

CONTROLLED ENERGY RELEASE BASED ON EXPLOSIVE POROUS SILICON

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ABSTRACT

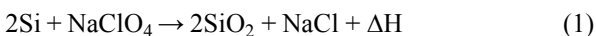
This paper reports on a novel method for controlled release of huge amount of energy stored in a functionalized porous silicon (PS) on a silicon chip. This is achieved by adjusting the size and the separation distance between locally defined areas of PS. Such an approach allows multiple sequential or single explosions with defined energy outputs. The confinement and sequential explosions were studied for different shapes and sizes of PS areas with different separation distances between them. A critical separation distance between PS sites is found for which the sequential explosions are achieved.

INTRODUCTION

The discovery of PS as explosive material [1] has initiated the development of integrated nanoscale solid state explosives onto Si chips since a massive explosion can be obtained even with a small amount of PS [2]. The explosive properties of PS have been investigated by many researchers in terms of PS morphology [2–4], oxidizers [3–5] and ignition methods [6, 7]. The reaction of PS and an oxidizer is an exothermic reaction which releases a huge amount of heat energy besides light, sound, pressure, ejected material and shock waves [5]. This indicates that a chip based system for long-term energy supply for electronic devices might be possible by using a suitable energy transformation principle such as Seebeck effect. However, a controlled energy release, both, locally and with respect to time, is essential to achieve this. The energy release of explosive PS and its activation energy is typically controlled via the employing oxidizer [3, 4] and thickness of native oxide on the surface of PS before loading the oxidizer [6]. However, here, we report on controlling the explosive reactions by a suitable pattern design so that an explosion event is either isolated on a specific PS area or transferred to an adjacent PS area.

BASIC OF EXPLOSIVE POROUS SILICON

The vast internal surface area ($> 500 \text{ m}^2/\text{cm}^3$) [8] has made PS a suitable fuel for explosion applications since around 20 % of Si atoms in a PS layer are located on the surface of pores [9]. Several oxidizers have been employed and tested. Among them, sodium perchlorate (NaClO_4) has the highest energetic efficiency since it is slightly less dense than Si and can completely fill the pores and stay inside them [5]. The energy output of a chemical reaction is theoretically estimated using standard enthalpies (ΔH) if the reaction kinetic and products are known. In the case of PS and NaClO_4 , the basic balanced reaction is described as [10]:



This can theoretically provide 1848 kJ/mol heat energy which is equal to 33 kJ/g per Si mass [11].

CONTROL AND GUIDE OF EXPLOSION

Thermal ignition is the simplest method to ignite an explosive PS. PS impregnated with NaClO_4 can be thermally initiated at temperatures between 133–400 °C [6, 7, 11, 12], depending on the used conditions. In the approach here, the released heat energy due to the chemical reaction between PS and NaClO_4 is used to ignite separated PS regions within a distance where heat transfer is sufficient for ignition - within a transferring distance (a) as it is shown in Fig. 1. Hence, by adjusting the size of PS structures, their energy outputs, the duration of explosion, and using suitable thermodynamic conditions (heat sinks or thermal isolation), the explosion of an explosive PS can be either transferred to the adjacent explosive PS ($a < a_{crit}$) or isolated ($b > a_{crit}$) by choosing a proper separation distance between them. Such an approach along with well-tailored sizes and separation distances of PS regions allow multiple sequential or single explosions with various explosive properties and different timing on a single chip.

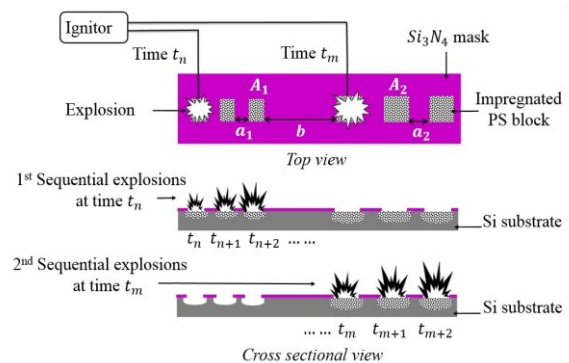


Fig. 1: Schematic representation of two sequential explosions with different output powers occurring at different times with an ignition for each sequence. A_1 and A_2 are PS areas, a_1 and a_2 are transferring distances, and b is the isolation distance.

HEAT TRANSFER SIMULATION

The heat transfer due to a released energy from an explosion was studied through a finite element simulation. A simple model was created in the Comsol 5.2 and simulated using heat transfer physics. A Si-chip containing $3 \times 3 \text{ mm}^2$ PS blocks with PS layer thickness of 20 μm and separation distance of 200 μm was set on top of an aluminum heat sink with dimensions of 80 mm \times 60 mm \times 1 mm (Fig. 2). The Cooper-Mikic-Yovanovich correlation was used as constriction conductance to the heat sink. The released energy using eq. (1) (4.14 J for 125.82 μg Si for the PS with 70 % porosity) from the first PS block was considered as the energy source for ignition of the second block. The energy was assumed to be released at a constant rate over 1

ms. The simulation was done for a total time of 5 ms with 1 ms steps. The energy started to be released at time 0. The temperature at a depth of 20 μm (Si directly below the PS area) is plotted as a function of the distance from the center of the exploding PS structure towards the adjacent block for different times (Fig. 3).

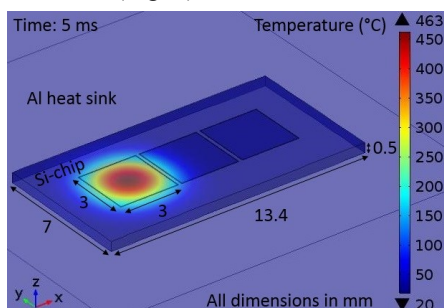


Fig. 2: Temperature distribution on a Si chip due to explosion of a PS block and thermal conduction.

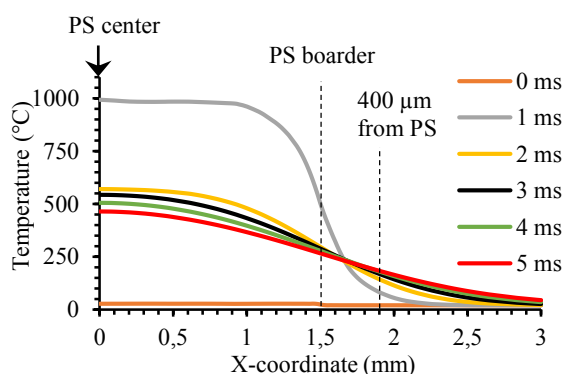


Fig. 3: Simulated temperature as a function of distance for duration of 5 milliseconds.

Even though a temperature up to 1000 $^{\circ}\text{C}$ was simulated directly below the exploding PS block, a temperature range of 220-190 $^{\circ}\text{C}$ was obtained at distances of 200-400 μm away from the exploding area at some millisecond after releasing the energy (Fig.3). This indicates that in theory, an explosive PS located at distances less than 400 μm from the exploding site could be thermally ignited considering the experimentally found temperature range (133-400 $^{\circ}\text{C}$). However, the experimentally released energy is about 3 times lower than the theoretical one [2]. Hence, the temperature calculated from direct heat transfer from PS to the underlying Si will be also around 3 times lower (73-63 $^{\circ}\text{C}$ at 200-400 μm). Nevertheless, thermal ignitions are still possible for distances up to 100 μm . Additionally, this simulation does not consider heat transfer from the hot gas above the exploded PS to the surrounding PS and other forms of released energy.

EXPERIMENTS

Porous silicon fabrication and impregnation

P-type $\langle 100 \rangle$ silicon wafers with resistivity of 1-10 Ωcm were patterned using silicon nitride (Si_3N_4) mask to achieve defined and separated PS areas on a single chip. Anodization was done in a double tank setup with a constant current density of 7-10 mA/cm^2 for 30 minutes in a 1:1 HF/ethanol solution in order to achieve optimal PS properties for explosions (around 70 % porosity and 20 μm

thickness [2]).

Freshly produced PS was impregnated with a solution of sodium perchlorate monohydrate and methanol (ratio of 1:10) using a micropipette (droplet method) before ignition. Depending on the size and number of PS structures on a chip, 1-4 droplets with the volume of 4-8 μl each was used. The impregnated chips were dried in a vacuum chamber containing silicone gel with a pressure of 0.2 bar for 7 minutes prior to explosions. The explosions were initiated within 1 minute after drying. The characterization was done via a thermal camera (FLIR A600, 200 fps) and a photodetector (OSD15-5T, 12 ns time response) combined with a TW-MF2CAB amplifier.

Critical separation distance to transfer an explosion

PS structures with different shapes (squares, rectangles, and circles) and areas (0.78-18 mm^2) were designed and generated to investigate the critical separation distances between exploding PS blocks to transfer an explosion from one PS block to another. Separation distances from 50 μm to 3200 μm were investigated. Due to the influence of masked (electrically isolated) area and design of PS structures (structures with different shapes, sizes and separation distance on the same wafer), the local current density for different structures was different from the global set current density (10 mA/cm^2) during the anodization process [13]. Hence, PS structures with different layer thicknesses (12-34 μm), and consequently with various porosities (60-80 %) were obtained by the anodization.

The first block of each sequence was manually ignited using a piezo spark explosions were characterized through their light outputs (Fig. 4).

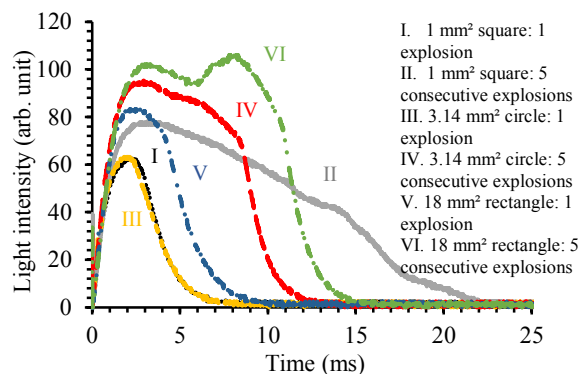


Fig. 4 Measured light output of the exploded PS with different shapes and sizes arranged in the sequences in which the distance change between each block followed an exponential order ($d = 50 \mu\text{m} \times 2^{n-1}$, n is the number of PS block in a row).

In most of the samples, 5 consecutive explosions were obtained. This corresponds to a separation distance of 400 μm between the explosive PS blocks up to which the explosions were transferred to the next blocks. The light output was larger and lasted longer for the consecutive explosions compared with the single block explosions. In addition, an increase in light intensity amplitudes was sometimes observed (curve VI) which can be due to a faster chemical reaction rate between PS and NaClO_4 at those specific regions [14]. In most cases, the maximum light output occurred around 2-3 ms after the ignition.

Sequential explosions

Based on the obtained critical distance ($400\ \mu\text{m}$), sequences of PS structures (squares and rectangles with areas of $9\ \text{mm}^2$ and $18\ \text{mm}^2$) with constant separation distances of $200\ \mu\text{m}$ and $400\ \mu\text{m}$ between each PS block were designed and generated. The sequences were arranged in “C”- and “2”-shape. By manually igniting the first block of each sequence, complete sequential explosions (7 explosions in a row) were obtained from both squares and rectangles arranged in “C”-shape, and also for both separation distances, $200\ \mu\text{m}$ and $400\ \mu\text{m}$ between each explosive PS block. Fig. 5 shows thermal images in the time frame of 0-25 ms for a sequence of explosions transferred from a $9\ \text{mm}^2$ PS block to an adjacent block with a constant separation distance of $200\ \mu\text{m}$ arranged in a “C”-shape. Even though the sampling time of the thermal camera (5 ms) does not allow correct measurement of sharp temperature peaks, the maximal measured temperature fits well with the simulated values by considering practical output energy ($10.8\ \text{kJ/g Si}$ [11]).

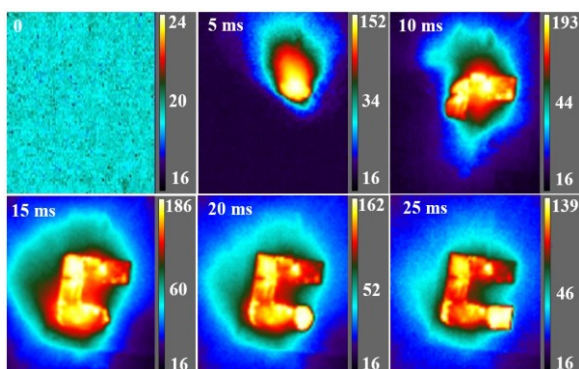


Fig. 5: Thermal images of transferring of explosions from one PS block to another in the “C”-shape arrangement (seven $9\ \text{mm}^2$ large PS blocks with constant separation distance of $200\ \mu\text{m}$).

For $9\ \text{mm}^2$ large square PS structures with a separation distance of $200\ \mu\text{m}$ arranged in a “2”-shape, 12 consecutive explosions out of 14 separated blocks were achieved. Moreover, for $18\ \text{mm}^2$ large PS rectangles with a separation distance of $400\ \mu\text{m}$, 10 consecutive explosions out of 11 separated blocks were obtained. Transferring of the explosion to the last patterns did not occur in all three tested samples. Light emission of sequential explosions with constant separation distances (Fig. 6) showed similar behavior as those with increasing distances (Fig. 4). The light intensity and duration were larger for 10 and 12 consecutive explosions compared with single ones (duration changed from 7 ms to 24 ms for single and 12 explosions in a row).

Storage of explosive porous silicon

For practical applications, the stability of explosive PS is a critical aspect. The surface of freshly etched PS is covered with Si-H groups. During the storage, Si-H groups are replaced by Si-O groups. This natural aging due to oxidation reduces the explosive reactivity of PS [6], meaning that PS loses its explosive properties under normal storage conditions. However, the aging effect can be overcome by impregnating the PS directly after anodization and storing the dried PS in a closed chamber containing silica gel, and then drying the sample once again in a vacuum before ignition.

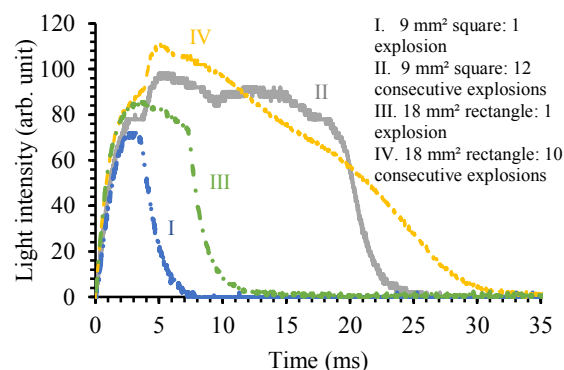


Figure 6: Measured light intensity of the sequential explosions with constant separation distances ($200\ \mu\text{m}$ in $9\ \text{mm}^2$ square, and $400\ \mu\text{m}$ in $18\ \text{mm}^2$ rectangles).

Using this method, freshly etched, one week, and six weeks old impregnated PS showed almost similar explosive behavior when they were activated by a spark. In contrast, no explosion was obtained from PS samples stored for one week and six weeks under normal conditions when impregnated and dried just prior to the ignition.

DISCUSSION

Based on the simulation results and the possibility of transferring of explosions from one exploding area to another at distances smaller than $400\ \mu\text{m}$, and stopping sequential explosions at larger distances, we conclude that thermal ignition is the most important principle in controlling of sequential explosions. Also, the long duration of consecutive explosions (Fig. 5 and 6) is a strong indication for a transfer process controlled by heat conduction (Fig. 3). The critical distance to transfer an explosion mostly depends on the thermal properties of the system. Chip thickness, and consequently the distance to the heat sink have an influence on the overall lateral temperature as observed from the simulation with different chip thickness up to $700\ \mu\text{m}$. Based on simulation results, thermal coupling of the chip to the heat sink also changes the temperature amplitude, and thus the critical distance.

Additionally, by comparing simulated heat temperature at the distance of $200\text{--}400\ \mu\text{m}$ away from the exploding site ($73\text{--}63\ ^\circ\text{C}$ obtained based on practical energy output, $10.8\ \text{kJ/g per Si}$) with the ignition temperatures reported in the literature ($133\text{--}400\ ^\circ\text{C}$), we conclude that despite the heat transfer from an exploding PS to the underlying Si, the heated air and gas above the exploding PS has to be taken into account too. In the used measurement setup, it is not possible to clearly distinguish between the temperature on the surface of a solid chip and the gas above the chip. Therefore, high-speed thermal cameras positioned at different locations around the exploding area are necessary to confirm the exact required temperature for ignition of an explosive PS.

Another aspect which has to be considered when comparing simulations and experiments is the amount of exploding PS. In most of the samples, even though the sequential explosions were achieved, only around half of the PS thickness was exploded. This means that the practical output energy of an exploding site is less than of what is considered in the simulation (where we assumed that the

total thickness of PS is exploding).

An important limitation of energy transfer is found from the observation that the last blocks of long sequences (11 and 14 blocks in a row) did not explode even for a distance smaller than the critical distance between each pattern. This can be explained by the reduction of energy production efficiency along a sequence of explosions resulting in a reduced temperature along the exploding path. Losing of the potential reaction energy by partially exploding PS, and degradation of the oxidizer by thermal influence may explain this degradation effect. Additionally, the variation of effective current density in anodization and thus different porosity has an influence on the produced energy during an explosion when comparing different layouts.

Even though it was possible to control the reaction of explosive PS by suitable pattern designs and to transfer explosive reaction from one PS area to another, the total transfer distance was limited to about 3.82 cm for twelve 9 mm² large square isolated PS blocks, and 6.36 cm for eleven 18 mm² rectangular PS blocks. This shows that the total distance over which the explosion is transferred (length of a chain reaction) is depending on the size of the exploding PS blocks, and is limited to some centimeters. For practical applications and chip sizes of around 1 cm², this is not a relevant restriction. However, using full wafers, a repeated ignition (e.g. by hot wire) of explosive PS blocks is needed for longer sequences of energy release.

CONCLUSION

Control and transfer of explosions using PS patterns with different shapes and sizes were studied. The energy released from the first pattern was used to ignite the adjacent pattern. A critical separation distance of about 400 μm between PS patterns to transfer an explosion to another explosive pattern as well as an isolation distance between patterns to stop the chain explosions were experimentally determined for the investigated structures. The obtained isolation and transferring distance were the same for all tested shapes; even though, the energy released of the explosions might have different profiles. Additionally, a simple finite element model was created to study the temperature change due to an exploding PS at different distances from the exploding site and for times between 0 and some millisecond. As the simulated temperature at the measured critical distance of 400 μm is slightly smaller than the lowest reported thermal ignition temperature (133°C), we conclude that additional heat transfer mechanism e.g. the heated gas above exploded PS has to be considered. The duration of releasing the energy of an exploding sequence can be controlled between some millisecond and some tens of milliseconds. Considering minimal and maximal volumes of exploding PS, the typical power output can be controlled over 3 orders of magnitude (e.g. 5 - 3000 W). For long term use, suitable preparation and storage of impregnated PS are necessary.

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