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Fabrication, characterization, and application in nanoenergetic materials of uncracked nano porous silicon thick films

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ABSTRACT

The porous silicon (PS) film has gained increasing attention in recent years as advanced nanoenergetic materials (nEMs). A simple fabrication method to prepare uncracked PS thick films was successfully realized with precisely controlled electrochemical etching, and the relationship between the current density and the concentration of electrolytes was found in its fabrication. Additionally, the capillary stresses resulted from the liquids in nanopores of PS films was another factor resulted in its crack. The nanopores composed of uncracked PS thick films distributed regularly and their diameters ranged from 2 nm to 6 nm. Its S_a (average roughness) of PS film surface was 6.53 nm, and its thickness ranged from 102.41 μm to 205.75 μm. The specific surface area was 587 m^2/g and the average diameter of nanopores was 4.3 nm. The PS film was found to be monocrystal and it was same as the substrate. The crack mechanism of PS films was discussed: the porous structure reduced the strength of PS films comparing the silicon bulk and the capillary effect hastened the crack of PS films. PS films filling with sodium percholorate in nanopores were ignited by laser and the stable combustion showed that they were advantageous to be applied as micro-electromechanical systems (MEMS) compatible devices, such as silicon-based chips of mircothruster and microigniter.

1. Introduction

The porous silicon (PS) was discovered by Uhlir in 1956 [1], but its first industrial application was applied as Silicon-on-Insulator (SOI) [2] structure with the development of Super Large-Scale Integration (SLSI) circuits in 1970s. From the discovery of the photoluminescence at room temperature [3–9], the PS has gained increasing attention [10–13] and it was applied as new functional materials, because of its unique chemical and physical properties compared to their bulk. Since then, the PS film has been researched in comprehensive fields [14–18] because of its novel properties, such as electronic, optical, mechanical and thermal properties. But the PS films applied in these fields are typical thin films and their thicknesses range from nanometers to microns, generally. As well-known, the cracks of PS films are common problems in drying. The crack is the serious disadvantages of PS films, and this problem confines its applications in many fields, such as nanoenergetic materials (nEMs) [19–23]. Several methods to fabricate PS films have been reported [24–26], but the crack of PS film is not completely solved, especially the PS thick films. Some reports indicated that the uncracked PS film is suitable materials to fabricated nEMs and nanoenergetic devices [27–30], because of a large enthalpy of reaction in its combustion and a compatibility with the MEMS technology in its fabrications. However, Parimi et al. [28] still found the random micro-crack pattern in fabrications of PS films. Therefore, it's necessary to research the fabrication of uncracked PS film. For this target, some researchers [31–33] studied the residual stress in drying of PS and the mechanisms involved in the crack of PS film. In addition, Dongsheng et al. [34,35] studied the supercritical drying technique to avoid the crack of PS films in drying process. But the supercritical drying technique is exorbitantly expensive and inconvenient. In this paper, we develop a simple method to fabricate uncracked PS thick film and this method does evidently reduce the cracking probability of PS thick film. Besides, their nanostructure and surface morphology are all tested by SEM, AFM and other essential instruments. The cracking reasons of PS films are also discussed from the nanostructures of PS films and the surface tension of electrolytes. The stable combustion of PS nEMs which is ignited by pulsed laser is shown in this work, and this combustion indicates that the PS film is advanced materials in nEMs devices, such as the full silicon-based matrix chips of mircothruster and microigniter.

2. Fabrications of uncracked PS thick films

PS film is fabricated on the polished surface of single crystal silicon wafers which is single polished, p-type, (1 0 0) crystallographic

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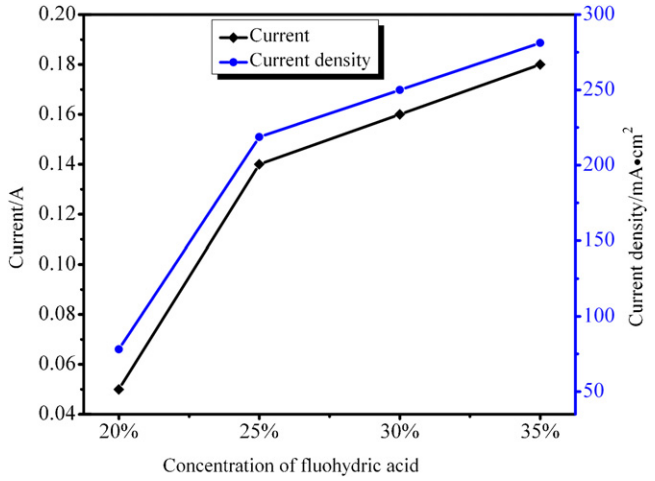

Fig. 1. Relationships between the maximum current densities and concentrations of etching solutions for fabrications of uncracked PS thick films.

orientation, B-doped, 0.1–0.3 Ω cm resistivity. The thickness of silicon wafer is 525 ± 25 μm. The etching chamber is purpose-built. Two plate electrodes are made of platinum (its purity is 99.95%). The electrolyte is a mixture of hydrofluoric acid (40%) and anhydrous alcohol at the ratio 3:1 (vol/vol). The current is supplied by direct current (DC) electrical source and the current density is 200 mA/cm^2. All the PS films are fabricated at room temperature.

Before fabrications of PS films, the silicon wafers are completely cleaned by the mixture of concentrated sulfuric acid (purity 98%) and hydrogen peroxide (purity 30%) in ultrasonic cleaner until there is not any small bubble on the surface of silicon wafer. Thoroughly, the silicon wafer is rinsed by demonized (DI) water. Then, the silicon wafers are cleaned by acetone in ultrasonic cleaner for 20 min. Next, the anhydrous alcohol is used to clean the substrate for 20 min, too. These three steps will remove the organic pollutants what contaminate the surface of silicon substrate. At the end, the substrate is cleaned by 20% hydrofluoric acid/DI water solution to remove inorganic pollutants, thoroughly rinsed by DI water. The cleaned substrates are preserved in anhydrous alcohol for applications.

The etching parameters have to be exactly controlled. The current density is related with the concentrations of etching solution, and the relationship between the maximum current density and the concentrations of etching solutions to fabricate the uncracked PS thick films is shown in Fig. 1. This compatibility is the key to fabricate the uncracked PS thick films. Fig. 2(a1) is the top view of the uncracked PS film, and Fig. 2(b1) is the top view of cracked PS film. From the sectional view of the uncracked PS film (a2 image in Fig. 2), we find that the uncracked PS film is an ensemble with the substrate and the PS film does not separate from the substrate. The thickness of uncracked PS film is over 100 μm and its thickness is shown in Fig. 6(a). But from the sectional view of the cracked PS film (b2 image in Fig. 2), we find that the PS film separates from the substrate, although its thickness is only about 10 μm. From Fig. 2, we can get that the thickness is not the key factor to determine the PS film will be cracked or not. This shows me that it's feasible to fabricate the uncracked PS thick film. By the experiments, the thickness of PS film is determined by three factors: the current density, concentration of etching solutions and etching time.

3. Results and discussions

3.1. Instruments and testing conditions of PS films

In experiments, surfaces and cross-sections of PS films are investigated using FESEM (ULTRA plus, ZEISS, Germany). The thicknesses

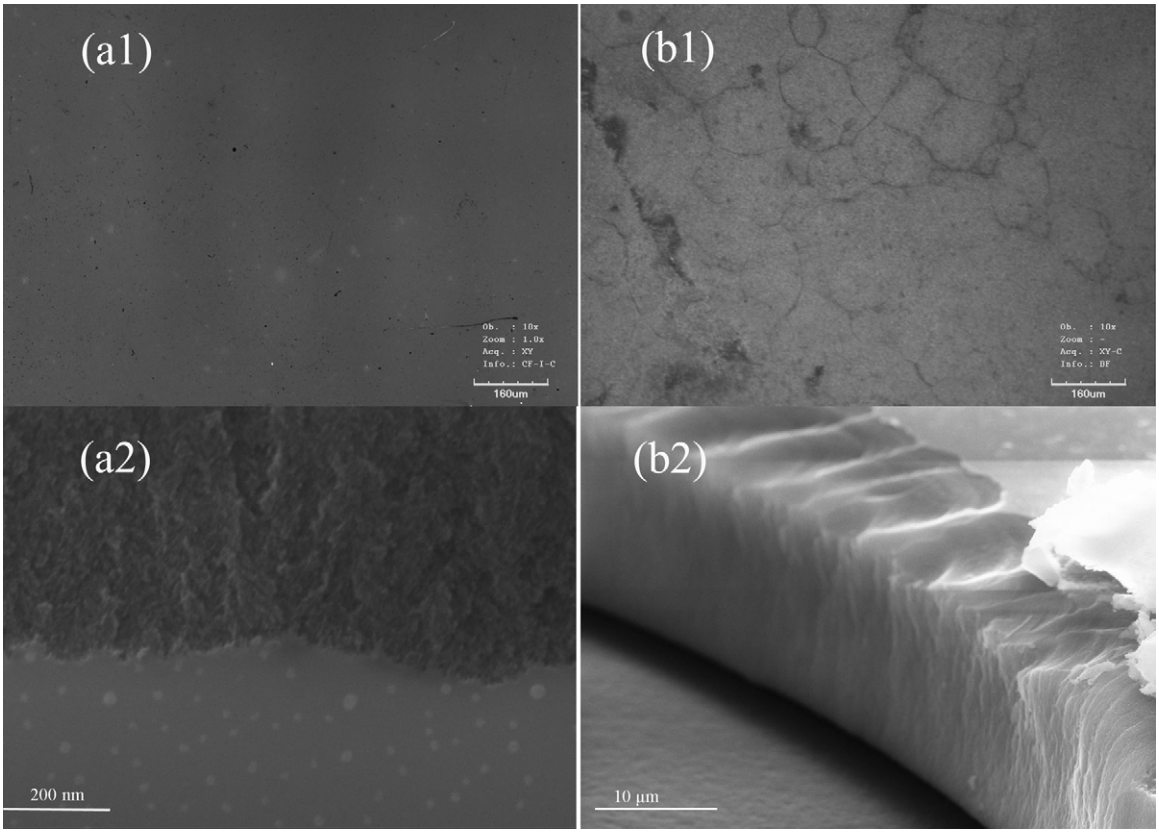

Fig. 2. FESEM images of uncracked and cracked PS thick films: (a) uncracked PS thick films and (b) cracked PS films.