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Fabrication, characterization, cathodoluminescence, and field-emission properties of silica (SiO_2) nanostructures

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ABSTRACT

High-quality one dimensional amorphous SiO_2 nanostructures with different morphologies (nanowires and starfish-like nanostructures) are synthesized through a simple catalysis-free approach and effective thermal evaporation process. The morphologies, microstructures, and compositions of the products are investigated by X-ray powder diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). A promising optical property (cathodoluminescence (CL) in a strong ultraviolet (UV) emission and a weak blue emission at room temperature) was detected in the as-synthesized nanostructures. Field-emission measurements show that the SiO_2 nanostructures may also be a promising FE emitter candidate if we can improve the conductivity and decrease the density of the nanostructures.

1. Introduction

Si-based nanoscale materials have attracted much attention in recent years due to their valuable semiconducting, mechanical, and optical properties, as well as their potential applications in mesoscopic research and nanodevices, such as one-dimensional quantum transistors, composites, and light-emitting diodes [1]. Recently, a variety of synthesis methods have been introduced, including chemical vapor deposition (CVD) [2,3], physical evaporation [4,5], sol–gel template method [6], carbon-assisted SiO_x nanowire growth [7–9], laser ablation technique [10], and so on, to synthesize versatile structures of SiO_2, such as nanowires, nanotubes, and regular spherical nanoparticles. Novel properties in the photoluminescence feature of stable ultraviolet (UV) emission and visible blue light from these SiO_2 nanowires have stimulated extensive interest, as it means that silica nanostructures could be utilized as promising photonic nanodevices (such as UV laser emitters) [11,12]. In another aspect, the SiO_2 nanowire is also considered as a good FE emitter because of its good chemical stability, high-aspect ratio and good compatibility with the Si devices; however, there have been fewer reports in regard to the field-emission (FE) properties of the SiO_2 nanowires [5].

Here, we describe a simple catalysis-free approach and effective thermal evaporation process at high temperature to synthesize silica nanostructures. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED) were used to characterize the structures, morphologies, and compositions of the samples. The cathodoluminescence and the field-emission (FE) were also used to investigate the optical and field emission properties.

2. Experimental Details

The synthesis of SiO_2 nanostructures was conducted in a vertical induction furnace, which consisted of a fused quartz

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tube and an induction-heated cylinder made of high-purity graphite coated with a carbon fiber thermo-insulating layer as shown in Fig. 1. The commercial silicon substrate (diameter: 15 mm; conduction type: n-type; thickness: 400 μm; crystallography: one side of the wafer was polished and orientated at <100> direction) was cleaned carefully using ultrasonic in alcohol and distilled water, separately, for 30 min, then the Si substrate was put directly on the top of the BN crucible (the polished side of the Si substrate faced downward and the unpolished side faced upwards, shown in Fig. 1). After the furnace was evacuated for 1 h (generally, the vacuum reaches around 6–8 pa), the crucible was subsequently heated to 1700 °C and kept for 3 h. Then the furnace was cooled to room temperature naturally. Large quantity of white thin films could be directly seen on the polished sides of the Si substrate.

The as-prepared products were analyzed by using powder X-ray powder diffraction measurements (PINT-ULTIMA) with CuKα1 radiation (λ=0.15406 nm), a Raman spectrometry (Horiba Jobin-Yoon T6400), a scanning electron microscope (SEM; JEOL, JSM-6700F) and a high-resolution field emission transmission electron microscope (TEM; JEOL, JEM-3000F) equipped with energy-dispersive X-ray analysis (EDX). After the structural and chemical examinations, spatially resolved CL measurements on SiO_2 nanostructures were carried out. CL spectra from the bundle and individual nanostructures were collected with a high-resolution CL system at an accelerating voltage of 10 kV and a current of 1.6 nA by using a scanning electron microscope (HITACHI S4200) with a field emission electron gun equipped with a CL system. The pressure in the specimen chamber was 10^{-4} Pa. All CL SEM-images and spectra were collected at room temperature under the same conditions. Also, the field-emission properties were studied at room-temperature in a high vacuum chamber (7×10^{-6} Pa) using a 1 mm^2 cross-section area copper anode. A dc voltage sweeping from 100 V to 1100 V was applied to the samples with a step of 10 V and a sampling time of 1 s.

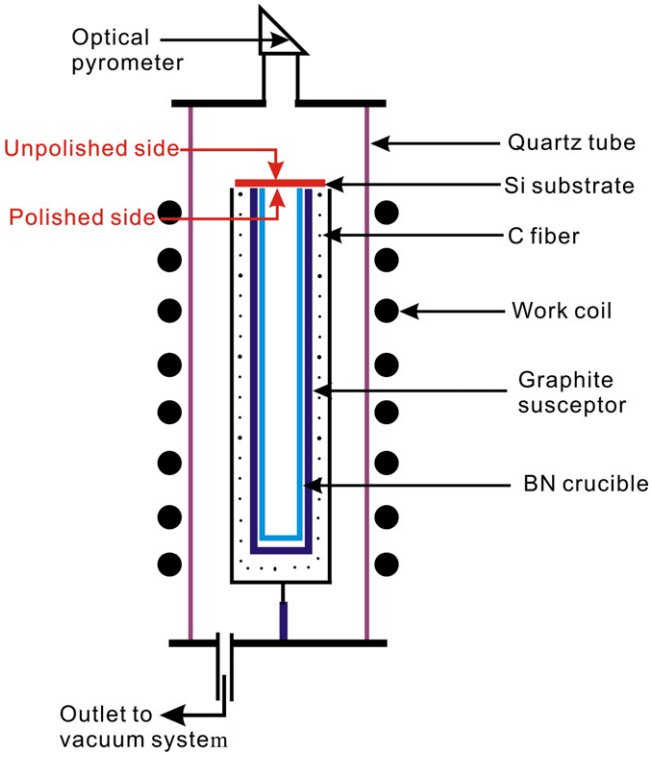

Fig. 1 – Apparatus for the synthesis of the SiO_2 nanostructures.

3. Results and Discussion

The X-ray diffraction (patterns) performed for the bundle of SiO_2 nanowires on silicon substrate are shown in Fig. 2(a). The sharp peaks are consistent with the standard orthorhombic end-centered cubic cell silicon (JCPDS 89-9056), which may be attributed to the exposure of some crystal faces from the Si substrates due to the thermal evaporation. The increased noise signals are probably coming from the amorphous body of the SiO_2 nanostructures; especially, a broad peak centered at about 22.5° may possibly relate to crystallographic direction and originate from the amorphous SiO_2. Fig. 2(b) displays the room-temperature Raman spectrum of the bundle of SiO_2 nanostructures which exhibits a broad peak at around 411 cm^{-1} and a steam-like peak at 700 cm^{-1}. Previously, Yu et al. [10] reported that the Raman spectrum of amorphous silica nanowires has two broad peaks located at approximately 450 cm^{-1} and 790 cm^{-1}, respectively; Goller et al. [13] found that the SiO_2 Raman spectrum of amorphous silica powders contains three peaks at 450 cm^{-1}, 480 cm^{-1} and 800 cm^{-1}; Li et al. [14] reported two steam-like peaks located at 430 cm^{-1} and at 790 cm^{-1}, respectively, from the nano-SiO_2 wires. Compared with the above literature, in our experiment, there is some shift in the peak location, which may be due

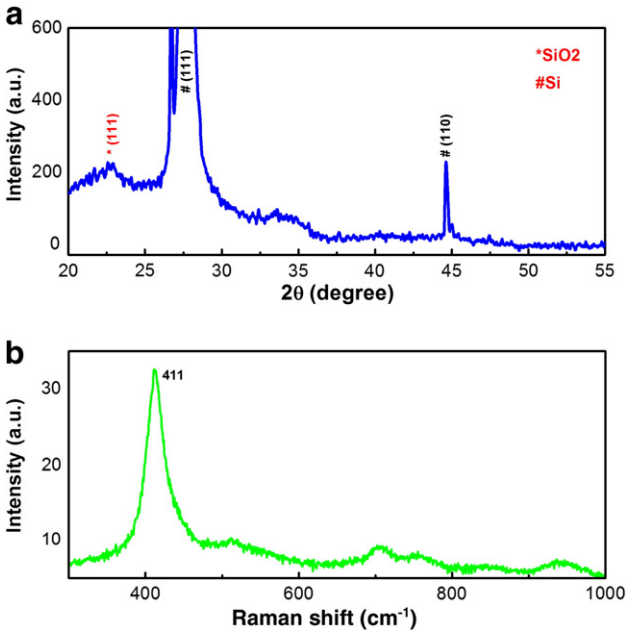

Fig. 2 – (a) X-ray diffraction of the bundle of SiO_2 nanostructures on the Si substrates; (b) Raman spectrum of the bundle of SiO_2 nanostructures at room temperatures on the Si substrates.