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Nanoporous Silicon Materials Achieved by Electrochemical Method and Applications

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ABSTRACT

Nanoporous materials have attracted extremely intense scientific attraction since the photoluminescence discovery at room temperature because of the quantum confinement effects. It is well known that in addition to the superior photoluminescence, nanoporous silicon materials prepared by the electrochemical method are promising materials for applications in catalysis, chemical, energy storage and biological sensing, due to its high porosity, modifiable surface, biocompatibility and biodegradability, which comprise with tunable optical porous Si structure and the applications such as biosensing, in vivo imaging, gas sensing and solar cells.

Therefore, the facile electrochemical methods employed to synthesize the nanoporous materials are marked, especially for nanoporous silicon materials aim to provide the crucial information about the relevant techniques to consider the eco-friendly developments for the future environmental risks to diminish.

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Introduction

Recent years, the huge scientific research effort has been put into nanotechnology, and with the development of nanotechnology, the technology related to human is dramatically changed, even included an extensively profound influence on our daily life. It is well known that nanoporous materials are a subset of nanotechnology, which is also a signifcant class with captivating applications such as sensors, drug delivery, catalysis, electrodes and molecular separation [1-16]. To date, the applications of nanoporous materials related to the biomedical have been extensively explored owing to its unique properties (such as tunable size of pores, large volume of pores, high specific surface area, feasible surface modification and chemical stability, etc.). Meanwhile, the structures of nanoporous materials also have fascinating conducting, magnetic and fluorescent properties resulted in attracting the abovementioned biomedical applications, for instance, optical sensors, electrochemical sensors, biomolecule determination, targeted therapy, drug encapsulation, controlled drug release, drug solubility improvement, theranostics, magnetic resonance imaging, fluorescent imaging, enzyme immobilization, gene transfer, nucleic acid protection, proteome analysis, adjuvants, implants, regeneration medicine, tissue engineering, etc.

It often defines the highly porous nanostructure with pore sizes ranging from a few nanometers to one hundred nanometers as nanoporous material. In line with the requirements of the International Union of Pure and Applied Chemistry (IUPAS), it can be categorized into three different types of pore on the basis of the diameter of pore: nanopores (< 2 nm), mesopores, 2 nm <pore size < 50 nm and macropores (> 50 nm). On such nanoscale, the nanoporous materials possess a series of the unique properties (such as quantum confinement effect, plasmonic, high surface to volume area and photonic etc. which are closely related to the materials [9,14,17-28]. Up to now, many efforts have been devoted to exploring different porous materials such as metal, ceramic, semi-conductor and organic [29-40].

Because of the contribution to the state-of-art synthesis strategies, bulk materials can be taken for preparing the porous materials with the cutting-edge techniques. Numerous types of pore morphologies along with the well-developed nanostructures have been proposed. Generally, pore morphologies consist of open pores which display a connection throughout the structure to the surface of the materials. Moreover, many different attractive pore shapes have been developed such as spherical, triangular, cylinder and sponge-like, etc. [41-48]. Furthermore, some nanostructured pores with the special characters, for instance, in the sinusoidal and wavy form can be explored with various controllable output waveforms fabricated by the electrochemical methods [49,50].

Methods for Synthesis of Nanoporous Materials

Etching-Dealloying

Etching such as dealloying process refers to a chemical process in which the alloy is partially dissolved by the selective etching [51]. In the alloys' system, a less noble element is dissolved by the etchants and leaves behind a noble alloy constituent and an open nanoporous structure. The evolution of nanoporosity during the dealloying has been explored with the relevant results published in Nature [52]. Study shows that the gold atoms are not dissolved and tend to cluster together to form Au islands, it opens up the pore and etches continuously throughout the bulk structure. Finally, the sponge-like porous Au is obtained after etching. Recently, fabricated a kind of nanoporous Au structures by dealloying Au/Ag. By HNO_3 dealloying etching, the particles nanoporous keep the shape and the density of the surface density successfully along with the particles volume shrinking to some extent resulted in the lattice defects and the plastic deformation of Au crystal structure [22]. It also indicates that the dealloying process is more efficient on the particles obtained by the liquid state process to obtain a more homogeneity of the AuAg alloy forming the particles.

Etching-Electrochemical Etching

In general, electrochemical etching is a common top-down approach to fabricate nanoporous materials. In electrolyte in two or three electrode configurations using a potenetiostat in this procedure, the bulk material is usually electrochemically etched, where by an applied voltage or current the pore is formed. The surface of the bulk materials reacts with the electrolyte (the etchants) to generate the pore structure and such reaction usually begins in the defect sites of the surface. Literature related to nanoporous materials by the electrochemical etching has been published: porous silicon (pSi), porous Ni, porous titania and porous alumina [4,11,53-61].

Templating Method

Templating method is a technique adopted to prepare porous materials by a sacrifice mold and fill with the target precursors into its void space. Generally, the electrochemical reduction or calcination is usually taken in order to turn it into the solid phase. Many materials such as porous silicon (pSi), porous anodic alumina can be taken as the sacrificial template [62,63]. In addition, due to the cylindrical pores in the porous anodic alumina, they can be filled with other materials to easily fabricate the well-defined nanorod or nanotube arrays [64]. Also, the photonic porous silicon with the rugated structure can be replicated its structure by filling other materials into the porous silicon e.g. metal and polymer [65-68]. It should be noted that other templating method such as the nanosphere lithography is a technique of the application of the nanospheres (silica or polystyrene) with diameter about 100 nm to 1 μm [69,70]. At the initial, the nanospheres are self-assembled by different methods involved the spincoating and the dipcoating on the substrate to form the ordered hexagonal structures. The structures can be a monolayer or a structure with three dimensions. The fabricated nanosphere nanostructure can be adopted as a template that can be filled into the void with various kinds of the materials afterwards (for instance filled the metal by the electrodeposition processing). In the process of the electrodeposition, metal ions in an electrolyte are reduced to metal and filled into the interstices of the nanosphere template. Subsequently, the nanosphere can be removed by the dissolution or calcination to obtain porous materials with the desired characteristics.

3 Porous Silicon (pSi)

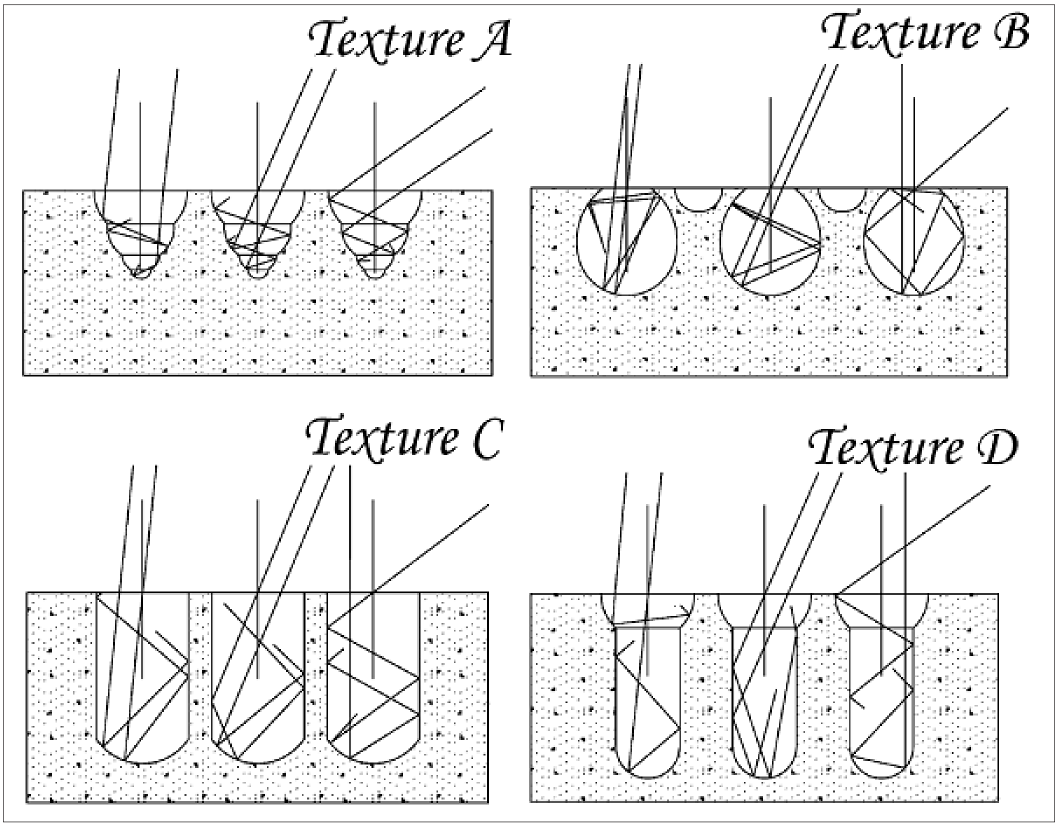

Figure 1: Different Geometrical Models with Macroporus Silicon Layers

The texture beneficial to the cost-effective solar cells can be achieved easily by chemical and electrochemical etching (as shown in Figure 1) with the multidimensional and multilayers macroporous crater-like surface. Also, the correlated mathematical model of the macroporous silicon of the real layer was explored [71].

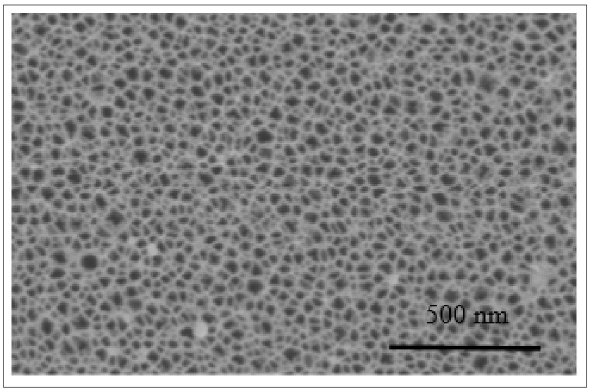

Figure 2a: Top view

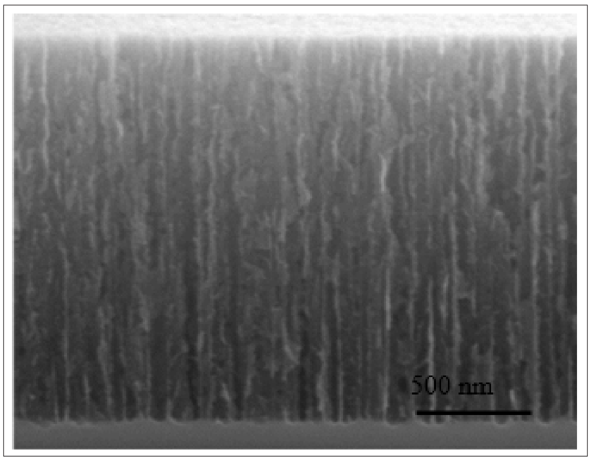

Figure 2b: Cross Section

Figure 2: FESEM images (a) top view (b) cross section of the porous silicon etched by ozone oxidization Porous silicon (pSi) has attracted the intense scientific research focus significantly since the discovery of photoluminescence at room temperature due to its quantum confinement effects [72,73]. In addition to the photoluminescence of pSi, the applications (biosensing, in vivo imaging and gas sensing of other properties (high porosity, tailorable surface, biocompatibility and biodegradability) of pSi have been well exploited [74]. Moreover, in the reflectance spectra the particular optical characteristics of pSi is extremely crucial to develop pSi-based sensor. It is well known that the single layer pSi displays Fabry-Pérot fringes and the modulated pSi multilayers with the waveform can fabricate into optical nanostructures for example Bragg stacks and rugated filters [75,76].

The top view and cross section images of the porous silicon etched by ozone oxidization at ozone of 1.5 SCFH for 20 min is shown in Figure 2. It shows that the pSi possess the high porosity with long and straight pores of the average diameter at 37 nm.

Synthesis strategies for pSi

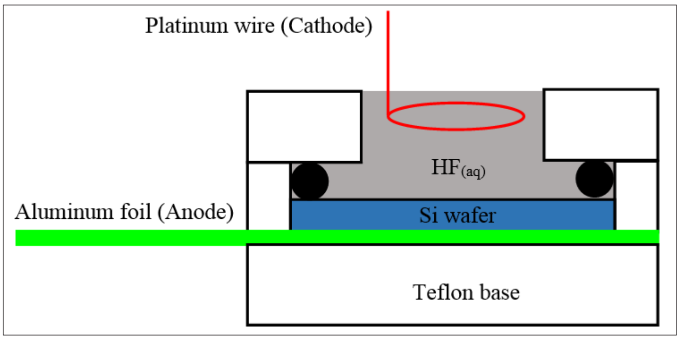

Figure 3: Schematic Drawing of Electrochemical Etching Process for Porous Silicon

Porous silicon is usually fabricated by the electrochemical etching process on the crystalline silicon wafer in aqueous hydrofluoric acid (HF) connected to potentiostat as shown in Figure 3. Usually pSi samples are fabricated with the silicon wafer in a solution of 48% aqueous HF: ethanol (3:1). For increasing the wettability, ethanol is commonly added to the etchant to enhance the etchant infiltration and reduce the bubble formation. The mechanism of pore formation related to silicon etching is expressed as follows [77].

$$Si+6HF+2hole+ \rightarrow H_2SiF_6+2H++H_2$$

Porous Silicon for Bioengineering-Biosensor

The attractive tunable pore sizes along with various optical nanostructures make the porous silicon a definitely promising candidate for bioengineering, especially in field of the biological sensing. One of the captivating biosensor is researched on the basis of the optical feature of pSi - an optical interferometric biosensor. The contribution of such pSi-based optical interferometric biosensor is based on Fabry–Pérot fringes which are the result of the peak maxima and minima of the reflection spectrum constructed by the constructive and destructive interference of the reflecting light from the top and the bottom of porous silicon layer. Results show that the change in the refractive index of the porous silicon matrix, as the peak shift of the effective optical thickness in the reflectance spectrum can be easily detected by the charge-coupled device (CCD) [78-83].

Porous Silicon for Solar Energy Applications

It is all well-known that in the field of photovoltaics pSi materials have attracted much attention, especially for solar cells. The relevant advantages are listed as follows: (1) Ease and low-cost fabricating pSi. (2) Tuning the band gap from 1.47 to 1.8 eV by controlling the density of pores along with optimizing the sunlight absorption. (3) Enhancing light trapping and reduce reflection loss with increasing the short circuit current. (4) Converting solar radiation of shorter wavelengths into longer wavelength photons which absorbed more efficiently by bulk Si [84,85]. More attractively all reported that the achieved efficiencies are over 20%, which one employed group IV reverse graded buffer layers grown on Ge/Si virtual substrates with a subsurface silicon porous layer to develop a GaAsP/SiGe tandem solar cell [86,87]. And the latter took the silver assisted wet chemical etching to implement a simple and fast etching process yet effective for nano-scale texturing of mc-Si surface.

Conclusion

Due to the ease and quick fabrication by the electrochemical methods, the porous silicon (pSi) has the attractive optical properties with the controllable and tuneable porosity and pore size along with the enhanced morphological properties of the large internal surface area and the versatile surface chemistry. Owing to such unique properties of nanoporous materials (high porosity, modifiable surface, good biocompatibility and biodegradability), the nanoporous silicon materials prepared by the electrochemical methods will play more and more significant role in the field of catalysis, chemical, energy storage, gas sensing, biological sensing and in vivo imaging. Moreover, the above-mentioned captivating properties of pSi fabricated by the electrochemical methods definitely make the porous silicon a promising candidate for solar energy applications in the coming future. Meanwhile, for the future environmental risks and the sustainable development, the eco-friendly techniques shall be explored further because of the chemical usage [88-99].

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