Research Article

Facile Synthesis of Nanoporous Amorphous Silica on Silicon Substrate

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Large-scale nanoporous amorphous silica nanostructure is fabricated via a simply etched approach and effective thermal evaporation process. The nanoporous amorphous silica was synthesized by a general and scalable process via etching by metal particles on the silica sheets. In this study, we elucidated how a nanoporous structure was performed and the addition of indium is the key factor that determined the formation of the nanoporous structures. The morphology and the sizes of the porous structure could be tunable by the sizes and the shape of the metal. We discovered a promising optical property in the as-synthesized nanostructures, which have a photoluminescence in an intensive ultraviolet emission as well as a broad visible emission at room temperature.

1. Introduction

Silica materials exhibit unique physical, mechanical, and chemical properties that make them attractive, for example, for heterogeneous catalysis [1–3], drug delivery [4], and composites [5]. Amorphous silica networks [6, 7] have a high surface area, low density [6], good dispersity, and unique morphology which could be widely used in the application of gas and liquid separation [8] and catalysis carrier [9]. The common method to get amorphous silica network is CVD and sol-gel process [10–13]. However, it is difficult to get pure inorganic oxides in the amorphous silica networks acquired by the sol-gel process, which includes the hydrolytic polycondensation of appropriate liquid precursors [14–16]. The obtained amorphous silica always contains hydroxyl (-OH) and ethoxy (-OCH2CH3) groups, and the structure is chemically instable because of the condensation of the remaining OH group. The pore size of an amorphous silica film by the sol-gel process is determined by the polymeric and colloidal routes, which is still a challenge to obtain pores of small size. And the sol-gel process uses high-cost precursors such as tetraethoxysilane (TEOS) and the drying of the gels, which is hard to get large-scale production [13]. A simple method to produce pure porous silica is essential for a number of applications [2, 17, 18].

The pore engineering on graphene sheets through carbothermal reaction provides a universal and economical
method for the synthesis of porous nanostructures [19]. Herein, we demonstrate a simple and scalable approach to the fabrication of large-scale, nanoporous amorphous silica structure. The nanoporous amorphous silica is formed via metal droplet etching that resulted in the vacancy formation. And the as-synthesized nanostructures have a strong ultraviolet emission in photoluminescence spectrum at room temperature.

2. Experimental

First, the nickel films were deposited on the silicon substrate by a high-vacuum magnetron sputtering systems. Before being deposited, silicon substrate is cleaned by acetone in an ultrasonic bath for 10 min, rinsed with isopropanol, and dried with argon. The deposition time of the nickel films is 20 min, and the constant power density of the nickel target is 5.3 W/cm². The gas pressure was maintained at 1.0 Pa during deposition, and Ar flow rate was adjusted to 100 SCCM. The silicon substrate covered with nickel film and indium powder was annealed at 1000°C for 3 hours. The pressure during the heat treatment was 0.001 Pa, and we naturally cooled the sample to room temperature in the furnace.

The morphology of the samples was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The samples were characterized using a TEM (Tecnai G2 F30, operated at 300kV) and SEM (Helios Nanolab 660i, operated at 20kV). The structure of samples was analyzed using grazing incidence X-ray diffractometer (GIXRD, PANalytical X'Pert ProCu Kα). The sample for TEM was dispersed using ultrasonic dispersion. The Raman spectrum of the samples was measured using a He-Cd laser with an excitation wavelength of 325 nm at room temperature.

3. Results and Discussion

3.1. Structure and Morphology Characterization. Figures 1(a) and 1(b) are the typical SEM images of the obtained silica film. Large-scale porous nanostructures with foam-like morphology were stacked on the silicon substrate. The nanoporous film with thickness from several tens of nanometers up to 1 μm and size can be scaled up by enlarging the silicon substrate. The pores in the network are not uniform, and the sizes of the pores vary from several nanometers to hundreds of nanometers. There is a direct relationship between the sizes of the pores and the diameters of the particles inside the holes. The statistical analysis of the size distributions for the particles and the corresponding holes indicates that the diameters of the particles inside and the sizes of the corresponding pores are linear. The pores always have similar shape like the particles inside. And the area of porous nanostructure decreased with the amount of particles increasing. The histogram shows that the majority of the particles have a diameter in range of 10 nm-400 nm. However, we cannot observe some particles in the smaller pores because the small particles are easy to be removed or covered by the silica films. There are two or more particles in the large holes. The results reveals that the particles are the determining factor in the formation of the nanoporous structure and it is possible to tune pore sizes and morphology of the nanostructure by tailoring the sizes and shape of particles. It is shown that the diameters of most droplets are within a range of 10-300 nm in the SEM image and the element ratio of the particle is Ni : In = 2 : 3 characterized by EDS. The results show that the formed Ni3In3 alloy particles have the diameters of tens of nanometers and a crucial effect on the formation of porous structures. The formation mechanism of the porous nanostructure will be discussed in the following section.

Figures 2(a) and 2(b) shows the TEM images of the nanoporous film. It is obvious that the nanostructure has network-like morphology. The porous nanostructure is composed of multilayer films with nanoporous structure, and the edges of the films reel up to a nanotube marked by an arrow in Figure 2(a). The particles which are shown from the SEM image are not observed in TEM images. Because the samples for TEM have been dispersed by ultrasonic dispersion, maybe the particles are gone during this process. It revealed that it is easy to remove the particles for pure porous amorphous silica by ultrasonic dispersion. No crystal structure was found in the high-resolution transmission electron microscopy mode, which suggests that the films are amorphous. It is demonstrated that the porous nanostructure includes silicon, oxygen, and copper that comes from the grid by EDS. Figure 3(a) is the XRD pattern of the porous nanostructures. The XRD pattern shows that the sample is amorphous in a 15°-35° region. The broad peak in the range of 15° to 30° in the XRD pattern always confirms that the silica is amorphous [20]. The small diffraction peak corresponds to the silicon substrate, and the other peaks could not be distinguished for the XRD pattern because of the broad amorphous peak. The SAED image of the porous nanostructures is shown in Figure 2(c). There is not any trace of crystal structure, and the highly diffusive ring pattern indicates that the structure is of a completely amorphous state. The result from the SEAD was in accord with TEM and EDS analysis of the porous compositions that indicated that the nanostructure contains only silicon and oxygen elements.

The photoluminescence (PL) spectrum of porous amorphous silica films is showed in Figure 3(b), excited by 325 nm wavelength. The porous silica has a broadband spectrum from ultraviolet to visible light. There are a sharp peak located at 358 nm (3.46 eV) and a broad peak in the 450 nm to 650 nm band. It is proposed that two folded coordination silicon lone pair centers (O-Si-O) and neutral oxygen vacancies (=Si-Si≡) are the sources of amorphous silica [21]. It has been indicated that the silica exhibits visible PL emission under UV excitation, resulting from the nonbridging oxygen hole centers and hydrogen-related species on the surface of silica [22–24]. These defects are clearly caused by the amorphous structure of the samples. These structure defects can be radiative recombination centers, and ultraviolet light emission in annealed SiO2 is already observed [21]. So the intensive ultraviolet light
emission from the porous amorphous silica is attributable to Si-O defects [25]. The ultraviolet emission silica films may be potentially used as promising UV laser emitters.

3.2. Growth Mechanism. In this study, most of the nanoporous nanostructures were presence of alloy particles in the pores as shown in Figure 1, indicating that nanoporous silica is etched by the metal nanoparticles; nanoscaled pores are generated on the silica film. To better explain the growth mechanism of the nanoporous silica, the possible mechanism of the porous amorphous nanostructure is proposed in Figure 4. The porous silica film is caused by Ni-In metal particles interspersed on its surface. In was liquefied at 157°C that is absorbed by nickel, and Ni$_2$In$_3$ is formed above 448°C. The melting temperature of Ni$_2$In$_3$ is 448°C; therefore, it is in a liquid form in the temperature of 1000°C. The heating process is long enough to reach saturation, and indium power is easy to evaporate during the thermal process. The oxygen atoms remaining in the low vacuum can form SiO$_2$ with silicon atoms at high temperature. Simultaneously, the indium atoms from the indium powder reacted with nickel to form Ni-In spherical island that resulted from the effect of the surface tension. The Si-O atoms are difficult to crystallize at low temperature, leading to the formation of the amorphous silica rather than crystalline silica. Nanoscaled pores could be observed under nanoparticles, validating the pore generation through the etching by the metal nanoparticles. The Ni$_2$In$_3$ alloy and silica are to a certain extent immiscible that EDS analysis indicated that the particles are only including Ni and In elements. The Ni$_2$In$_3$ alloy can be removed easily and leave a stable and porous phase left. Indium is critical for the formation of porous silica, and the obtained nanostructure could be nanowire with Ni-Si alloy at the top of the wire, if no catalyst indium was added during thermal process in our previous literatures [26, 27].

4. Conclusion

In this study, we demonstrated a feasible method to produce nanoporous amorphous silica by using the alloy particles as
nanoscale etcher. The pore sizes varied from hundreds to several tens of nanometers, and the thickness of nanostructures is up to micrometers. The alloy droplet is the key factor that determined the formation of the nanoporous silica, and the sizes of the pores are linear with those of the alloy droplet insides. The amorphous silica has a strong peak in the

Figure 2: (a, b) TEM images of nanoporous silica. (c) The SAED of nanoporous silica. (d) The EDS analysis of the nanoporous silica.

Figure 3: (a) XRD pattern of nanoporous silica networks. (b) The PL spectrum of obtained simples.
ultraviolet band and a weak visible peak that may be caused by the defect centers in amorphous silica. The porous amorphous silica films would be a good UV emitter in applications such as light-emitting diodes or displays.

Data Availability

All the data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Luo Hui and Huang Yongquan contributed equally to this work.

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