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Synthesis and photoluminescence properties of aligned Zn_2GeO_4 coated ZnO nanorods and Ge doped ZnO nanocombs

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Abstract

Aligned Zn_2GeO_4 coated ZnO nanorods and Ge doped ZnO nanocombs were synthesized on a silicon substrate by a simple thermal evaporation method. The structure and morphology of the as-synthesized nanostructure were characterized using scanning electron microscopy and transmission electron microscopy. The growth of aligned Zn_2GeO_4 coated ZnO nanorods and Ge doped ZnO nanocombs follows a vapor-solid (VS) process. Photoluminescence properties were also investigated at room temperature. The photoluminescence spectrum reveals the nanostructures have a sharp ultraviolet luminescence peak centered at 382 nm and a broad green luminescence peak centered at about 494 nm.
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1. Introduction

The study of different ZnO nanostructures has attracted much research attention because it is one of the most promising materials for the fabrication of optoelectronic devices operating in the blue and ultraviolet (UV) region, owing to a direct wide band gap (3.37 eV) and a large exciton binding energy (60 meV) [1,2]. Creation of ZnO nanostructures of various sizes and shapes would be of interest in terms of realizing functional nanosystems. A lot of different methods have been reported for the fabrication of aligned ZnO arrays. But previous efforts to synthesize aligned ZnO nanostructures needed expensive substrates or complex experimental procedures and sometimes produced polycrystalline materials. Exploring simple, cheap methods of synthesizing aligned ZnO nanostructures remains a challenge [3]. Herein, we have synthesized aligned Zn_2GeO_4 coated ZnO nanorods by a simple thermal evaporation method.

Besides aligned Zn_2GeO_4 coated ZnO nanorods we also obtained Ge doped ZnO nanocombs simultaneously. Using a thermal evaporation method, various kinds of ZnO nanostructures have been synthesized under specific growth conditions by Wang's group [4–10], including nanowires, nanorods, nanocombs, nanorings, nanohelixes, nanosprings, nanobows, nanobelts and nanocages. Among these structures, nanocomb structure, which is a good example of the hierarchical nanostructures [11,12], has attracted much attention for the applications to nano-cantilever and nano-laser array [13,14]. ZnO comb-like structure has been synthesized by many groups. The important difference between this

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work and the others is that we synthesized Ge doped ZnO nanocombs. Ge is an indirect band gap semiconductor with smaller energy difference between the indirect gap and the direct gap (DE = 0.12 eV), and smaller effective masses for electron and hole pairs. These characteristics lead to the expectation that it is much easier to change the electronic structure around the band edge [15]. ZnO has been doped with many elements such as In, Ga, Sn, Al [16–18], but only few reports on Ge doped ZnO. In our work Ge was used as dopant, we also report the photoluminescence of the product. In addition, details about the synthesis, growth mechanism and properties are also discussed in this paper.

2. Experimental

Zn (purity, >99%) powders and Ge (purity, >99%) powders were mixed with a molar ratio of 1:1 and then the mixture mixed with graphite as the source material. Then the source material was put in an alumina boat and inserted into a horizontal furnace. Several pieces of Si (1 1 1) plates were placed at downstream positions of the source material used as substrates to collect product. Finally, the entire assembly was heated to 950 °C and maintained at this temperature for 50 min. A mixed gas which contained Ar and H_2 was used as carrier gas before the temperature reached 950 °C. When the system reached 950 °C a mixed gas which contained Ar and O_2 was used instead. The carrier gases flowed constantly at a rate of 50 standard cubic centimeters per minute (sccm). After the reaction was finished, the furnace was cooled down to room temperature. A white product was found on the substrate. The reaction temperature is about 600 °C.

The morphologies and structures of the as-deposited product were characterized and analyzed by field-emission scanning electron microscopy (FE-SEM) (JEOL model JSM-6700F), high-resolution transmission electron microscopy (HRTEM) (JEOL model 2010, operating at 200 kV), and selected area electron diffraction (SAED). Their components were measured via energy-dispersive X-ray spectroscopy (EDS) attached in the HRTEM system. A photoluminescence (PL) spectrum was measured using a He–Cd laser (325 nm) as the excitation source at room temperature.

3. Results and discussion

The XRD pattern of the as-synthesized sample is shown in Fig. 1. Most of the strong peaks in this pattern can be readily indexed to hexagonal wurtzite ZnO with cell constants comparable to the reported data (Joint Committee on Powder Diffraction Standards, JCPDS Card No. 79-0205). There are two peaks which formed from Zn_2GeO_4 compound, but they overlap the ZnO peaks. Except for the SiO_2 peaks from the substrate, no other impurity peaks exist.

The as-synthesized product of our work contained aligned nanorods and double-sided nanocombs. The morphologies do not varied too much in the whole area. Fig. 2(a) shows the full view of as-synthesized nanostructures.

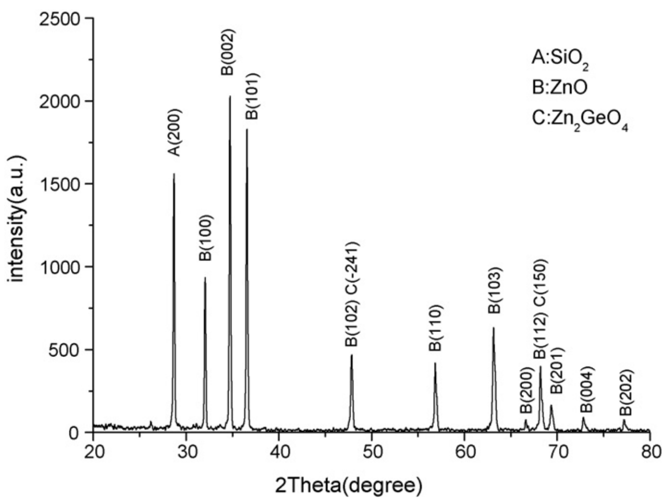

Fig. 1. The X-ray diffraction pattern of the product. The SiO_2 peaks come from the substrate.

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