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Large-scale fabrication of sunflowers-like ZnO nanostructures on patterned sapphire by aqueous solutions

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Large-scale sunflower-like ZnO nanostructures are synthesized on the patterned sapphire by aqueous solutions. Due to the geometry of patterned sapphire, ZnO nanostructures are grown along the upper base and sidewall region on the frustum of a cone shaped sapphire forming sunflower-like morphology as a whole. Photo-fluorescence luminance (PL) spectrum of the sunflower-like nanostructures shows an excellent luminescence property. The large-scale periodical sunflower-like characteristics, make them useful for potential applications in ultra-sensitive gas sensing and exciton based photonic devices.

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Keywords: ZnO, Sunflowers-like ZnO nanostructures, Aqueous solutions

1. Introduction

One-dimensional (1D) ZnO nanostructures have been attracted much attention over the past few years due to their novel properties and the potential applications in optoelectronics and device miniaturization [1-6]. Well-controlled growth of the nanomaterials is essential to the production of nanodevices. [7-9]. Up to now, nanostructures of ZnO including prismatic, needle-like, ellipsoidal, tetrapod-like, nanorod, nanofiber, nanobelts, and nanotubes have been prepared by various physical and chemical methods[10-16]. Among these methods, vapor–liquid–solid, chemical vapor deposition, and thermal evaporation are the three major vapor methods to fabricate these materials. However, complex procedures, sophisticated equipments, or rigid experimental conditions are involved in these vapor methods. In addition to these methods, solution chemical route including solvothermal, hydrothermal, self-assembly, and template-assisted sol–gel process became a promising option for large-scale production nanoscale materials due to the simple, fast, and less expensive virtues [17-18]. Noteworthy, in order to enhance the multi-functionality and tailor aesthetic morphologies, synthesis of complex nanostructures especially nanoflowers have attracted many researchers. However, to our knowledge, large-scale fabrication of periodical ZnO sunflowers with prominent optical properties prepared by solution chemical routes has not been reported till now.

In this paper, patterned sapphire is used to grow sunflower-like ZnO nanostructures through simple aqueous solutions. Due to the geometry of patterned sapphire, ZnO nanostructures are grown along the upper base and sidewall region on the frustum of a cone shaped sapphire forming sunflower-like morphology as a whole. Photo-fluorescence luminance (PL) spectrum of the sunflower-like nanostructures shows excellent luminescence properties.

2. Experimental

The patterned sapphire substrates were obtained by standard photolithography combining with inductively-coupled plasma etching. Structural characteristics of as-grown ZnO nanostructures were investigated using X-ray diffraction (XRD). Field emission scanning electron microscopy (FE-SEM Hitachi S-4800) were used to investigate the morphology. Room temperature photoluminescence(PL) was performed using ACCENT RPM4000 with excited wavelength of 266 nm laser as the excitation source.

To fabricate periodically patterned sapphire substrate, a 150-nm-thick nickel (Ni) layer was deposited by E-beam evaporation on top of the sapphire substrate. The dimension of the frustum of a cone (R=5μm r=4μm, R is the radius of the lower base and r the radius of the upper base, spacing=1.5μm) was fabricated using a standard photolithography process and inductively-coupled-plasma etching. The Ni mask was finally removed to complete the frustum of a cone patterned structure. The ZnO seeding layer was deposited on patterned sapphire by radio frequency(RF) magnetron sputtering at room temperature for 5 min. Then the ZnO seed-coated substrate was heated to 400°C in air for 5 min. In a typical experiment an equimolar(0.05M) aqueous solution of zinc acetate [$Zn(C_2H_3O_2)_2$] and hexamethyltetramine($C_6H_{12}N_4$) was prepared. All chemical reagents in the experiments were of analytical grade(AR) and used without further purification. The seeded sapphire substrate was putted into the above solution of 95°C for 5h. After deposition, the sample was cleaned with deionized water and then dried in an air atmosphere.

3. Results and discussion

Fig. 1 (a)-(c) show the typical FE-SEM images of the patterned sapphire. Fig.1(a) displays pattern sapphire with low magnification. Fig.1(b) and (c) corresponds to the single unit of the patterned sapphire with top-view and cross-section view respectively. As can be seen from the figure, the distribution of patterns is very regular, and the shapes and sizes of the patterns are uniform.

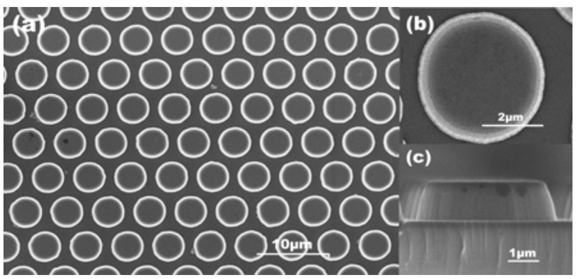

Fig. 1. Typical SEM images of the periodically patterned sapphire. (a) The surface morphology of the periodically patterned sapphire with low magnifaction (b) (c) Top-view and cross-sectional SEM image of the single unit.

Fig. 2 shows the XRD pattern of the nanostructures. Two obvious diffraction peaks are shown, which match the hexagonal structure of wurtzite ZnO according to the standard card (JCPDS 36-1451). And the peaks correspond to the $(10\bar{1}0)$, and $(11\bar{2}0)$ facets in the wurzite ZnO structure. Meanwhile, the (0002) diffraction peak is much sharper and stronger, indicating the ZnO cystallites are highly oriented with their c-axis being perpendicular to the sapphire substrate. The presence of $(10\bar{1}0)$ peak is due to the designed patterned sapphire make the nanostructures grow along the frustum of a cone upper base and sidewall after precoating ZnO seeding layer.

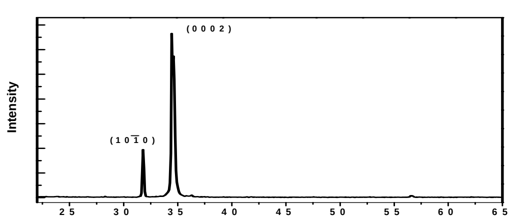

Fig. 2. Typical XRD pattern of the nanostructures.

Fig. 3 (a) displays the ZnO nanostructures grown on patterned sapphire with low magnification. The nanostructures show sunflower-like nanoarrays morphology and distribute regular along the patterned sapphire. The patterned sapphire direct ZnO to form sunflower-like nanostructures due to the multiple nucleation on the frustum of a cone surface. It is known that the nucleation on bare and smooth substrates requires relatively higher energy (or supersaturation degree) than the crystal growth. The presence of precoated ZnO seeding layer can eliminate this process, thus maintain higher supersaturation degree during the crystal growth. Hence obtained ZnO nanostructures exhibit higher crystallinity. Fig. 3(b) is the image of a ZnO nanoflower with high magnification. From the enlarged image, each flower is composed of nanorods along the top base and sidewall of the frustum of a cone. The nanorods are around 1μm in length and diameter about 100-200 nm. Meanwhile, some larger nanorods with diameter around 400 nm surround the edge of top base forming by self-organized growth.

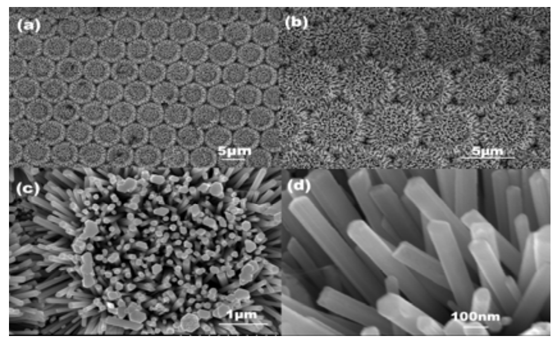

Fig. 3. FE-SEM images of ZnO (a) overall morphology at low resolution (5000×). (b)(c) High magnification image view of a typical sunflower-like ZnO on the top surface and sidewall.

The optical properties of the ZnO nanostructures were studied by means of room temperature PL measurement. The typical PL spectrum is shown in Fig. 4. The PL spectrum is characterized by two emissions, a strong and dominant sharp peak around 380 nm with a narrow FWHM value of 13.62 meV and a negligibly weak, broad peak centered around 650 nm. The peak observed at around 380 nm in the UV region is due to free exciton emissions, while the weak, broad peak in the visible region is attributed to deep level emissions, which are associated with oxygen vacancies, and interstitial zinc or zinc vacancies [19-20]. The strong UV and weak green bands imply good crystal quality and low concentration of defects in the ZnO nanostructures.

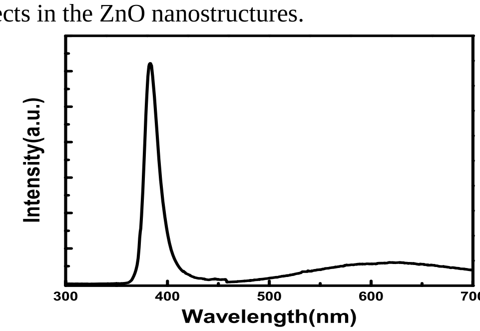

Fig. 4. Typical PL spectra of ZnO sunflower-like nanostructures using 266 nm laser as a source excitation.

4. Conclusions

In summery, we have synthesized sunflower-like ZnO nanostructures on patterned sapphire through simple aqueous solutions. ZnO nanostructures are grown along the upper base and sidewall region on the frustum of a cone shaped sapphire forming sunflower-like morphology as a whole. The large-scale sunflower-like characteristics, make them potential applications in ultra-sensitive gas sensing and exciton based photonic devices.

Acknowledgments

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