

Mechanisms of Silicon Combustion in the pSi–O₂ and pSi–NaClO₄·H₂O Systems

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1 Introduction

The ability of porous silicon to support oxidative reactions leading to combustion and explosion was established about twenty years ago [1], but because of the high propagation velocities these physicochemical transformations (10^2 – 10^3 m/s), it is difficult to understand their mechanisms. Here are briefly described the combustion modes of the pSi–O₂ system in processes occurring at velocities of three orders of magnitude below (~ 1 m/s). The analysis of these processes and post combustion SEM-diagnostics of samples showed that porous silicon is, in fact, a block of densely packed elements of solid fuel. Such system, with supply of a energy pulse is transformed, at the expense of destructive mechanical deformations, to suspension with multiple increase of the surface and jumpwise increase of a mass rate of combustion. The propagation of the combustion process in the pSi–NaClO₄·H₂O system at different parameters of the porous layers structure and coefficients of stoichiometry is investigated. The phenomena of the jumps of the front of combustion of the sample were observed (formation of the "precursors"). It is indicated that the probable cause of their occurrence is the interaction of longitudinal acoustic waves caused by thermomechanical deformations of the pSi. In the absence of remote precursors, the combustion velocity reaches 1800 m/s.

2 Combustion of Silicon in the pSi–O₂ System

By virtue of the ability of porous silicon (pSi) to support oxidation reactions that lead to combustion and explosion, in [2] the processes of combustion of pSi layers at initial pressures of oxygen medium P up to 33 bar have been studied and the combustion conditions have been described.

Fig. 1 show post combustion cross-sectional SEM images of samples for different combustion conditions. In aerosol combustion a porous layer is destroyed almost completely, therefore to understand the mechanisms of aerosol formation and combustion we present the data of experiments conducted at small and medium pressures of oxygen (combustion conditions, porous layer thickness h , and porosity p are given in Fig. 1).

In the case of *smoldering* combustion, a porous layer retains the initial thickness h , though the SEM image structure resembles a cracked three- (a) or two-level (b) laying. In the latter case, an almost undestroyed $h/3$ -thick porous layer is located under two layers of elements. A minor degree of destruction is explained by the fact that it occurs mainly under the effect of secondary combustion fronts propagating across the samples having a substantially smaller velocity and heat release and not producing, in the porous layer, stresses capable of imparting to breakaway elements an impulse sufficient to eject them to a gaseous medium

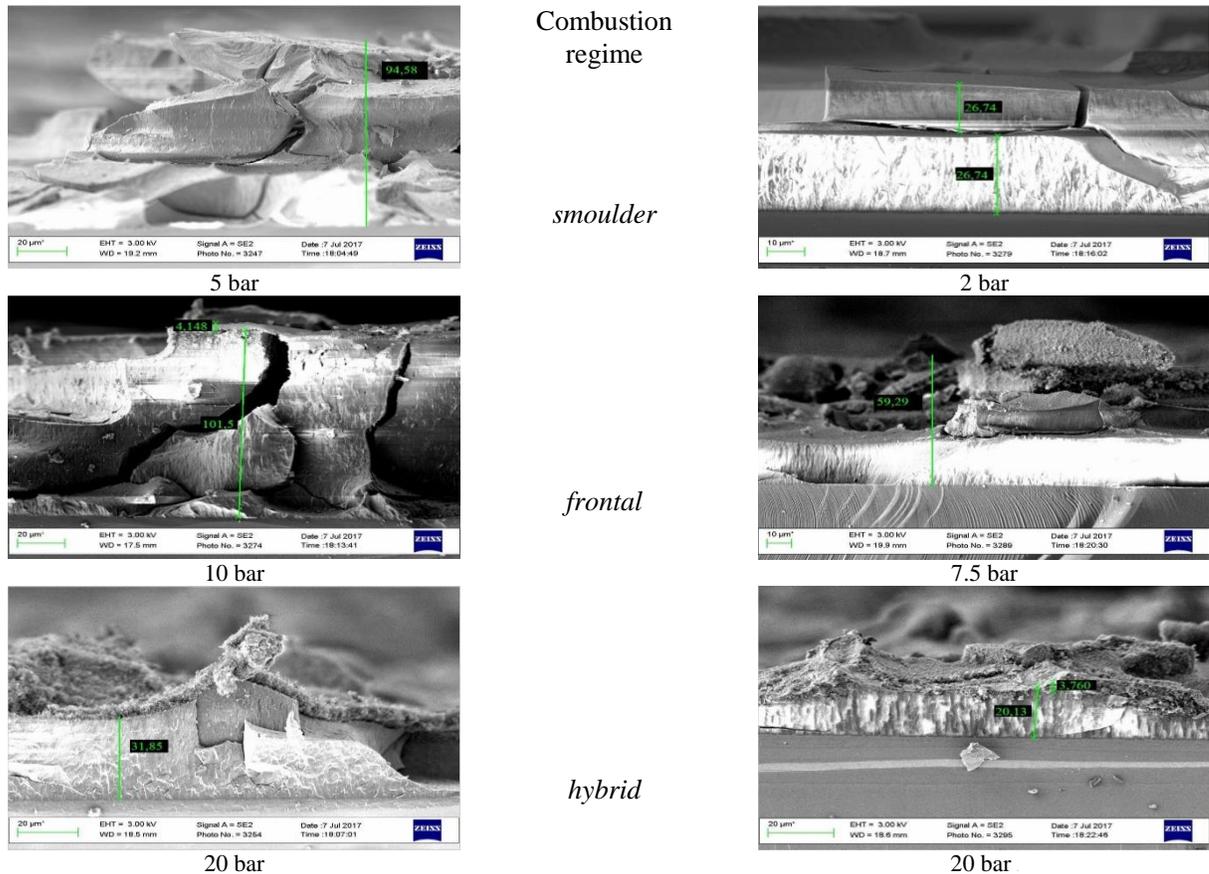


Figure 1. Post combustion cross-sectional SEM images of samples from wafers of Conditions: a) 6 ($h = 104 \mu\text{m}$, $p = 0.52$) and b) 7 ($h = 61 \mu\text{m}$, $p = 0.70$). The initial pressure of O₂ is given under the photos

In the case of *frontal* combustion, the character of its effect on the samples is different. For conditions 6, a layerwise position of elements is replaced by a system of almost vertical cracks over the entire depth of the porous layer, with the elements being interconnected with neighboring ones by irregularities separating them, which makes ejection of elements into the gaseous medium difficult. For conditions 7, losses in the porous layer are already noticeable. It is seen from the remaining elements that a layerwise structure of the type of two-level laying formed in the case of layer destruction was less pronounced than in the case of smoldering. The layer of undestroyed porous material was retained partially, though on some portions it is absent up to a single-crystal substrate.

In the *hybrid* regime, the surfaces of both samples are covered by a 4- μm -thick layer of particles of the products of aerosol combustion with nanosized (from 40 nm) spheres of silica. Spheres of micron fraction (to 7 μm) are seen. The degree of porous layer destruction in the sample of conditions 6 is rather high.

Judging by the shape of the surface, destruction was accompanied by the formation of a system of cracks typical of frontal combustion. However, in this case, thermomechanical stresses were much higher which resulted in high-volume ejection of particles to the gaseous medium. On some portions the porous layer is destroyed and almost entirely carried away, in the remaining portions there are crests with height of up to $h/3$. A similar picture is observed on the cut of the specimen of Conditions 7.

Let us describe the processes occurring on ignition and combustion of pSi in oxygen. It is known that about 20% of the Si atoms are located at the surface of the nanocrystals of porous layer [3]. When freshly prepared, the internal surface of porous Si is almost completely covered by hydrogen, which play the role of a buffer between Si atoms and molecular oxygen, thus preventing the oxidation reaction. Thus, to proceed with the fast oxidation of the internal Si surface further hydrogen atoms have to be removed by energy transfer to neighboring Si-H_x sites [4].

At the moment of spark discharge in a silicon wafer, including the porous layer, Joule heating occurs, which leads to a substantial overheating of the breakdown region. Since thermal conductivity of porous silicon is, as a rule, by an order of magnitude smaller than that of crystalline one [5], heat liberated in the porous layer does not practically pass to the substrate, the layer is heated-up strongly and thermal deformations and mechanical stresses occur in it, thus leading to the formation of cracks both in the layer and at the boundary with the single crystal.

In this case, according to [4], the strain energy of a mechanically continuous medium can be high enough to rupture Si-Si bonds and form free radicals, as well as remove hydrogen atoms from the surface due to their weaker vibronic coupling with the nanocrystal core. Besides, when cracking in the porous layer, new surfaces that are not covered with hydrogen and oxygen atoms appear and are ready for oxidation. Therefore, if there is a temperature in the region of violation of the original structure that is sufficient for the exothermic reaction of hydrogen oxidation, and later – for the interaction of oxygen molecules with unsaturated Si bonds, *in situ* combustion of particles begins, which on flaring up of individual particles passes to radial frontal one.

If heat release in frontal combustion is slight, combustion propagation can stop or, on reaching the sample boundaries, can proceed along the sample edges where the combustion surface is larger. In this case, due to increase in heat release, the warm up of the porous layer near the edges begins, which is accompanied by thermomechanical deformations and stresses (due also to the increase of the solid phase volume during oxidation) and cracking of the porous layer, i.e., the appearance of elements with the developed surface along the boundaries. This leads to the formation of combustion fronts directed from the edges of the sample to its axis.

If heat release in frontal combustion is large enough for a stationary process, i.e., it suffices to disturb the integrity of the porous layer and formation of elements with the developed surface, frontal combustion occurs over the entire width of the sample. In this case, the rate of combustion is virtually proportional to the pressure of oxygen, i.e., just the oxidizer pressure in the samples of the same regime is a limiting factor of the process.

The character of combustion changes qualitatively from the moment when, with increase of the oxygen pressure, the amount of released heat becomes sufficient for mass ejection of particles formed in porous layer cracking. Initially, the region of particle ejection lags behind the front of heterogeneous combustion. Additional warming-up of the porous layer is likely necessary (supposedly due to propagation of combustion to lower layers) in order to create stresses in the material, which are able to not only destroy some region of the porous layer but also provide an impulse for "catapulting" hot particles into the gaseous medium. As the pressure increases, warming-up of the porous layer becomes stronger and the zone of particle ejection approaches the front of heterogeneous combustion and catches up with it.

The onset of the aerosol phase of combustion is accompanied by a sharp increase of its mass rate. This is due to the fact that in transfer of burning particles of the porous layer into the gaseous medium the surface of combustion increases substantially, whereas heat removal decreases sharply. The temperature of particles increases rapidly thus causing drastic enhancement of the process.

It should be noted that with increase of P by dozens of percent the mass rate of combustion increases several orders of magnitude. In this case, the velocity of combustion propagation increases with pressure virtually linearly. Thus, aerosol combustion practically does not affect this process, which confirms its unoriginality relative to the frontal heterogeneous combustion. Porous silicon layer is properly a block of densely packed elements of solid fuel. Such system at pressures of oxygen more than 15 bar and with supply of a small energy pulse is transformed, at the expense of destructive mechanical deformations, to suspension with multiple increase of the surface and jumpwise increase of the mass rate of combustion. Such behavior is caused by ejection of these elements to the gaseous medium with subsequent aerosol combustion of these particles; here the amplitude of the jump is determined by the degree of dispersion of fuel particles and by the pressure of oxidizer.

3 Combustion of Silicon in the pSi–NaClO₄·H₂O System

solid-fuel systems. Samples of pSi with a length of up to 85 mm a The fact that even in oxygen the combustion of pSi is rather intense indicates its promise as a fuel for nd width 5 mm were used in the experiments. Based on recommendations and results of works [6, 7] sodium perchlorate was selected as solid-fuel oxidizer. Aqueous alcoholic solutions of sodium perchlorate were used for its introduction into the porous structure. A solution of 50 g of NaClO₄ in pre-mixed mixture of 27.8 g of H₂O and 22.2 g of C₂H₅OH was effective for introduction. Samples with a porous layer were immersed in narrow tubes filled with an oxidizing solution for various times (up to 40 min).

After removing the samples from the tubes, the liquid from their surfaces was removed using filter paper. Samples were weighed three times: immediately before immersion in the solution, after removing the surface liquid and immediately after drying (samples usually held in an oven at 40–43 °C for 30 minutes). The specified temperature regime of drying, due to the safety requirements of the process, leads to the fact that in the pores of silicon not anhydrous sodium perchlorate is formed (it crystallizes from an aqueous solution at a temperature above 52 °C [8]), but its monohydrate. In this case, the reaction of silicon oxidation is described by the following equation:



with maximum energy efficiency of mixture equal to 9.6 kJ/g [6].

The experiments were carried out on the setup described in [2]. The sample was placed in a chute under a protecting polycarbonate cover without use of a steel working chamber. Table 1 lists a number of parameters for wafers with pSi layer.

Figure 2 shows the results on combustion propagation through the samples. The values of h and p , specific surface S_{spec} , and a mean width of pores b are indicated on the graphs. The positions of the main fronts are denoted by symbols of different colors which correspond to the number of the experiment. The vertical lines of the same color show the regions of combustion before the main front (Fig. 2a-c). Figure 2d presents the regions where combustion takes place after passing the main front; here pink vertical lines correspond to the experiments denoted by red symbols and blue vertical lines to the experiments denoted by dark blue symbols. The following parameters are given for specific experiments the numbers of which here and in what follows are denoted by the bold italic font: the coefficient of stoichiometry φ calculated based on the actual amount of monohydrate of sodium perchlorate $m_{\text{oxid ac}}$ contained in the pores

($0.5 \leq m_{\text{oxid ac}} / m_{\text{oxid}} \leq 1$); heat of combustion Q related to the total mass of fuel (at $\phi = 1$) + ballast (excess pSi) + water, nonevaporated from the solution, per the same surface unit [J/cm^2] and combustion temperature T [K].

Table 1: Characteristics of porous layers and estimates of maximum values of the mass and power parameters of pSi–NaClO₄·H₂O systems for KDB-12 wafer

wafer	h , μm	p	S_{spec} , m^2/g	b , nm	m_{pSi}/s , mg/cm^2	$m_{\text{oxid St}}/s$, mg/cm^2	m_{sol}/s , mg/cm^2	m_{oxid}/s , mg/cm^2	ϕ_{min}	q/s , J/cm^2
14	58	0.73	384	6.1	3.7	7.3	6.0	3.4	2.1	50
20	59	0.71	437	4.0	4.0	8.0	6.0	3.4	2.4	49
17	91	0.64	667	4.0	7.6	15.3	8.2	4.7	3.3	67
18	105	0.68	472	5.1	7.8	15.7	10.1	5.8	2.7	83
29	128	0.50	347	5.1	14.9	29.8	9.0	5.2	5.8	75

Note: S_{spec} is the specific surface of pores; m_{pSi}/s is the mass of the porous skeleton per unit of the porous layer surface s submerged in the oxidizer solution; m_{oxid}/s and m_{sol}/s are the maximum masses of NaClO₄·H₂O oxidizer and of its solution, respectively, in the porous layer per unit surface s ($m_{\text{oxid}}/m_{\text{sol}} = 0.574$ for the described oxidizer solution); the subscript St denotes stoichiometric combustion ($\phi = 1$) in the porous layer; q/s is the maximum energy capable of liberating in combustion of porous layer particles per unit surface s , proceeding from the quantity m_{oxid}/s .

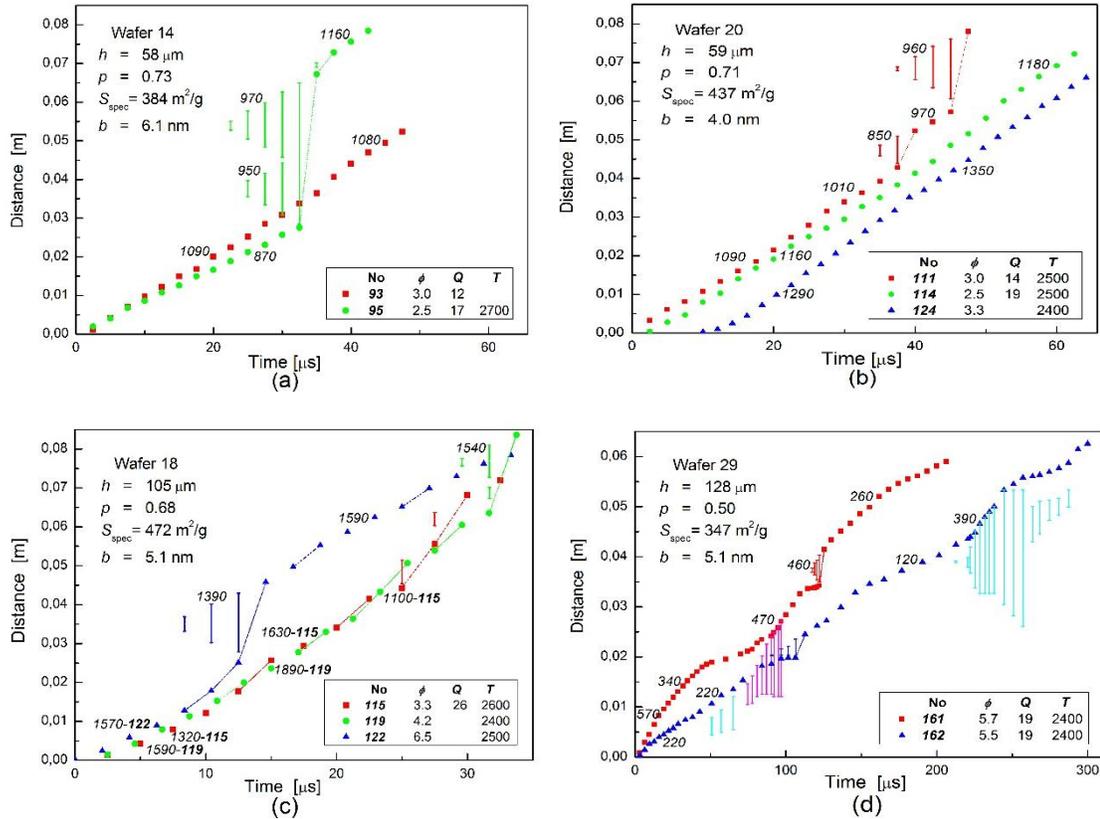


Figure 2. Special features of combustion of Si–NaClO₄·H₂O systems with different characteristics of porous layers formed in conditions: a, b) 4; c) 6; d) 8

Figure 3 gives the frames of videorecording illustrating special features of the studied processes shown in Fig. 2. The frontal propagation of combustion with points of self-ignition originating before the primary front – precursors – (experiment **95**) is presented in Fig. 3a. Figure 3b shows the propagation of the secondary process in the rear of the degenerating primary front (experiment **161**).

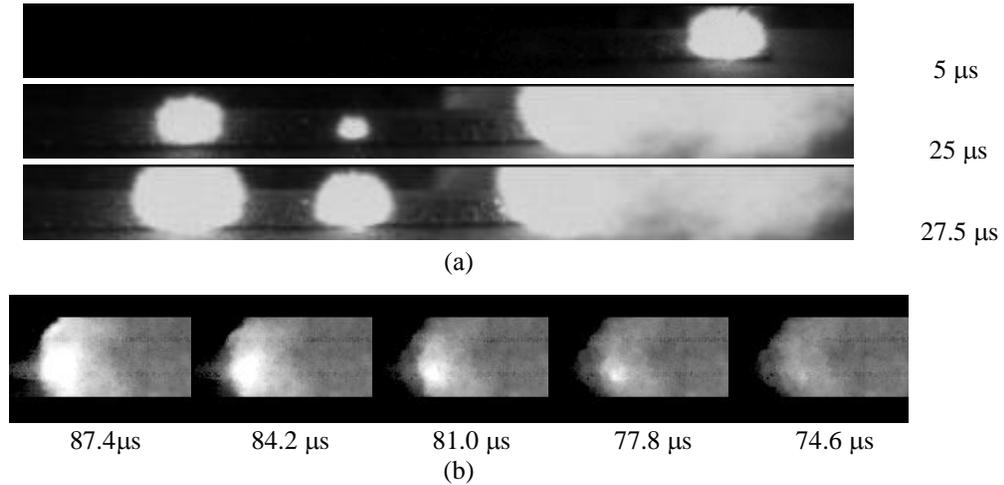


Figure 3. Propagation of combustion along the samples (from right to left) in the experiments: a) **95** (wafer 14, DC FASTCAM SA-X2, 400,000 fps), b) **161** (wafer 29, DC FASTCAM SA-Z, 630,000 fps). The time of the moment of ignition is given near the photos

Table 2 presents the results on combustion of samples cut from wafer 17 with the largest specific surface of combustion (the characteristics of the porous layer see Table 1). In the given series, the maximum velocity of combustion in the absence of remote precursors amounts to 1780–1810 m/s and is obtained for samples with $\phi = 4.1$ –4.3.

Table 2: Characteristics of combustion of samples made of wafer 17

Exp. No	98	100	102	104	106	107	109	110
ϕ	4.1		3.6	3.9	4.3	4.1	4.6	4.7
L , mm	48	47	58	56	68	65	72	71
t_{comb} , μs	33	34	36	35	46	35	39	50
$V_{\text{comb } 0}$, m/s	1100	1240	1280	1120	1250	1250	1470	1410
$V_{\text{comb end}}$, m/s	1780	1600	1560	1530	1810	1700	1420	1460
Q , J/cm^2	24		27	24	26	29	19	19
T , K	2500	2400	2500	2500	2300	2400	2300	2300

Note: L is the length (from the point of ignition) of the porous layer with the oxidizer being introduced; t_{comb} is the time from the moment of the start of front glowing to reaching the end of the porous layer with the oxidizer; $V_{\text{comb } 0}$ and $V_{\text{comb end}}$ are the initial and final velocities of combustion, respectively.

4 Discussion

An analysis of the results presented indicates that combustion of the pSi–NaClO₄·H₂O system takes place by, at least, two orders of magnitude faster than that of the pSi–O₂ system. Stationary combustion at a high velocity is typical of porous layers of small thickness (Fig. 2a, 2b). This occurs probably due to fragmental destruction of the porous skeleton directly before the front as in the case of above-described

aerosol combustion in oxygen. At weaker energy release thermomechanical loads on the porous layer lead to the propagation of stresses through the system that increase with time. Probably the concentration of these stresses related, for example, to the reflection of the longitudinal acoustic wave from the edge of the crystalline substrate can lead to self-ignition at a distance of several widths of sample from the main front (see the left combustion zone at a distance of 36 mm from the main front in Fig. 3a). In turn, superposition of two longitudinal waves – one from the main front and another from the front of the flared-up combustion zone approaching it at a slightly higher velocity – is likely the reason of the origination of a new point of ignition (see the central zone of combustion in Fig. 3a) in the loop region of counter-propagating disturbances. The appearance of new points of ignition before the combustion front was first observed in [9]. Churaman et al. [9] explained "supersonic" velocities of combustion propagation (in both cases exceeding 5000 m/s) just by the jump of the front by 2–3 cm at a frequency of videorecording 250,000 fps. In our case, the appearance of remote points of ignition before the front at weak energy release is caused by the sample geometry, when in the phase of compression the longitudinal wave reflects from the single-crystal wall with high acoustic resistance the intensity of the wave increases.

The character of combustion propagation changes with increase in the porous layer thickness (Fig. 2c). Now, the points of ignition before the front originate practically in each experiment. In most cases, precursors near the main front are localized. It is likely that at a high initial rate of energy release (which is caused by a large specific surface of the skeleton of the system) the destruction of the skeleton before the front with the formation of the cloud of fuel particles intensifies the combustion process so that in the undestroyed part of the skeleton near the front there stochastically originate pulse mechanical stresses that are capable of causing self-ignition of this part. At smaller energy release the development of remote points of self-ignition is most likely.

The observed stable increase of the velocity of combustion for samples from wafer 17 is explained, probably, by a large surface of pores and also by a high heat of combustion Q . To our mind, due to intense destruction of the porous skeleton before the front and due to the ejection of the cloud of fuel fragments, these factors provide practically regular pulse stresses that cause the appearance of precursors in the vicinity of the main front.

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