

SELF-CATALYTIC FABRICATION OF ZnO MICRO- AND NANO-TETRAPODS

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Abstract: Tetrapod-like zinc oxide (ZnO) micro and nanorods were produced on oxidized silicon substrates by thermal evaporation of Zn/ZnO powder mixture. The synthesis procedures were carried out at 1050°C in air, and there is no any catalyst used. The fabricated ZnO tetrapods were quite uniform, high yield, good crystallinity, and especially had very strong UV and green photoluminescence at room temperature. The forming and photoluminescence mechanisms of the tetrapods were considered.

1. Introduction

ZnO has been realized as an excellent functional material for many fields of application. Novel superstructures of ZnO, such as nano comb-, propeller-, tetrapod-, teeth-like shapes [1-5], promise a great deal of interesting physical property, and can be used as special building blocks, components for micro/nanosystems. Recently, in the world, many attempts have been made to synthesize, characterize and apply ZnO tetrapod-like structures [2-5]. Authors of [2] found that the sintering temperature of their ZnO-glass varistors were evidently lowered because of the higher activity of tetrapod (TP) ZnO nanopowders. Low-field electron emission and the technological usefulness of ZnO TPs synthesized by rapid heating of zinc pellet was reported in [3]. Room-temperature photoluminescence (PL) of ZnO TPs prepared by oxidation of zinc powders [4] or evaporation of ZnCO₃ powder [5] was clearly observed and it showed the potential ability for fabricating light-emitting devices in nanoscale optoelectronics. For the nice application prospects, the synthesis procedures, forming mechanisms and physical properties of ZnO TPs are continually studied and developed.

In this paper, we report our efficient route for synthesis ZnO TPs and the beginning discussion on their structural, photoluminescence properties.

2. Experimental

Our synthesis method is based on a vapor transport process and a simple experiment setup shown in figure 1. The source material for evaporation is a mixture of high purity zinc metal (Zn) and zinc oxide (ZnO) powders (molar ratio 2:1). The source material and the SiO₂/Si substrates were placed inside a quartz tube, the source material was located at the closed end while the substrates were arranged toward the opened end of the tube. The quartz tube was inserted to a horizontal furnace in air ambient. The temperature of the source material was ~1050°C, of

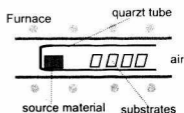


Fig.1. Experiment setup for synthesis of ZnO tetrapods

the substrates was in range 850-950°C. The temperature was kept for 1.5 hour, and then naturally cooled down to room temperature. After the experiment, white fluffy products of mass yield were found on the substrates and the quartz tube. The products covered on the substrates were collected for characterization. Morphology and crystal structure of the products were characterized by scanning electron microscopy (SEM) (JEOL JSM 5410 LV) and X-ray diffractometer (Bruker D5005). Photoluminescence of the samples were recorded by a spectrofluorometer (FL3-22 Jobin-Yvon).

3. Results and discussion

X-ray diffraction (XRD) patterns of the synthesized products show characteristic diffraction peaks of hexagonal wurzite ZnO crystal phase, there is no any diffraction signal of impurity (fig.2).

The typical SEM image shown in fig.3 illustrates the tetrapod-like shape of the synthesized ZnO products. Each tetrapod is composed of four ZnO micro/nanorods - legs of tetrapods - with the diameter of about 500÷2000 nm and length of several micrometers, this sizes depend on the location of the substrate in the quartz tube of the synthesis process. All the legs of the TPs have smooth surface and particularly have hexagon end planes, as can be seen in the SEM image (fig. 3).

Hexagonal wurzite cell of ZnO presents a polar oxide (or zinc) [001] plane and an electrically-neutral non-polar [100] plane, as shown in the inset picture of figure 2. The polar plane is metastable and thus favors a fast growth rate, while the non-polar face has higher stability [6]. We believe that in our synthesis conditions ZnO nuclei formed in the typical hexagonal wurzite structure and fast grew up layer-by-layer along the c-axis ($\langle 0001 \rangle$), therefore resulted in hexagonal shape, end planes and single crystalline of the legs of the ZnO TPs.

Both vapor-liquid-solid (VLS) and vapor-solid (VS) processes could occur in our synthesis procedures because at the synthesis temperature (850-950°C), ZnO solids, ZnO_x ($x < 1$), Zn liquids could exist together and play as the self-catalysts for the growth of ZnO micro/nanorods (the legs of TPs) [1, 5]. However, the VS mechanism may dominate due to that Zn and ZnO_x liquid droplets (with boiling point of 907°C) easily transit to gaseous state at the synthesis temperature. The explanation for the forming of the tetrapod-like morphology is still an exciting problem for worldwide research. May be, the volcanic oxidation of Zn powder plays an important role leading to the growth of the ZnO TPs. Four legs of each TP may form and lengthen from one starting ZnO nucleus.

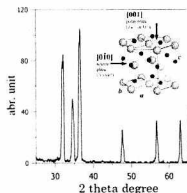


Fig.2. XRD pattern of ZnO tetrapod products ; The inset is the hexagonal unit cell of ZnO [6]

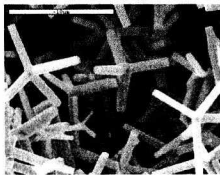


Fig. 3. A typical SEM image of the synthesized ZnO products

Room-temperature photoluminescence spectra of the ZnO TPs excited with a 335 nm light (from a 450W Xenon lamp) were shown in Fig. 4. Very intense emission peaks at 388 nm (UV) and 495 nm (green) were observed in all the synthesized samples. The first narrow peak at 388 nm can be attributed to excitonic recombination. This UV peak is red shift in comparison with the 380 nm peak of usual cases of ZnO. The broad peak at 495 nm is mainly due to oxygen vacancies (inducing deep levels) in the ZnO crystals [7]. The ZnO materials of our case formed in the zinc-rich (oxygen-deficient) condition, especially for the positions near the source material and far from the opened end (air ambient) of the synthesis quartz tube (fig.1). The further distance from the opened end of the tube, the higher probability of forming oxygen vacancies, thus the green emission increases and the UV emission is partially quenched (fig. 4). The representative excitation spectrum of the 495 nm emission peak (fig.5) indicates the optical semiconductor nature of the ZnO TPs with the clear excitonic absorption peak at 381 nm. Good excitonic optical transitions can reveal the high purity and good crystallinity of the ZnO products.

4. Summary

We have fabricated tetrapod-like ZnO micro/nanorods by a simple experiment setup. The synthesis process, forming mechanism and physical properties of the ZnO tetrapods are still the land for active researches in coming time. Very high intense ultra-violet and green photoluminescence at room temperature of our synthesized ZnO tetrapods exposes the potential for fabricating micro and nanoscale light-emitting devices.

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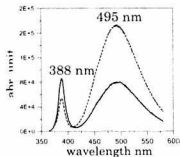


Fig.4. PL spectra of the ZnO TPs formed near (solid line) and far from (dotted line) the opened end of the quartz tube.

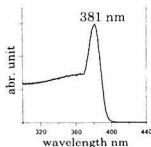


Fig.5. Excitation spectrum of the synthesized ZnO TPs.