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Nanostructured zinc oxide thin film by simple vapor transport deposition

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ABSTRACT

Zinc oxide (ZnO) nanostructures find applications in optoelectronic devices, photo voltaic displays and sensors. In this work zinc oxide nanostructures in different forms like nanorods, tripods and tetrapods have been synthesized by thermal evaporation of zinc metal and subsequent deposition on a glass substrate by vapor transport in the presence of oxygen. It is a comparatively simpler and environment friendly technique for the preparation of thin films. The structure, morphology and optical properties of the synthesized nanostructured thin film were characterized in detail by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) and photoluminescence (PL). The film exhibited bluish white emission with Commission International d'Eclairage (CIE) coordinates $x = 0.22$, $y = 0.31$.

1. Introduction

Zinc oxide is a promising wide direct band gap II-VI semiconductor having variety of applications in the field of optoelectronics. It has a stable wurtzite structure with a band gap of 3.37 eV and excitonic binding energy of 60 meV. Several interesting structures of this material have been demonstrated. Nanotubes [1], nanowires [2], nanorods [3], nanoribbons [4], nanoflowers [5] tetrapods [6] and nano belts [7] are some among them. ZnO nanostructures are used in the fabrication of blue light emitting diodes [8], field effect transistors [9], ultra violet laser diodes, sensors [10], etc. Nanostructured zinc oxide thin films can be prepared by different methods. Some of them are Pulse laser deposition (PLD) [11], metal organic chemical deposition [12], spray pyrolysis [13], oxidation of metallic zinc [14], ion beam assisted deposition [15], sol–gel method [16], sputtering [17] and molecular beam epitaxy [18]. Most of the above mentioned techniques require vacuum and catalyst, resulting in a difficult process with complex apparatus. We prepared our film without any catalyst or vacuum. Here we report a simple vapor transport deposition method for the growth of zinc oxide thin film with nanostructures of different morphology, using zinc metal and oxygen.

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2. Experimental method

Our experimental arrangement (Fig. 1) consists of a high temperature, double chamber and split type furnace with two heating zones. The furnace is programmable to attain different temperatures in both the chambers so that the heating process can be controlled. A quartz tube of 5 cm diameter was inserted into the furnace. Granulated zinc taken in a quartz crucible was kept inside the tube near the end in the high temperature zone. A microscopic glass slide cleaned using chromic acid was placed near the other end in the low temperature zone at a distance of 32 cm from the sample.

The metal was heated in steps till 1100 °C in 4 h 30 min. Oxygen supply at a moderate level was established through the aluminum coupling at the sample end of the quartz tube. Zinc vapor produced in the high temperature zone was oxidized to form ZnO. They were subsequently transported and condensed on to the glass substrate kept at 350 °C in the low temperature zone. The sample was allowed to cool to room temperature with oxygen supply keeping up to a temperature of 850 °C.

The X-ray diffraction spectrum of the ZnO film was obtained with Cu Kα radiation using Bruker AXS D8 advance X-ray diffractometer. Photo luminescence was recorded using Horiba Scientific FluoroMax-4 spectrofluorometer. A field emission scanning electron microscope (FESEM), JEOL JSM 7600F, was employed for examining the morphology and energy dispersive X-ray spectroscopy (EDX) analysis of ZnO nanostructures. TEM images of the sample were recorded using a FEI-Titan – 80–300 kV microscope.

3. Results and discussion

Fig. 2 shows the XRD pattern of the synthesized products on the glass substrate. All the diffraction peaks in the figure can be indexed to the known hexagonal wurtzite structure of ZnO matching with JCPDS file number 75-0576. The XRD shows a significant difference in the $(10\bar{1}0)$ peak intensity suggesting a preferential growth along that direction. The lattice parameters are calculated using the relation

$$d_{hkl} = \frac{1}{\sqrt{\frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}}}$$

It is found that $a = b = 2.72$ Å and $c = 5.03$ Å. The narrow width and strong intensity of ZnO peaks indicate that the products are of high purity and crystallinity.

External morphology of the ZnO nanostructures are studied using FESEM. Our sample consists of a large number of rods with varying diameter, tripods, tetrapods and several irregular structures. From the previous reports it is found that through vapor phase synthesis process, ZnO nano structures with different morphologies often grow mixed together, if no catalyst is used. Fig. 3(a)–(c) are the low magnification images which show formation of different types of structures like rods, tripods, tetrapods, etc. Also the distribution of structures is not uniform, crowded as well as scattered in different regions due to non uniformity of thin film. The EDX spectrum (Fig. 3d) confirmed the formation of ZnO.

Fig. 4 represents the high magnification images of some isolated structures in the ZnO thin film. The nanorods, which are merged together have an approximate length of 5 μm (Fig. 4a). Some of them are found to be isolated having an approximate length of 2 μm. The tripod is composed of three planar arms of nearly equal length and size, grown from a common core. The three arms of the tripod are symmetrical with an average length of 750 nm and the angle between the arms around 120°. The width for the arms at the center is around 300 nm (Fig. 4b). Such higly symmetrical planar tripods are rarely reported. For the tetrapod, it is expected that the fourth arm is produced by the merging of a rod on the tripod (Fig. 3).

The crystal structure of the sample was also studied by TEM. Fig. 5 shows the TEM images obtained on an isolated tripod, in Fig. 5(a) a bright-field TEM images is displayed, with dimensions of 1.2 μm in each arm. The inset in (a) shows the selected

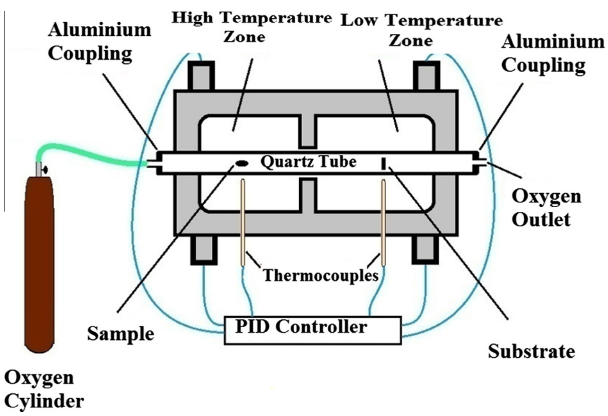

Fig. 1. Experimental set up.