

# Study on the Stability of Porous Silicon Energetic Materials

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**Abstract:** Porous silicon has been widely studied due to its high explosion characteristics, less harm to the environment and compatibility with all silicon based production processes. At present, it has been used in military, national defense and other fields. In this paper, porous silicon was prepared by electrochemical anodic oxidation. The electrolysis time was 35 min, the current density was 50 mA/cm<sup>2</sup>, and the electrolyte was HF: DMAC=5:1 (volume ratio). The effects of silane coupling agents (KH550 and KH560) and cathodic reduction treatment on the life of porous silicon were investigated. The results show that the life of porous silicon chips treated by cathodic reduction+KH560 is longer, and the morphology of porous silicon chips treated by cathodic reduction+KH560 is better.

**Keywords:** Porous silicon, Electrochemical anodic oxidation, Stabilization.

## 1. Introduction

Porous silicon has rich morphological characteristics and excellent properties, such as large specific surface area, high resistivity [1], photoluminescence, electroluminescence and good biocompatibility, and has good application prospects in MEMS, sensors, medicine and other fields [2]. Porous silicon as the substrate has the characteristics of high explosiveness, less environmental harm of explosive products and compatibility with all silicon based production process, which is widely used in small initiation devices [3]. In the decades since the discovery of the luminescent properties of porous silicon, researchers have studied the optical, electrical, physical, chemical and other properties of porous silicon [4].

When the newly prepared porous silicon sample is placed in air, its surface will react with oxygen, which will reduce the reactivity of porous silicon. With the increase of time, the structure and some characteristics of porous silicon will also change, affecting the actual use. The research results show that the fresh porous silicon surface contains a large number of Si H<sub>x</sub> (x=1,2,3) bonds [5], which are very active. When the sample is stored in air, the oxygen in the air will destroy the Si H<sub>x</sub> bond, and hydrogen passivation is gradually replaced by oxygen passivation, which eventually changes the performance of porous silicon. In addition, if the prepared porous silicon is separated from the liquid and dried naturally in air [6], the solution will volatilize from the pores during the drying process, and the porous silicon will crack, or curly capillaries will fall off from the substrate, damaging the original morphology of porous silicon. This process only takes a few minutes [7]. If porous silicon cannot be dried and stored in the air and has a flat and smooth surface [8], other processes cannot be carried out on the surface of porous silicon, which seriously affects the explosive performance of porous silicon and greatly limits the application of porous silicon [9].

In order to prolong the storage time of porous silicon, electric heater is used to provide heat source by using cathodic reduction surface treatment technology, anodic oxidation treatment technology, silane coupling agent KH550, KH560 treatment and other methods [10] to evaluate the maintenance of the explosive performance of porous silicon under different

treatment methods.

## 2. Reagents and Methods

Monocrystalline silicon wafer is provided by Emei Semiconductor Materials Co., Ltd. of Dongfang Electric Group, which is n-type P-doped monocrystalline silicon wafer with resistivity of 2~4 Ω·cm, crystal plane direction<100>, and thickness of 500~550 μm. Cut to 1.0 cm × 1.0 cm square machining unit. During transportation and storage, a small amount of silicon oxide layer (mainly composed of SiO<sub>2</sub>) or dust will gradually form on the surface of monocrystalline silicon wafers, as well as other impurities such as grease. These impurities on the silicon surface will have a certain impact on the deposition process. Therefore, monocrystalline silicon wafers need to be pretreated before chemical reduction deposition.

Soak them in acetone and ethanol solution for five minutes respectively, take them out and soak them in 10% hydrofluoric acid for 10 minutes, and finally soak them in acid pickling solution (hydrochloric acid, hydrogen peroxide, deionized water, volume ratio 1:1:5), alkali pickling solution (salt ammonia water, hydrogen peroxide, deionized water, volume ratio 1:1:5) at 70 °C for five minutes, and then wash them dry for standby.

After pretreatment, silicon wafer is used as anode and platinum wafer as cathode during electrochemical anodizing. The electrolyte used is the mixed solution of hydrofluoric acid and DMAC, the volume ratio is 1:5, the current density is 50mA/cm<sup>2</sup>, and the electrolysis time is 35min. After the preparation, dry it in a vacuum drying oven at 60 °C for 5min.

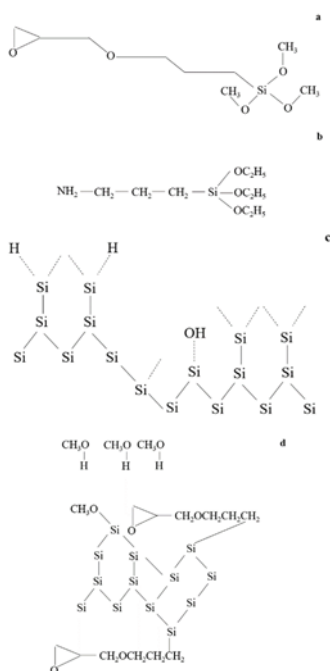
## 3. Conclusion

Electrochemical anodizing conditions for preparing porous silicon: electrolysis time 35 min, current density 50 mA/cm<sup>2</sup>, electrolyte HF: DMAC=5:1. Two methods, silane coupling agent (KH550 and KH560) and cathodic reduction, were used to stabilize the porous silicon chips. After treatment, the porous silicon chips were stored in vacuum. With natural conditions and vacuum storage as the blank control group, the explosion characteristics of porous silicon chips compounded

with 1.2mol/L gadolinium nitrate/ethanol solution under seven conditions were tested.

Vertically, the explosion strength of porous silicon energetic materials generally decreases with the increase of storage time. This is because the freshly prepared porous silicon is unstable, and the surface is covered with a large number of highly active Si-Hx. With the increase of storage time, the oxidation of the porous silicon surface becomes more and more serious, and the dehydrogenation of Si-Hx occurs, so that Si-Hx is replaced by Si-Ox. The energy intensity of porous silicon energetic materials is related to the number of Si-Hx. Therefore, with the decrease of active hydrogen, the trigger energy required for the reaction of porous silicon energetic materials increases. However, in order to ensure the same test conditions, the detonation energy provided each time is the same, which cannot meet the requirements of the detonation energy of porous silicon energetic materials with a long storage time, leading to poor explosion test effect.

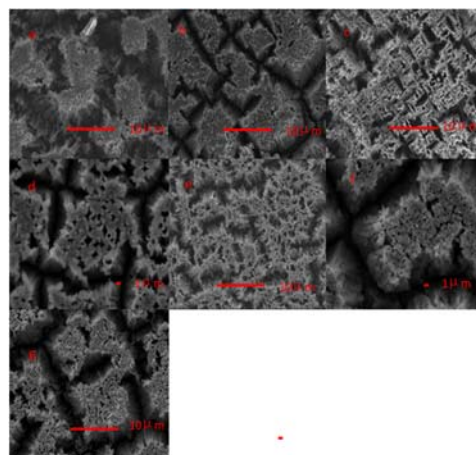
By comparing the explosion performance of porous silicon energetic materials under the same storage time and different stabilization conditions, the porous silicon energetic materials using cathodic reduction treatment+KH560 still have good explosion characteristics after long vacuum storage conditions and composite ignition with gadolinium nitrate. Cathodic reduction treatment is to move the F<sup>-</sup> in the porous silicon energetic material to the anode under the effect of electric field during reverse power supply, while pulling H<sup>+</sup> to the cathode, promoting the combination of silicon suspension bond and H<sup>+</sup> to form a more stable Si-H bond, weakening the original possible oxidation reaction, reducing the F<sup>-</sup> left in the porous silicon energetic material, eliminating the corrosion of fluoride ions on silicon, and ensuring the morphology of surface porous silicon. The bubbles of porous silicon energetic material soaked in KH560/ethanol appear for a short time and disappear after only a few minutes. The color of porous silicon layer becomes light, showing light yellow.



**Figure 1.** a. KH560; b. KH550; c. suspended keys on porous silicon surface; d. Eliminate suspended bonds on porous silicon surface

The storage life of porous silicon energetic materials can be prolonged by the treatment of porous silicon energetic materials with silane coupling agents, because the oxygen containing groups in silane coupling agents replace the hydrogen atoms adsorbed by silicon atoms on the freshly prepared porous silicon energetic materials. The silicon atom in the silane coupling agent is combined with the unsaturated silicon atom on the surface of the porous silicon energetic material to eliminate the hanging bond on the surface of the porous silicon energetic material. At the same time, a new alkyl protective layer with strength much higher than the hydrogen atom layer adsorbed on the surface of the porous silicon energetic material is formed on the surface of the porous silicon energetic material to prevent oxygen and other oxygen from oxidizing the porous silicon energetic material during storage, so as to stabilize the porous silicon energetic material. At the same time, because the alkyl group forms the protective layer on the surface of the porous silicon energetic material, it is completely different from the silicon oxide on the surface of the porous silicon energetic material. The alkyl group protective layer will not affect the reactivity of the porous silicon energetic material.

From the perspective of explosion performance, silane coupling agent KH560 is better than silane coupling agent KH550. The reason may be that the porous silicon is prepared by oxidation in the electrolyte mainly composed of hydrofluoric acid. Although the porous silicon layer is cleaned after electrolysis, it is still acidic in fact. KH550 is an alkaline solution. Neutralization reaction occurs during the treatment of the porous silicon layer, which will reduce a certain amount of Si-H bonds, thus affecting the storage performance. Then the explosion effect is reduced; Although silane coupling agent KH560 is also weakly acidic, KH560 is soluble in water, and hydrolysis reaction occurs at the same time. The hydrolysis reaction releases methanol, which can squeeze the ethanol that cannot be cleaned from the pores during the electrolytic preparation of porous silicon, thus generating more Si-H bonds. The Si-H bonds are replaced by more stable functional groups on the silane coupling agent, forming an alkyl protective layer, which has a stronger protective effect on the porous silicon layer, and the explosive performance is greatly stabilized.



**Figure 2.** SEM of the surface of porous silicon a. Natural; b. Vacuum; c. KH560; d. Cathodic reduction+KH560; e. KH550; F. Cathodic reduction+KH550; g. Cathodic reduction

The scanning electron microscope characterization results of porous silicon morphology under different stabilization conditions under the same storage time are as shown in Fig.

3.2. It can be seen that the porous silicon layer under natural conditions and vacuum conditions is seriously cracked, and the pore structure is difficult to observe, resulting in poor composite effect with oxidants and poor explosion effect; The porous silicon layer treated with silane coupling agent KH550 can prevent cracking, but the holes are small and uneven; The morphology of porous silicon layer treated with silane coupling agent KH560 is well preserved. There are few cracked areas, which are spongy. There are many holes with uniform distribution. The dense holes absorb more oxidants, ensuring good explosion performance after treatment with KH560.

To sum up, porous silicon energetic materials treated with silane coupling agent KH560 still maintain explosive properties after 25 days of vacuum storage.

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