

## Highly explosive nanosilicon-based composite materials

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We present a highly explosive binary system based on porous silicon layers with their pores filled with solid oxidizers. The porous layers are produced by a standard electrochemical etching process and exhibit properties that are different from other energetic materials. Its production is completely compatible with the standard silicon technology and full bulk silicon wafers can be processed and therefore a large number of explosive elements can be produced simultaneously. The application-relevant parameters: the efficiency and the long-term stability of various porous silicon/oxidizer systems have been studied in details. Structural properties of porous silicon, its surface termination, the atomic ratio of silicon to oxygen and the chosen oxidizers were optimized to achieve the highest efficiency of the explosive reaction. This explosive system reveals various possible applications in different industrial fields, e.g. as a novel, very fast airbag igniter.

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### 1 Introduction

Silicon (Si) is a common material for high-tech industry and is mainly employed for applications in electronics. Additionally different types of MEMS devices (micro electro mechanical systems) based on Si have been developed recently. Since industrial facilities for mass-production of Si-based systems have already been established, new application technologies should be compatible with these production lines.

Explosions belong to the most impressive chemical reactions. Their efficiency depends on the energy yield and the rate of the chemical reaction as well as on the spatial configuration of the interacting species [1]. There is a variety of mechanisms responsible for the ignition and development of explosive reactions. In solid explosives like trinitrotoluene (TNT) the interacting atoms are confined in one molecule resulting in an enormous efficiency of the explosion when the detonation shock wave activates all interacting reaction partners almost instantaneously. Bulk silicon was never considered as a basis for energy carriers or explosive materials. Contrary to carbon its reaction product is solid and its oxidation rate is limited by the relatively slow diffusion of oxygen through the silicon dioxide layer at the Si surface [2]. However, the potential yield of energy of the exothermic reaction of silicon and oxygen is higher than that of the most common carbon-based explosives.

Porous silicon (PSi) has remarkable morphological properties which result in the enormous increase of the oxidation reaction rates which are crucial for explosive reactions. PSi layers are assembled from nanometer-sized nanocrystals and have a large internal surface area (up to  $10^3 \text{ m}^2/\text{cm}^3$ ) [3]. Therefore the spacing between silicon and oxidizing atoms is at the atomic scale. For as-prepared samples this internal surface is almost completely covered with hydrogen and the concentration of hydrogen atoms can be as high as  $10^{22} \text{ cm}^{-3}$ . Other properties of PSi, such as porosity and pore sizes, can be easily adjusted to

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achieve a stoichiometric mixture of interacting atoms. The surface can be long-time stabilized against natural oxidation by annealing PSi in oxygen ambient. Furthermore, PSi has a sponge-like structure which builds up the skeleton for the oxidizer. Therefore it serves simultaneously as a reactive and a packaging material. Ordinary pyrotechnical materials are usually mixed powders pressed together to form pellets. In this case mixtures of fuel and oxidizer on a molecular scale will never be achieved. This results in a slower reaction rate than for PSi/oxidizer systems.

PSi is known as reactive material since 1992 when the fast combustion reaction of PSi immersed in nitric acid has been discovered [4]. According to our measurements the timescale of this reaction is in the millisecond range. Later explosive oxidation of PSi layers in liquid oxygen at cryogenic temperatures has been found to be roughly 1000 times faster [5] because before the explosion the pores were completely filled with liquid oxygen. Afterwards, a composite solid state system based on PSi layers having pores filled with gadolinium nitrate operating at room temperature has been demonstrated [6].

In this paper we review our efforts towards developing of a new type of energetic materials based on PSi layers. Our systems combine PSi and several oxidizers. They are mechanically stable, applicable at room temperature, ignitable in a common and controllable way, and long-term stable. They show a reproducible and predictable reaction rate and energy output. Furthermore, it is compatible with standard mass-production technologies of silicon industry. The first concrete industrial application is content of a research project in collaboration with industrial partners at the moment. First tests have demonstrated that  $2 \times 2 \text{ mm}^2$  PSi-based explosive elements can initiate booster charge of a standard airbag. We believe that these energetic materials can be employed in airbag ignition systems.

## 2 Sample processing and their properties

### 2.1 Experimental details

PSi is formed by electrochemical etching of crystalline bulk silicon wafers in a mixture of hydrofluoric acid (HF) and ethanol [3]. For industrial applications two parameters are crucial: the thickness of the layers and their growing rate. To achieve the highest explosive power on the smallest area the layer has

**Table 1** Preparation conditions and resulting parameters of the PSi layers.

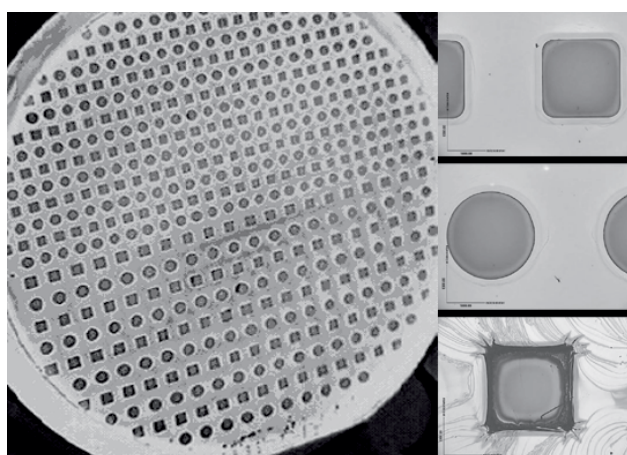
type of wafer (doping level)	current density (mA/cm <sup>2</sup> )	etching time (min)	thickness (μm)	growth velocity (μm/min)	porosity (ρ in %)
P <sup>++</sup> 1–15 mΩ cm	43.5	30	70	2.32	59.1
	60.9	30	90	2.98	60.3
	87.0	30	112	3.73	71.0
	43.5	60	138	2.30	59.1
	60.9	60	170	2.82	65.8
	87.0	60	193	3.22	cracked
P <sup>+</sup> 10–30 mΩ cm	43.5	30	72	2.40	54.9
	60.9	30	94	3.13	58.8
	87.0	30	120	4.00	66.7
	43.5	60	132	2.20	59.0
	60.9	60	160	2.65	67.4
	87.0	60	–	–	cracked
P <sup>–</sup> 1–1000 mΩ cm	20.0	40	57	1.43	49.3
	30.0	30	63	2.09	49.6
	43.5	20	58	2.90	50.3
	20.0	80	116	1.45	50.1
	30.0	60	125	2.09	51.0
	43.5	40	105	2.62	59.0

to be as thick as possible and the porosity has to be adjusted to achieve a stoichiometric mixture with oxidizing molecules. For ordinary electrochemical etching procedure the current density is kept constant. Different current densities, doping levels of the bulk silicon wafers and etching time result in porous layers having specific thickness and porosity (see Table 1 for details). We found that under constant etching current conditions PSi layers become mechanically unstable after a certain etching time which is shorter for higher current densities. The maximal depth of mechanically most stable  $p^{++}$  PSi layers which can be achieved is about 200  $\mu\text{m}$ .

To produce layers having larger thicknesses we developed a “gradient-break-etching” technique. At the beginning we start with higher current density (up to 120  $\text{mA}/\text{cm}^2$ ) to have larger pore diameters. This allows the hydrogen gas generated during the etching to escape from the pores more easily in later etching stages. In time the current density was gradually decreased because the etching solution needs longer time to penetrate inside the pores at later etching stages. Additionally, we inserted breaks in the etching process to allow hydrogen to be released from the pores and give the etching solution time for concentration equilibration at the front of etching. Due to this technique it is possible to etch complete  $p^{++}$  4"-wafers up to thickness of nearly 500  $\mu\text{m}$ . Clearly this electrochemical etching process is extendable to larger wafers. The porosity of the PSi structure must be adjusted for the finally chosen oxidizer. The highest energy yield of the reaction is assured when the oxidation reaction is complete. This implies a stoichiometric ratio of  $\text{SiX}_2$ , where X is oxygen or sulfur, and can be realized for PSi layers having porosity in the range of 70% for most of oxidizers used.

## 2.2 Single explosive element processing

Industrial production of single explosive elements requires the processing of full Si wafers and includes a few steps. It requires a HF-resistive mask on top of the Si wafer for spatially-selective etching. The second step includes porosification of the wafer and filling the porous elements by an oxidizer. Finally, the wafer should be cut in the regions where porous silicon is not present to avoid ignition. In order to get small, single explosive elements  $\text{Si}_3\text{N}_4$ -masks were prepared on 4"-wafers (Fig. 1) using LPCVD technique.  $\text{Si}_3\text{N}_4$  is resistive against HF and for 500  $\mu\text{m}$  thick elements an 800 nm thick mask is sufficient to avoid direct etching of the underlying substrate. However, we found that etching of a single thick element is not a straightforward procedure. While for elements having rounded corners the mask remains stable at sharp mask corners its cracking appears due to highly inhomogeneous current flow and under-



**Fig. 1** Left: fully processed  $\text{Si}_3\text{N}_4$  masked 4"-Si wafer. Right: shape of single elements surrounded by stable mask (upper two images) and the unstable mask at the sharp corners of the single element (lower image).

etching of wafer. Because the pores at the edge of the mask are tilted to the surface of the wafer they can propagate below the mask on the distance comparable with the thickness of the layers. This is certainly a restriction for the mask design because spacing between single elements has to be adjusted for the following cutting procedure.

### 2.3 Stabilization of the PSi surface

The long-term stability of the explosive device requires a stability of the PSi surface against aging. The surface can be long-time stabilized via thermal annealing the PSi in an oxygen ambient resulting in a passivating oxidized surface layer. At annealing temperatures below 250 °C the oxygen is mainly back bonded to surface Si atoms and the PSi surface remains organophilic. This process can be called artificial aging because after one year of natural oxidation in air the amount of surface-bound oxygen is roughly the same. At higher temperatures the oxygen will also be bonded directly to the surface, making it more hydrophilic. While annealing at lower temperatures where oxygen is mainly back bonded to the surface does not noticeably influence the layers reactivity, tempering at high temperatures (up to 700 °C) decreases the efficiency of the reaction. Furthermore, naturally aged samples which were exposed ~10 years to the air react as freshly prepared ones.

## 3 Realization of the explosive system impotente

### 3.1 Possible oxidizers

Due to packaging and long-term stability reasons only solid oxidizers incorporated into the pores of PSi have been explored. The most efficient oxidizers are perchlorates, since they have high oxygen content and are relatively stable in comparison to other oxidizers, e.g. chlorates. Therefore, we have chosen perchlorates as first choice for oxidizer. Unfortunately, most of the perchlorates contain crystal water and are hygroscopic (see Table 2). Non-hygroscopic perchlorates are  $\text{KClO}_4$  and  $\text{RbClO}_4$  but they are not solvable in common solvents. We found that perchlorates are much more efficient for explosive interaction than the analogue nitrates. We didn't find any other oxidizer comparable with perchlorates but, because the energy yield of the reaction is very high, less efficient oxidizers can be sufficient for the possible industrial applications. On one hand, crystal water and hygroscopic nature of perchlorates are certainly disadvantages because they cause problems with long term stability of the samples. On the other hand, according to our experience it seems that at least the crystal water is necessary for stabilizing the salt inside of the pores. For instance,  $\text{NH}_4\text{ClO}_4$  is not hygroscopic and contains no crystal water but after evaporation of the solvent it also creeps away of the pores.

All of the oxidizers investigated are summarized in Table 2 and the most promising for explosive interaction are marked in bold. One of the most efficient oxidizers is found to be  $\text{NaClO}_4$ . It contains only one crystal water and is not as hygroscopic like most of perchlorates. If a water-free packaging can be guaranteed,  $\text{NaClO}_4$  is the best solution for the industrial application as airbag initiator. If water-free packaging according to requirement of the automotive industry cannot be guaranteed for a time period above 20 years, sulfur is the most efficient, stable, non-hygroscopic oxidizer we found up to now.

### 3.2 Pore filling procedures

Standard commercial oxidizers are produced in the form of powders whose grain sizes significantly exceed the pore diameter. Therefore, several different methods were employed to fill the pores of PSi with oxidizer. The simplest method is filling the pores from an oxidizer-containing solution.

We were using different solvents such as water and organic liquids with different concentrations of oxidizers inside. Due to the organophilic surface of PSi water does not penetrate into the pores, so it cannot be used as solvent. Therefore we used mainly small alcohol molecules. Methanol and ethanol

**Table 2** Possible oxidizers, solvents where they are most efficiently dissolved and the major properties relevant to stability and reactivity of the system. Solvents: Me – methanol, Et – ethanol, Ac – acetone. HP – ignition on the hot plate. EL – electrical ignition (current flows through the wafer). SIB – standard ignition bridge. + – successful ignition.

oxidizer	solvent (solubility)	remarks	explosion		
			HP	EL	SIB
perchlorates (most efficient, but if solvable also hygroscopic)					
$\text{Ca}(\text{ClO}_4)_2 \times 4\text{H}_2\text{O}$	Me (237 g/100 g)	strongly hygroscopic	+	+	+
	Et (166 g/100 g)		+		
$\text{NH}_4\text{ClO}_4$	Me (6 g/100 g)	does not stay inside of the pores;	+		
	Et	therefore weaker reaction	+		
	Ac (>6 g/100 g)		+		
$\text{LiClO}_4 \times 3\text{H}_2\text{O}$	Me (182 g/100 g)	does not stay inside of the pores,	+	+	
	Et (152 g/100 g)	takes a while to come to the	+		
	Ac (137 g/100 g)	surface	+	+	
$\text{NaClO}_4 \times 1\text{H}_2\text{O}$	Me (~181 g/100 g)	less hygroscopic and stay inside	+	+	+
	Et (<181 g/100 g)	the pores (standard)	+		
$\text{AgClO}_4 \times 1\text{H}_2\text{O}$	Me	sample becomes white, AgCl?	+		
	Et	afterwards black	+		
$\text{Fe}(\text{ClO}_4)_3 \times \text{XH}_2\text{O}$	Me	most hygroscopic, but also high-	+		
	Et	est oxygen yield	+		
$\text{KClO}_4$	Me (<1.7 g/100 g)	not solvable in any common	—		
	Et (<1.7 g/100 g)	solvent	—		
	Ac (<1.7 g/100 g)		—		
nitrates (in general reaction is less efficient than for perchlorates and hygroscopicity is comparable)					
$\text{Ca}(\text{NO}_3)_2 \times 4\text{H}_2\text{O}$	Me (>54 g/100 g)	strongly hygroscopic	+		
	Et (54 g/100 g)		+		
$\text{NH}_4\text{NO}_3$	Me (17 g/100 g)	does not stay inside of the pores	+		
	Et (4 g/100 g)		—		
$\text{LiNO}_3 \times 3\text{H}_2\text{O}$	Me (good)	very weak reaction, may be due	+		
	Et (good)	to relatively low solubility	+		
	Pyridine (37 g/100 g)		+		
$\text{AgNO}_3 \times \text{H}_2\text{O}$	Me	sample becomes white-grayish	—		
	Et	and is no more reactive	—		
$\text{KNO}_3$	Me	bad solubility, therefore no reac-	—		
	Et	tion	—		
others (not that efficient like perchlorates but non-hygroscopic and solvable)					
$\text{KMnO}_4$	Me (good)	oxidizes slowly the alcohol	—		
	Et (good)		—		
	Ac (good)	microexplosions, weak react		+	
$\text{K}_2\text{Cr}_2\text{O}_7$	Me (not good)	bad solubility, therefore no reac-	—		
	Et (worst)	tion	—		
sulfur	$\text{CS}_2$ (good)	the only non-hygroscopic mate-	+	+	+
	melting	rial which stays inside the pores,	+	+	+
$\text{HClO}_4$	$\text{H}_2\text{O}$	easy filling from melting			
	$\text{H}_2\text{O}/\text{Et}$	also no slow oxidation, PSi re-	—		
		mains stable over time	—		

combine good solubility of the oxidizing salts (see Table 2) and the organophilic behavior. We used a sequential filling method to achieve highest possible mass of oxidizer confined in the pores and a stoichiometric ratio of oxygen to silicon. By gravimetric measurements we found that filling of the pores three times is sufficient for a 30%  $\text{Ca}(\text{ClO}_4)_2$  solution in methanol to reach stoichiometric filling. Additional fillings do not further increase the mass of the oxidizer. For saturated solutions of  $\text{NaClO}_4$  and  $\text{Fe}(\text{ClO}_4)_3$  it is sufficient to fill the pores two times. The highest filling factors achieved were ~50% of total pore volume. This is enough to realize the stoichiometric ratio of  $\text{SiO}_2$  for  $\text{Ca}(\text{ClO}_4)_2$ . The major problem of this filling method is that salts solvable in organic liquids are always hygroscopic.  $\text{KClO}_4$  which is the oxidizer most frequently used in pyrotechnics is not hygroscopic but its solubility in water is only 17 g/l and even lower in alcohol. For sulfur an organophilic and nonpolar solvent,  $\text{CS}_2$ , was used.

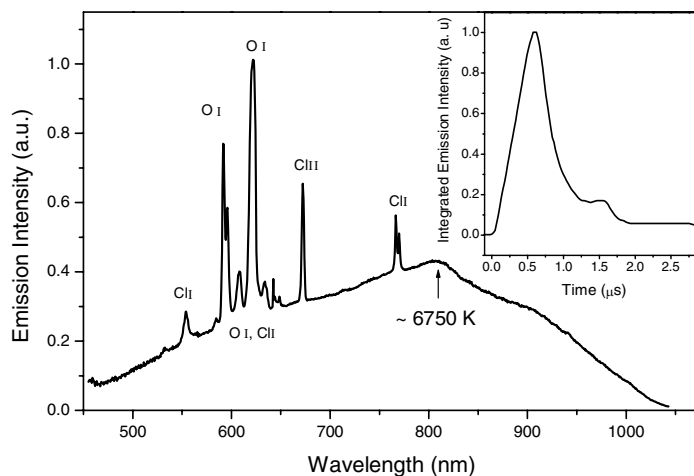
The best method to fill the pores will be one using melted oxidizer. However, we found that this is not always possible. If the melting temperature of the oxidant is higher than the ignition temperature this method cannot be applied. Ignition temperatures for different oxidizers were determined to be in the range of 460–540 °K. To decrease melting temperatures we performed experiments with salt eutectics. For the nitrates low temperature eutectics are well known, e.g.  $\text{KNO}_3/\text{NaNO}_3$  (21.9 mass%  $\text{NaNO}_3$ ) has melting point at 383 K. Unfortunately, a high surface tension of the eutectic prevents its penetration into the pores. However, melted sulfur successfully fills the pores. Sulfur has a rather low melting point, 386 K and is well wetting the PSi surface. The filling factors achieved with this method are comparable to the filling from solution, but are in the case of sulfur not sufficient to reach the stoichiometric ratio of  $\text{SiS}_2$ . Sublimation and physical vapour deposition techniques were also considered for sulfur. The filling factors achieved were significantly less than for filling from melting and therefore, these filling techniques seem not to be promising.

### 3.3 Ignition techniques

According to our experiments PSi-based explosives can be ignited thermally, electrically or optically. The essence of all the ignition methods is to produce hot spots to initiate the reaction locally, which afterwards ignites the rest of the sample. Thermal ignition was performed with a hot plate. We note that below a certain heating rate the oxidizer decomposes and our system does not explode. Thus, the active sample should be rapidly heated up to the ignition temperature. Electrical ignition is a standard method for industrial application. We used for the explosive element a standard Ni/Cr or  $\text{HfH}_x$ -bridges on a ceramic substrate as igniters. A single current pulse (2.5 A, 2 ms duration, according to standard specification of the automotive industry) heats up the bridge and evaporates Ni/Cr or explodes  $\text{HfH}_x$ . This ignites the PSi layers filled with oxidizer via ejection of plasma or hot particles. Since PSi has a low thermal conductivity these bridges cannot be placed on the top of PSi layers directly. Therefore, a heat conducting ceramic substrate below the ignition bridge has been used to avoid heating of the layers generated by periodic current pulses which are required by a standard permanently running automotive airbag test called “non-fire condition”. Optical ignition with a pulsed YAG-laser was used for the measurement of the detonation wave propagation speed. A single pulse has been found to be enough to initiate the explosive reaction.

## 4 Analysis of Si-based explosive system

The energy yield of the explosive reaction has been determined via calorimetric bomb-test only for calcium perchlorate up to now. This oxidizer has been chosen due to its high solubility in methanol and its high oxygen content. The energy yield for freestanding layers etched from  $p^+$ -wafers at a nearly stoichiometric ratio of silicon and oxygen has been found to be 7.3 kJ/g. For comparison the energy yield for TNT is roughly 4 kJ/g and the most powerful explosives known so far falls below 8 kJ/g. We would like to mention that our system is still not completely optimized and potential energy yield can be even higher. The propagation speed of the detonation wave parallel to the surface of PSi layers was deter-

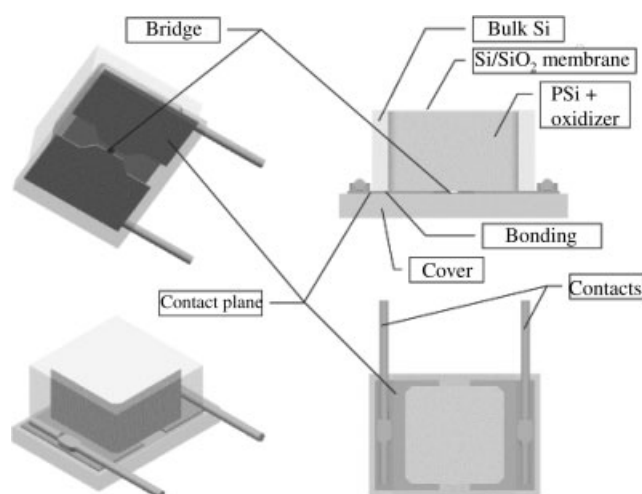


**Fig. 2** Spectrum of flash and temporal evolution of its integrated intensity during explosion.

mined by laser reflectivity measurements. The explosion was ignited by a single laser pulse in one place of the layer and reflectivity variation of a second displaced laser beam has been analyzed. We estimated the propagation velocity of the one-dimensional detonation wave to be  $>2000$  m/s.

An intense flash emitted during the explosion allows us to estimate the time of the reaction. We found that the reaction finishes in only 500 ns for the detonation (see inset of Fig. 2) while the reaction takes time from 1.5 to 50  $\mu$ s for deflagration, depending on the morphology of layers. The emission after the rising part of the flash kinetics represents a cooling step due to expanding hot gases/particles which react slightly after the main detonation event.

Figure 2 shows the spectral dependence of the time-integrated intensity of the optical flash. This experiment has been performed with a single spectrometer combined with a Si charge coupled device allowing measuring the complete spectrum of the optical flash after a single explosion event. The emission spectrum includes a wide band located in the near infrared spectral range as well as a few sharp plasma lines. It can be seen that the system is far from thermodynamic equilibrium. Plasma lines belong to states of the atomic components of the mixture having different ionization levels (indicated in Fig. 2) and the “quasi-blackbody” temperature was estimated from the spectrum shown in Fig. 2 to be roughly equal to 6750 K.



**Fig. 3** Sketch of the PSi-based airbag initiator construction.





**Fig. 4** Left side: Picture of a single PSI-based explosive element (bottom), a prototype of the airbag igniter (upper left) in comparison with a Eurocent coin. Right side: Image of the ignited single explosive element.

## 5 Construction of PSi-based airbag initiator

One of the possible constructions of the PSi-based airbag initiation element is shown in Fig. 3. It consists from two main parts, the explosive part and the electrical ignition part. An electrical pulse-driven heating bridge is deposited on the heat-conductive ceramic plate and two pins provide connection to the electrical circuit. The PSi layer filled with solid oxidizer is bonded to ceramic plate and is in direct thermal contact with the bridge. Bulk Si remaining after the etching of the single element provides geometrical confinement of the PSi layer and its isolation from the environment.

Finally, Fig. 4 is introduced for clarity. It demonstrates simultaneously the size of the single explosive element, prototype of the airbag igniter and the geometrical scale of the explosion of this single element. We would like to mention that this igniter can successfully initiate a standard industrial airbag.

## 6 Conclusions

We presented results of our efforts to develop a new type of composite energetic material based on porous silicon nanostructures. These systems combine PSi and several oxidizers and are mechanically and chemically stable. They can be operated at room temperature and are ignitable in a controllable way by electrical current pulse according to industrial specifications. Their production technology is compatible with standard mass-production technologies of the silicon industry. The prototype of airbag igniter on the basis of this nanoenergetic material has been realized in collaboration with industrial partners. The future technological steps should include on-chip construction of operating electronics, deceleration sensor and explosive element.

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