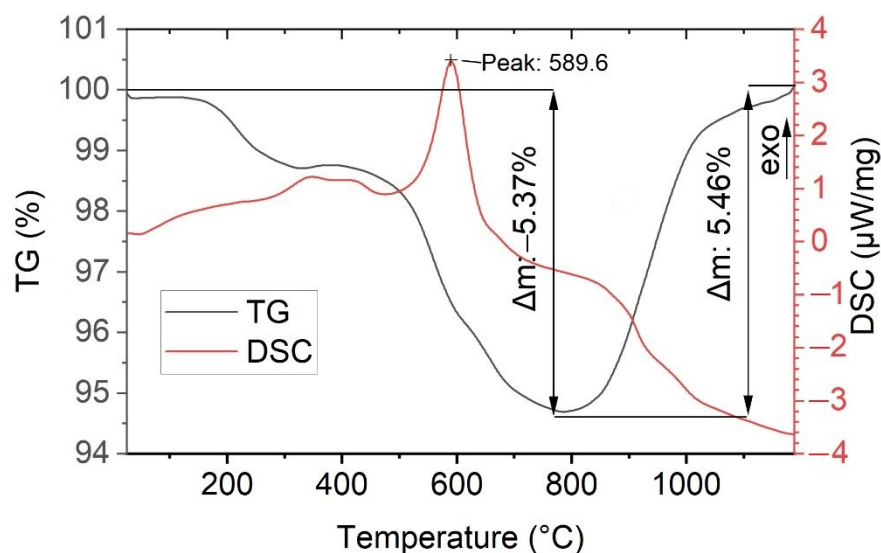


Figure 6. Thermal analysis curves for the powder obtained from PEGS and Al: 1—Thermogravimetric (TG) curve; 2—Differential Thermal Analysis (DTA) curve.

According to the given results (Figures 5 and 6), the initial stage of the heating of all samples is accompanied by an endothermic effect with a minimum in the range up to 100 °C. The endothermic effect is probably connected with the removal of the remaining volatile organic compounds.

On the thermogram of the powder that was obtained from polyethylhydrosiloxane without additives, an additional exothermic effect was recorded: ~520 °C, apparently related to the combustion of organic residues. A second endothermic peak (741.6 °C) was also observed, which may be related to the decomposition of organic residues.

The thermogravimetric (TG) curve analysis shows that the heating of the initial powder that was obtained from polyethylhydrosiloxane without additives is characterized by a strong mass loss of ~10.3%.

On the thermogram of the powder that was obtained in the presence of aluminum, at temperatures above 100 °C, the thermoanalytical DSC curve deviates from the zero line towards exothermic processes. The passage of the differential curve above the baseline can be explained by the difference in the specific thermal conductivity of the sample and the reference. The presence of aluminum in the sample increases its thermal conductivity.

The thermogram shows three exothermic effects: 345 °C, 427 °C, and 589 °C. The first peak (345 °C) is weakly expressed and is probably related to the combustion of organic residues. The second peak (427 °C) is also weakly expressed and may be related to the formation of limited pre-eutectic α -solid solutions of the silicon-containing component in aluminum crystals. The most intense exothermic effect in the temperature range 510–625 °C (maximum at 589.6 °C) is related to the formation of silicon and its dissolution in aluminum. Silicon has a high solubility in aluminum at the eutectic (α -Si) temperature of 577 °C, and under non-equilibrium conditions the appearance of the eutectic temperature is observed already at a silicon content higher than 0.05% [17]. Taking into account the temperature of the onset of the exothermic effect (510 °C) and the data of the X-ray phase analysis of the powder that was obtained from PEGS with the addition of aluminum powder and heat-treated at 570 °C (Figure 3), it can be noted that the appearance of crystalline silicon begins before the eutectic temperature: in the region of solid-phase reactions.

When the temperature rises above 650 °C, the transfer of the DSC curve into the region of endothermic processes is observed. This is caused by heat absorption during aluminum melting ($T = 660$ °C), decrease in the specific thermal conductivity of the sample (due to a decrease in the amount of metallic Al in the system), decomposition of the substances with the formation of oxides, and shrinkage of the sample during thermal analysis.

The analysis of the thermogravimetric (TG) curve also indicates that a multi-step process takes place during the heating of the powder containing aluminum. The mass change of -5.37% is due to the combustion of some components and the reduction of Si from SiO_2 , and the mass increase of 5.46% after 800 °C is due to the formation of oxides. At 1100 °C, amorphous Al_2O_3 is transformed into crystalline, and at 1250 °C, polymorphic transformation of quartz into cristobalite occurs.

The results of the differential thermal analysis data indicate a complex dependence of the reaction on the process temperature that is associated with changes in the properties of the reacting substances. Therefore, determining the kinetic features of the reaction of the reduction of crystalline silicon using TG and DTA data is difficult. The use of the proposed low-temperature method for producing polycrystalline silicon by the metal-induced crystallization of silicon–carbon powder provides, compared to the results of previous studies, the advantage of reducing the synthesis temperature of silicon–carbon powder from 1100 °C to 570 °C [13,14].

4. Conclusions

The production of powder systems of crystalline silicon by the method of aluminum-induced crystallization of amorphous silica-containing powder that is obtained from organosilicon compounds at a relatively low temperature (570 °C) is possible in the presence of carbon atoms. The carbon component ensures the formation of fine crystalline phases and the beginning of their growth at the initial stages of the process. In the future, carbon atoms will burn out, but an increase in the content of the crystalline phase in the reaction between silica and aluminum is possible without the participation of carbon. In the absence (insufficient amount) of a carbon component from an amorphous silica-containing powder modified with aluminum, only amorphous products are formed during the annealing process (570 °C). An assumption has been made about the activating effect of the carbon-containing phase at the initial stages of crystallization processes. The considered kinetic features of the reaction of the reduction of crystalline silicon will make it possible to control the process and influence the qualitative composition of the resulting crystalline powders.

The obtained results regarding the increase in the degree of crystallinity of silicon–carbon structures during synthesis by the metal induction method will make a significant contribution to the understanding of the crystallization processes of silicon–carbon structures for various technical applications and the control of their degree of crystallinity. The use of polyethylhydrosiloxane liquid as an organosilicon raw material makes it possible to obtain both powdered crystalline silicon systems and film systems, due to its film-forming properties, as well as the presence of active hydrogen groups in the structure. The produc-

tion of film systems, including on flexible non-crystalline substrates, is possible to achieve by applying a thin layer of a suspension consisting of finely dispersed metal particles in a polyethylhydrosiloxane dispersion medium to the substrate and subsequently annealing. The content of evenly distributed, finely dispersed metal particles in a silica-containing matrix will make it possible to obtain polycrystalline silicon at low temperatures. This work is of great practical importance for the production of microelectronics and solar energy elements, as well as the production of silicon composites, chemical catalysts, and coatings. Further research should certainly be continued in the direction of reducing the crystallization temperature and obtaining film systems on flexible substrates.

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