Hydrothermal synthesis and photoluminescence properties of SnO2 nanowire array and pinecone-like nanoparticles on ITO substrate

Junfeng Yan *, Manzhang Xu, Fengjiao Zhang, Xiongfei Ruan, Jiangni Yun, Zhiyong Zhang *, Fuyou Liao

School of Information Science and Technology, Northwest University, Xi’an 710127, PR China

A R T I C L E   I N F O

Article history:
Received 25 September 2015
Received in revised form
11 November 2015
Accepted 18 November 2015
Available online 23 November 2015

Keywords:
Nanoparticles
Nanowire array
Hydrothermal method
Luminescence
Crystal structure

A B S T R A C T

The SnO2 nanowire array and pinecone-like nanoparticles were synthesized on the indium tin oxide (ITO) substrate via a simple hydrothermal process. The microstructure and morphology of the samples indicated that both nanowire array and pinecone-like nanoparticles were composed of rutile SnO2 nanowires. Furthermore, a reasonable growth mechanism of SnO2 nanowire array and pinecone-like nanoparticles was proposed, and the molar concentration ratio of NaOH to SnCl4 of the precursor solution played a key role in the morphological evolution. Finally, the photoluminescence properties and the ultraviolet–visible absorbance spectrum were investigated. The band gap of SnO2 nanowire array was about 3.43 eV, which was consistent with the emission peak of PL spectrum.

1. Introduction

Metal-oxide semiconductor materials with one-dimensional (1D) nanostructure have attracted considerable interest due to their small sizes, high specific area and special physical and chemical properties [1]. Peculiarly, more attention has been paid to 1D well-ordered, aligned and dense nanoarray on a given substrate due to its superior performances and wider applications in light-emitting diodes [2], and Li-ion batteries [3] etc. SnO2 is an environmental friendly n-type metal-oxide semiconductor and numerous methods like chemical vapor deposition [4], template [5] and hydrothermal approaches have been proposed for the fabrication of SnO2 nanoarray motivated by its potential applications [6]. In particular, the hydrothermal process is increasingly important due to its low-cost and time-saving properties. In this respect, Liu et al. [7] reported a new paradigm that SnO2 nanorod array was prepared on large-area flexible metallic via hydrothermal process. Wang et al. [8,9] hydrothermally synthesized SnO2 nanoflower array on the indium tin oxide (ITO) substrate and SnO2 nanorod array on Ti substrate coated with a thin SnO2 buffer layer by magnetron sputtering method. Although a series of SnO2 1-D nanoarray has been successfully synthesized on various substrates, the fabrication of well-aligned, homogeneous and dense SnO2 nanowire array and pinecone-like nanoparticles directly grown on ITO substrates which has not been realized.

In this paper, SnO2 nanowire array and pinecone-like nanoparticles were firstly fabricated by hydrothermal method through altering the molar concentration ratio of NaOH to SnCl4 (alkali-salt-ratio) of the precursor solution. In addition, a reasonable growth mechanism of the samples was proposed, and their photoluminescence (PL) properties were discussed in detail.

2. Experimental

The SnO2 nanowire array was prepared through a simple hydrothermal process in an autoclave. In brief, NaOH solution (10.08 mmol) dripped into SnCl4·5H2O solution (0.84 mmol) drop by drop to form the precursor solution. Then, 28 ml of precursor solution was transferred into a 40 ml stainless steel Teflon lined autoclave. The ITO (10 × 10 mm2) was immersed into the precursor solution and was transferred into a 40 ml stainless steel autoclave. The ITO (10 × 10 mm2) was immersed into the precursor solution and was transferred into a 40 ml stainless steel autoclave. Finally, the ITO substrate was purged in deionized water for several times and dried in air for further characterization. The pinecone-like SnO2 nanoparticles were also obtained from 8.4 mmol of NaOH solution under the same experimental procedure.

The microstructure and morphology of the obtained products were characterized by x-ray diffraction (XRD, D/Max2550VB + PC, Rigaku, Japan), transmission electron microscope (TEM, JEM-3010, JEDL, Japan) and scanning electron microscopy (SEM, JEM-3010, JEDL, Japan), respectively. The photoluminescence (PL) properties...
were represented by the fluorescence spectrophotometer (Fluo-
oMax-4p, HORIBA Jobin Yvon, USA). The ultraviolet–visible (UV–vis) diffuse reflectance spectrum (DRS) was recorded with a UV–vis–NIR spectrophotometer (Cary 4000, VARIAN, USA).

3. Results and discussion

3.1. Microstructure and morphology

The crystal structure of the nanowire array and pinecone-like nanoparticles were determined by XRD patterns which are shown in Fig. 1. All the diffraction peaks were consistent with the index of the tetragonal rutile phase of SnO2 (space group P42/mnm (136), JCPDS file no. 41-1445). Except for the SnO2-related diffraction peaks, the diffraction peaks of the ITO substrate also could be observed.

Fig. 2 shows the SEM images of the as-prepared SnO2 nanos-
structures. The freestanding and homogeneous SnO2 nanowire was arranged neatly on the substrate, whose diameter was about 32 nm (Fig. 2a and b). Nevertheless, once the concentration of NaOH in precursor solution was decreased, for this reason a large scale of pinecone-like hierarchical structures with uniform morphology were formed on the substrate (Fig. 2c). Each piece of cone scale of the pinecone-like SnO2 nanoparticles was consisted of a bunch of nanowires with uniform diameter (32 nm) as shown in high-magnification SEM image Fig. 2d. Undeniably, the diameter of SnO2 nanowire array was slightly larger than that of pinecone-like hierarchical structures, suggesting that the concentration of NaOH in precursor solution played a key role for the morphological evolution.

The TEM images of the SnO2 nanowire array and pinecone-like nanoparticles are shown in Fig. 3. Fig. 3a and c confirm that the SnO2 nanowire array and pinecone-like nanoparticles were indeed composed of nanowires. The corresponding high-resolution transmission electron microscopy (HRTEM) images of the nanowire are shown in Fig. 3b and d, respectively. The spacing of the lattice fringes of the nanowire is about 0.329 nm and 0.336 nm, which can be indexed as the (110) plane of rutile SnO2, hence the nanowire of the as-prepared products all grow preferentially along [110] direction.

3.2. A reasonable growth mechanism

Based on the above characterizations, a reasonable growth mechanism of SnO2 nanowire array and pinecone-like nanoparticles can be proposed. The major reactions can be formulated as follows [10]:

\[ \text{Sn}^{4+} + 4\text{OH}^- \rightarrow \text{Sn(OH)}_4^{2-} \]  
\[ \text{Sn(OH)}_4^{2-} + 2\text{OH}^- \rightarrow \{\text{Sn(OH)}_6\}^{2-} \]  
\[ \{\text{Sn(OH)}_6\}^{2-} \rightarrow \text{SnO}_2 + 2\text{H}_2\text{O} + 2\text{OH}^- \]

SnO2 nanowire array and pinecone-like nanoparticles are formed with different nucleation mode. The former nucleates on the given substrate while the latter nucleates in space. When the alkali-salt-ratio is 10, the basic cells of crystalline growth [Sn (OH)] can fold together to form a multi-twin central nucleus. The multi-twin central nucleus is a spherical aggregate with multiple nuclei which can adjust their state under environmental driving force. On the one hand, under the environmental driving force, the multi-twin central nucleus can adjust to a two-dimensional circular surface. On the other hand, the two-dimensional multi-twin central nucleus can randomly absorb together by van der Waals force, accompanying with the nuclei growing along the preferred orientation in parallel with the normal of the two-dimensional circular surface. Thus, the pinecone-like SnO2 nanoparticles is obtained. However, once the alkali-salt-ratio is raised to 12, and the excessive OH ions can easily absorb on the surface of the nuclei. Under the action of coulomb repulsion, the nuclei does not form a spherical aggregate in the strong convection space but disperse homogeneously on the ITO substrate by Van der Waals force and grow preferentially along [110] direction to shape SnO2 nanowire array. For investigating the growth mechanism, a series of experiments were carried out along with an alkali-salt-ratio gradient from 10 to 13 and morphology evolution of SnO2 was clear and definite (see supplementary material).

3.3. Photoluminescence

The PL spectra of as-prepared products are measured with an excitation wavelength of 325 nm. Fig. 4a shows the PL spectra of the SnO2 nanowire array and pinecone-like SnO2 nanoparticles, and both of the spectra have been de-convoluted following Gaussian profile fitting. It can be seen from the PL spectrum of SnO2 nanowire array exhibiting a strong UV–vis light emission centered at 364 nm and a blue light emission band centered at 438 nm, which consist of four emission peaks centered at 364, 418, 452 and 504 nm. Compared with the pinecone-like SnO2 nanoparticles, the luminescence intensity is similar. Furthermore, an interesting phenomenon shows that there is a blue shift of 26 nm for all three visible emission peaks between the nanowire array and pinecone-like nanoparticles.

Broad luminescence bands from ultraviolet to visible light region have been reported from SnO2 nanostructures at room temperature [8,11–13]. The UV emission at 364 nm is near band edge emission and matched with the effective band gap calculated from the UV–vis absorbance spectrum, which was attributed to the surface localized exciton emission considered to originate from the radiative recombination of exciton at the surface region of the SnO2 [14,15]. However, the cone scale of pinecone-like SnO2 nanoparticles was consisted of a bunch of nanowires, which might reduce the surface of SnO2 and result in the decrease of the intensity centered 364 nm, even disappear. The emission peaks at 392 and 426 nm, which is consistent with the results of the literature [13,16,17] attributing to electron transition mediated by

![Fig. 1. XRD patterns of the SnO2 nanowire array (a) and pinecone-like nanoparticles (b).](image-url)
defects levels in the band gap (such as oxygen vacancies) and the luminescence centers formed by such tin interstitials or dangling in the as-prepared SnO₂ samples, respectively. The emission in the visible region at 478 nm is related to a shallow energy level, such as doubly ionized oxygen vacancies [13]. The blue shift for the three visible emission peaks of the nanowire array may be caused by different band gaps between pinecone-like nanoparticles and nanowire array due to the different morphologies and sizes [18].
While, the weak emission intensity of the pinecone-like SnO$_2$ nanoparticles may be caused by the abundant nonradiative action. The absorption of SnO$_2$ nanowire array is illustrated in Fig. 4b. The effective band gap values obtained from the UV–vis absorbance spectrum for the SnO$_2$ nanowire array is 3.43 eV (362 nm), which is in agreement with the emission peak of PL (364 nm).

4. Conclusions

In summary, SnO$_2$ nanowire array and pinecone-like nanoparticles have been fabricated via a simple hydrothermal process. The microstructures, morphology and room-temperature PL properties and UV–vis DRS have been characterized, and a reasonable growth mechanism has been proposed. It is found that the alkali-salt-ratio of the precursor solution plays a key role in the morphology evolution. The PL spectra of the pinecone-like SnO$_2$ nanoparticles and SnO$_2$ nanowire array exhibit a faint blue light emission centered at 436 nm and a strong UV–vis light emission centered at 364 nm and a blue light emission band centered at 438 nm, which is in agreement with the effective band gap values.

Acknowledgment

This work was supported by The National Natural Science Foundation of China (No. 61306009), the Key Project of Natural Science Foundation of Shaanxi Province (No. 2014JZ2-003), the Natural Science Foundation of Shaanxi Province (No. 2015JM6274) and the NWU Graduate Innovation and Creativity Funds (YZZ14117).

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2015.11.082.

References