# Investigation of self-sustained burning of the *n*-type porous silicon-based composites with barium perchlorate

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The exothermic chemical conversion of energetic composites based on porous silicon, prepared by electrochemical etching of a single-crystal *n*-type silicon wafer, and barium perchlorate was studied using high-speed video filming. It is found that the mixtures under study can show either local chemical conversion, which occurs in and around the initiation spot, and the self-sustained propagation of the exothermic reaction over the material volume. After subjection of the energetic composites to compression in a closed container, it became possible to determine the upper estimate of the chemical reaction front propagation speed, equal to 89 m/s, and classify the process as burning.

**Keywords:** porous silicon, energetic composite, barium perchlorate, exothermic reaction, self-sustained burning, burning rate.

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## 1. Introduction

Current trends in the use of porous silicon (PS) in creation of energetic materials involve separating the porous layer from the parent substrate, to which PS remains attached after the substrate has been chemically or electrochemically treated. In particular, this step makes it possible to create pasty or encapsulated energetic composites (ECs) [1], as well as prepare crystalline quantum dots from a powdered PS layer, which can independently serve as a fuel [2]. Over the last five years the ECs based on fragmented PS [3–5] have been actively developed (combustion of PS with sodium perchlorate monohydrate in various atmospheres is currently being studied): the dynamics and regimes of this process have been studied, ignition times and pressure pulses in the atmosphere at a fixed distance from the ignition source have been found, and the burning rates of such EC and their dependence on the coefficient of stoichiometry and humidity of sodium perchlorate monohydrate have been calculated. The characteristic combustion rates of EC based on fragmented PS with the selected oxidizer in an air environment are in the range of 1000−2500 m/s [3,4].

The majority of studies on physical and chemical properties of PS-based ECs were carried out using single-crystal silicon wafers *p*-type conductivity (see [6] and the above-mentioned works [2–4]). This result is explained by the specificity of electrochemical etching of silicon wafers of *n*-type, which consists in the need for additional intense illumination. The authors of paper [7] conducted a study of the influence of conductivity type and specific resistance of silicon wafers on the microstructure of PS obtained by electrochemical etching and the burning rate of EC. For high- and low-alloy Si plates with a resistivity of 0.001−0.005 and 2−5 Ohm · cm, the combustion rates of EC with sodium perchlorate were 5.4−11.0 and 314−372 m/s.y The increase in the combustion rate by 2 orders of magnitude was explained by the formation of a structure of disordered microcracks in PS, through which convective heat transfer occured.

This study provides an insight on the process of combustion of a PS-based EC, prepared from single-crystal silicon wafers *n*-type conductivity, and barium perchlorate. Information on the use of this perchlorate salt as an oxidizing agent is very limited. The fabricated EC was distributed among extended containers: open and closed, which made it possible to compare the nature of the exothermic reaction in conditions of unlimited and limited volumes.

## 2. Experiment

### 2.1. Preparation of PS

To obtain the porous silicon (PS), a single-crystal wafer of *n*-type silicon was used, characterized by the following parameters: Czochralski growth method, arsenic dopant, diameter of 150 mm, thickness of 640−660 $\mu$m, crystallographic orientation (111), specific resistance

**Table 1.** Geometry, shape and material of containers for EC

| Name of sample | Shape, material container | Internal length, mm | Internal width, mm | Thickness of wall, mm |
|---|---|---|---|---|
| AP-1 | Parallelepiped, aluminum | 49 | 4 | 1 |
| CT-1 | Cylinder, food-grade silicone | 60 | 2 | 2 |
| CT-2 | Cylinder, food-grade silicone | 60 | 2 | 2 |

**Table 2.** The masses of EC in the studied samples, as well as the values of the mass ratio (F:O) and bulk density characterizing them before and after compaction in the container

| Name of sample | Mass of EC, mg | Mass ratio (F:O) | Initial bulk density, g/cm$^3$ | Bulk density after compaction, g/cm$^3$ |
|---|---|---|---|---|
| AP-1 | 76.3 | 0.55 | 0.68 | – |
| CT-1 | 73.0 | 0.58 | 0.42 | 0.63 |
| CT-2 | 72.4 | 0.58 | 0.42 | 0.61 |

2.64 mOhm · cm. The selected wafer was subjected to double-sided electrochemical etching in a mixture of ethanol and 46–49 % aqueous hydrofluoric acid (special purity grade, grade 27-5), taken in a volume ratio of 1:1, for 60 min. The anode current density was 69 mA/cm$^2$. The separation of the porous layer from the substrate was done manually.

The textural properties of the resulting etching product were determined by low-temperature nitrogen adsorption at 77 K, performed using analyzer ASAP 2020 (Micromeritics, USA). The specific surface area and pore volume were determined using Barrett-Joyner-Halenda method. The average pore size was estimated as the ratio of the specific pore volume $V_{\text{pore}}$ multiplied by 4 and the specific pore surface area $S_{\text{pore}}$.

The specific volume of pores $V_{\text{pore}}$ with sizes from 2 to 500 nm, calculated from the nitrogen desorption isotherm, was used to find the degree of porosity $P$ of the prepared PS according to the formula

$$P = \frac{V_{\text{pore}}}{V_{\text{pore}} + 1/\rho_{\text{Si}}} 100\,\%, \qquad (1)$$

where $V_{\text{pore}} = 1.013$ cm$^3$/g, silicon density $\rho_{\text{Si}} = 2.33$ g/cm$^3$. Then, the value $P \approx 70\,\%$. The average pore size, also calculated from the desorption branch of the isotherm, made 7.24 nm and allowed the prepared PS to be considered mesoporous according to the classification introduced by the International Union of Pure and Applied Chemistry (IUPAC).

## 2.2. Samples preparation

To prepare the EC, the PS layers, crushed in a mortar to a powdery state, were mixed with a solution of barium perchlorate in ethanol. The remaining solvent was removed in the dry-box ShS-10-02 SPU (JSC „Smolenskoye SKTB SPU“, Russia) operating at 45 °C. The drying stage was followed by sieving the finished EC through a nylon mesh with an approximate mesh size of 0.25 mm. In order to ensure safety, the mass of EC required to perform the experiment was divided into several portions, prepared alternately and characterized by an individual value of the mass ratio (fuel:oxidizer) (hereinafter abbreviated as (F:O)). In this way, more than 500 mg of EC were obtained; for its individual portions, the mass ratio (F:O) ranged from 0.55 to 0.59.

The EC containers were prepared on the basis of an aluminum U-shaped profile, as well as tubes made of food grade silicone. The AP-1 open-top container was made from an aluminum profile by sealing its ends. Two pieces of tube of equal length were given the names CT-1 and CT-2. Construction nails with a diameter of 2.5 mm and pre-cut tips were used as plugs. The EC containers geometry data are given in Table 1 below. It should be emphasized that the names of the samples coincide with the selected names of the containers.

Table 2 gives the masses of EC in AP-1, CT-1 and CT-2 containers. Table 2 also contains the calculated values of the mass ratio (F:O) and bulk density of EC before and after compaction in containers. It should be noted that the compaction of EC in the sample AP-1 was not performed.

## 2.3. Initiation and registration of chemical transformation of EC

During the experiment on initiating and recording the chemical transformation (CT) of EC, the prepared samples were fixed in the stationary holders. The AP-1 sample

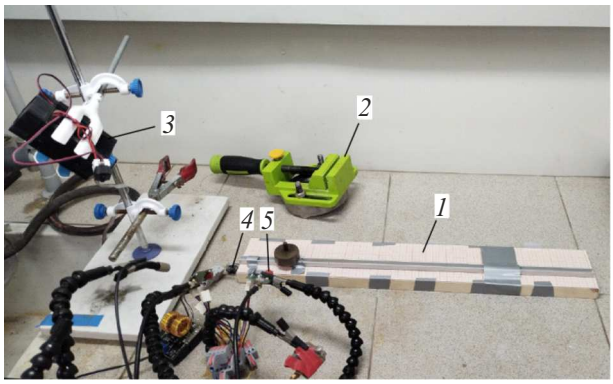


**Figure 1.** Photo of the experimental setup for initiating and recording the chemical transformation of the PS EC. Setup components: *1* — holder for samples CT-1 and CT-2, *2* — quick-release vice KITOKI BG-625702, *3* — laser diode GH04C05B9G in housing, *4* — copper induction coil used for thermal initiation of chemical transformation, *5* — photodetector FPU100-3. Near the left edge of the aluminum U-shaped profile, fixed on the stand, there is a punch, which can also be seen in Figure 4 and 5.

was clamped in a quick-release vice KITOKI BG-625702, which was attached to a massive metal disk-shaped base. Samples CT-1 and CT-2 were placed inside an aluminum U-shaped profile with an internal width of 6 mm, which was attached to the stand by a reinforced adhesive tape. The stand was made from a wooden board with dimensions $20 \times 80 \times 500$ mm (height × width × length), covered with 1 mm thick organic glass over coordinate marking paper.

The chemical transformation of AP-1 sample was carried out by irradiation of the EC surface with a continuous output of laser diode GH04C05B9G with a wavelength of 440 nm (SHARP, Japan). To initiate samples CT-1 and CT-2, a thermal method was used with a copper induction coil, inside which a tube plug was placed to close the end or to seal the EC. Regardless of the method of chemical transformation initiation, the part of the EC located on the extreme periphery of the container was exposed. The experiment was conducted in a workroom atmosphere; relative humidity was not intentionally controlled. The photo of the experimental setup is shown in Figure 1.

Chemical transformation was registered using a high-speed camera Evercam 1000-8-C (LLC SRC „Promyshlennaya optika“, Russia). The high-speed camera settings were controlled using VSCAM-CONTROL module of Platform VSCAM 1.0 software. The following parameters were selected for the experiment: image resolution — $1280 \times 304$ pixels, brightness — 76, contrast — 192, frame rate — 2694 fps (Frames Per Second), exposure time — 1/2700 s, intensification — 1, recording mode — cyclic, the preset number of frames after the „stop“ command was 300. The value of the last parameter was determined so that the number of frames stored in the high-speed camera's memory before and after executing the „stop“ command would be the same. This choice ensured that events were registered before the trigger was activated. The „stop“ command was supplied to the control contacts of the high-speed camera from TTL-output (Transistor-Transistor Logic) of the digital oscilloscope DS2302A (RIGOL, China) upon activation of the trigger when the signal rose to — 1.53 V in channel № 1 to which the photodetector FPU100-3 was connected (LLC „ACIA Polytekhnik“, Russia). The images characterizing the chemical transformation of EC for CT-1 and CT-2 samples had a bit depth of 10 and 8 different values. The video fragment containing the CT EC event was saved as still frames in TIFF format. Also, using VSCAM-CONTROL module, it was possible to add a configurable text label to output files.

## 3. Results and discussion

### 3.1. Sample AP-1

The response of AP-1 to the initiation is appropriate to compare with the similar behavior of the test samples T-1 and T-2, prepared to test the reactivity of the used EC. The containers T-1 and T-2 also had the shape of a parallelepiped with an open top, but differed from AP-1 container in dimensions: the internal length of each container was 56 mm, internal width — 2 mm, internal height — 4 mm. It should be noted that the internal height of the container AP-1 was equal to 5 mm. Samples T-1 and T-2 contained 52.3 and 96.3 mg of EC with a mass ratio (F : O) of 0.56 and 0.55, respectively; bulk density was not calculated.

As can be seen in Figure 2, in contrast to the test samples T-1 and T-2, sample AP-1 demonstrated self-sustaining propagation of the exothermic reaction from the left end of the container, near which the laser radiation was focused, to the right end. Samples T-1 and T-2 showed the same ignition pattern: local chemical transformation of the EC occurring in the area of the initiation.

After the first unsuccessful attempt to initiate the chemical transformation the samples T-1 and T-2 were tested again. This explains the presence of a second or increased volume air gap between the EC parts in containers. The most likely cause of failure during initiation of the chemical transformation of EC in samples T-1 and T-2 is the different bulk density of composites, which in turn is associated with the critical diameter of combustion; the nature of this relationship depends on the nature of the explosive [8]. As is known, when the diameter of the EC in the container is less than the critical value, heat loss to the environment exceeds the amount of energy released during the exothermic reaction; extinction is observed. The study of the discovered effect (stop/spread of combustion in EC) will be continued using an expanded set of aluminum containers with more varied values of internal width and height, as well as containers for conical EC [9].

### 3.2. Samples CT-1 and CT-2

Figure 3 shows the containers CT-1 and CT-2, as well as AP-1 after successful initiation of chemical transformation

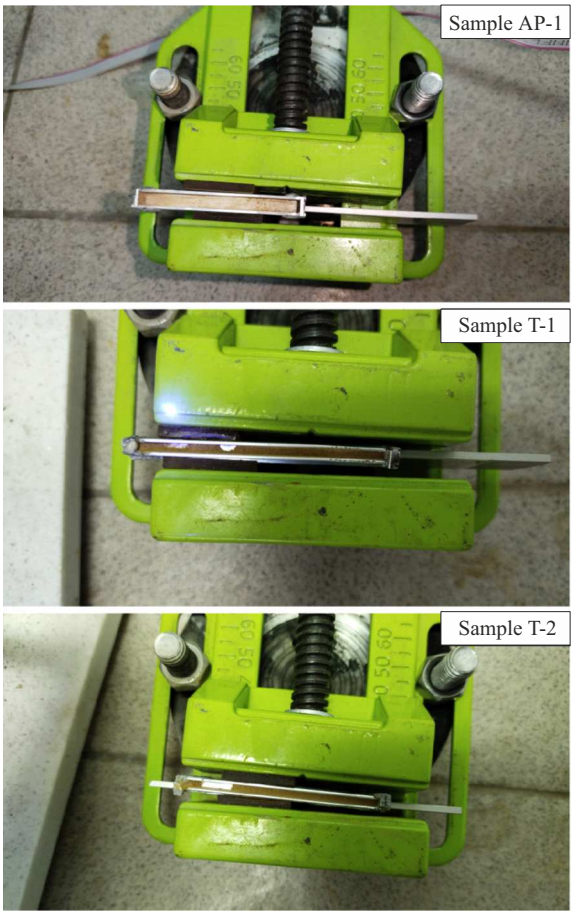


**Figure 2.** Samples AP-1, T-1 and T-2, fixed in the quick-release vice KITOKI BG-625702, after exposure to initiating laser radiation.

of EC. The propagation of chemical transformation of EC in the tube samples was observed only after compaction of EC, which was expressed in an increase in bulk density from 0.42 to 0.63 g/cm$^3$ for sample CT-1 and from 0.42 to 0.61 g/sm$^3$ for sample CT-2. Compaction was carried out manually using a 2 mm diameter construction nail with the tip removed. The length of the composite in the container was determined by the distance between two plug-nails: for sample CT-1 it was 55 and 37 mm before and after compaction, respectively, in sample CT-2 the EC was compacted from 55 to 38 mm. As an additional characteristic, the degree of porosity of the EC may also be indicated, equal to the ratio of the voids volume to the material volume: for both samples, this parameter was $\sim 82\,\%$ before compaction and $\sim 73-74\,\%$ after compaction.

Figure 4 shows the stop frames characterizing the proceeding chemical transformation (CT) for the sample CT-1. In the stop frame *1*, a flash is visible, the nature of which is mainly associated with CT of EC and partly with the heating of the sealing plug. The position of the reaction front is located in the area of the strip of reinforced adhesive tape used to secure the sample in the holder and can therefore only be determined approximately. In the stop frame *2* the reaction front of the CT, determined by the edge of the light flash relative to the beginning of

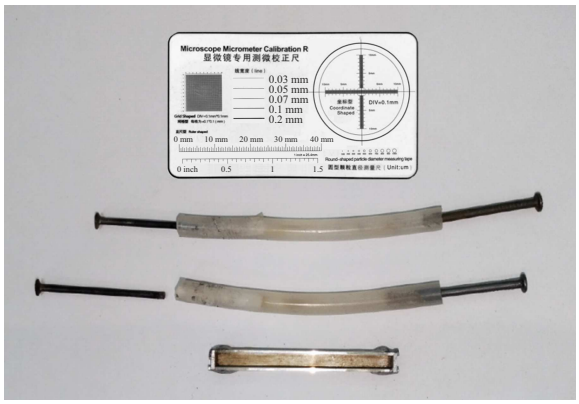


**Figure 3.** Containers of CT-1 (top) and CT-2 (middle), as well as AP-1 (bottom) after completion of the experiment on initiation and registration of the chemical transformation of EC based on the porous silicon and barium perchlorate. Thermal initiation of samples CT-1 and CT-2 was carried out by heating the left, i. e. sealing, plug of smaller diameter, as evidenced by the whitening and opacity of the material. As a result of the experiment, the integrity of the container CT-1 was damaged.

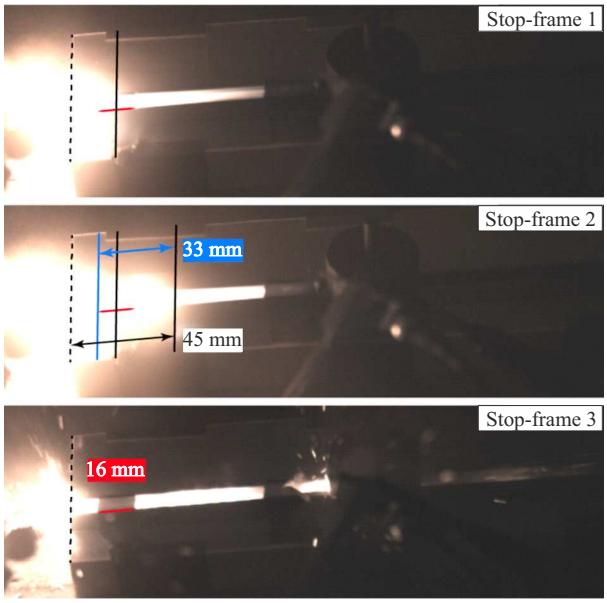


**Figure 4.** Proceeding chemical transformation for CT-1 sample of the EC. The time interval between stop frames *1* and *2* is 370 $\mu$s, stop frames *1* and *3* are separated by 5.55 ms. The black dotted line shows the edge of the wooden board, 80 cm long, corresponding to the beginning of the holder. Solid black lines mark the position of the exothermic reaction front, determined based on stop frames. The red line shows the width of the 16 mm strip of reinforced tape used to hold the sample inside the aluminum U-shaped profile. The blue solid line shows the left edge of the mentioned strip of tape. The black (blue) double arrow is used to indicate the distance from the edge of the holder (the left edge of the tape strip) to the position of the reaction front on the stop frame *2*.

the holder, already goes beyond the EC position. This conclusion is made based on the fact that after compaction of the EC, its length in the container was 3.7 cm. Note that before the initiation of CT, the end of the sealing plug, which was in contact with the EC, was aligned with the beginning of the holder. Thus, an upper estimate of the transformation propagation rate in EC for CT-1 sample can be given by dividing the distance from the left edge of the adhesive tape strip to the reaction front position on the stop frame *2* equal to $\sim 33$ mm, by the exposure time of the high-speed camera. Accordingly, the propagation rate of the self-sustaining exothermic reaction for sample CT-1 does not exceed 89 m/s, which allows us to classify the registered process as combustion. A layer-by-layer combustion is known to be the first stage of transition from combustion to explosion in porous energetic materials [8,10]. The pressure differential between the combustion source and adjacent layers of material, which occurs when the outflow of gaseous combustion products is limited by the shell walls, causes the hot combustion products to filter through the pores deep into the non-reacting substance. Ignition of the inner surface of pores by gaseous combustion products corresponds to the transition to convective combustion. At this stage, the rate of combustion propagation through the material increases sharply.

It should also be taken into account that as a result of sifting the EC, only maximum particle size of the material, equal to 0.25 mm, was fixed. At the same time, for mechanically activated EC based on silicon particles and solid-state inorganic oxidizers, it has been established that the rate of reaction propagation depends on the size of the silicon particles: the transition from micro- to nanoparticles of Si leads to higher combustion rate of the energetic material by more than 2 orders of magnitude [11]. The dependence of the reaction front propagation rate on the porosity degree and specific surface area of the PS layer is also well known for EC, for which the contact of the PS with the parent substrate is saved after etching [12,13]. The study of the EC particle sizes impact on the rate of propagation of the chemical transformation front is an individual scientific task.

As can be seen in Figure 5, already in the first stop frame characterizing the CT of the EC for sample CT-2, the CT reaction front is located almost at the edge of the composite, compacted to a length of 38 mm. Considering the previously made estimate of EC reaction propagation rate, it can be stated that the following stop frame, recorded with a time difference of 370 $\mu$s, is unsuitable for determining the propagation rate of the chemical reaction front in EC.

The fundamental possibility of creating cylindrical samples for which a self-sustaining propagation of the chemical transformation of EC along the container length is observed allows us to positively evaluate the prospects for preparing longer samples of similar geometry. The authors conducted preliminary experiments to produce such samples using containers 10 cm long and of 2 mm internal diameter made of food-grade silicone, as well as containers 25 cm long and

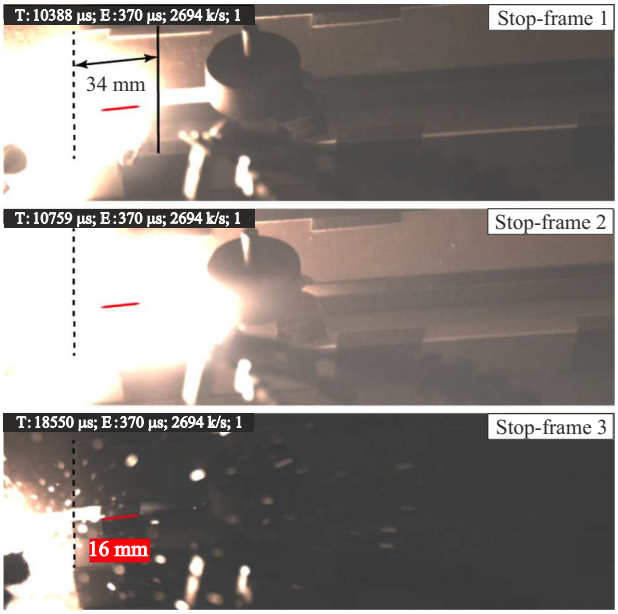


**Figure 5.** Chemical transformation of EC for CT-2 sample. The designations and choice of colours are similar to those introduced in Figure 4.

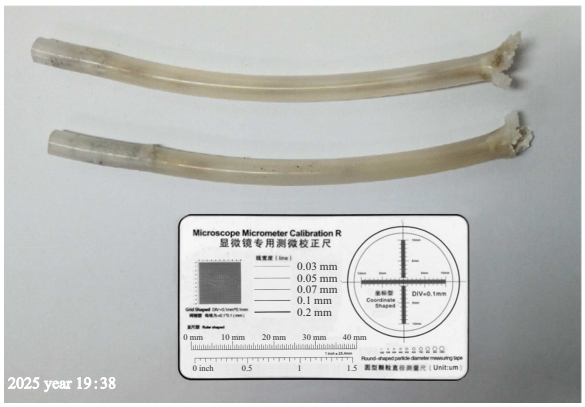


**Figure 6.** Elongated test samples demonstrating feasibility of self-sustaining propagation of chemical transformation of EC over distances greater than 5 cm.

of 1 mm internal diameter made of stainless steel. In both cases, ECs were prepared with a mass ratio (F : O) close to that which characterizes the energetic material used in this study. The EC, also prepared on the basis of single-crystal silicon wafers with *n*-type conductivity, was placed into silicone containers; photos of the containers after chemical transformation are shown in Figure 6. Details of the study conducted using steel containers will be reported separately.

## 4. Conclusion

In this study, an exothermic reaction in a PS EC obtained by electrochemical etching of a single-crystal *n*-type silicon

wafer and barium perchlorate was investigated. A self-sustained combustion process propagation was observed both in case of using an open container for EC and when sealing the ends of this container. Using high-speed video recording, an upper estimate of the CT front propagation rate for EC composites in a confined space was determined and found 89 m/s. Further research will be aimed at determining the critical combustion diameter of such ECs and establishing the dependence of CT rate on the particle size distribution of the energetic material.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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