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Control growth of catalyst-free ZnO tetrapods on glass substrate by thermal evaporation method

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ABSTRACT

Novel three-step directions of glass substrate for catalyst-free growth of ZnO tetrapods (ZnO-Ts) without using catalyst or seed layer via thermal evaporation method were investigated. In this study, controlled synthesis of ZnO-Ts was achieved through glancing angle deposition by three-step directions of glass substrate with inclination angles of 0°, 45°, and 90° toward the gas flow at a growth temperature of 650 °C. The effects of substrate inclination angles on the morphological, structural, and optical properties were systematically investigated using field emission scanning electron microscopy, X-ray diffraction, UV–vis spectroscopy, and photoluminescence spectrum. Results showed that the substrate tilt angle is one of the most critical control parameters in determining the nucleation and growth of ZnO-Ts. This new approach provides a cost-effective and simple method for the synthesis of tetrapods, which can be useful in various optoelectronic applications and solid-state devices.

1. Introduction

Zinc oxide (ZnO) nanostructure is an II–VI compound semiconductor with a direct and wide energy band gap (3.37 eV), a native n-type, and a high exciton binding energy [1]. In addition, ZnO nanostructure is low cost, non-toxic, high thermal stability, high transmittance in the visible region, and can be easily fabricated [2]. Therefore, ZnO has been extensively used in various fields, such as optoelectronics [3], environmental science [4], actuators and piezoelectric transducers [5], catalysts [6], and solar cells [7]. Many chemical and physical methods are available and can be used to prepare ZnO nanostructures, such as magnetron sputtering (RF) [8], atomic layer deposition [9], spray pyrolysis [10], sol-gel method [11], pulsed laser deposition [12], and thermal evaporation[13].

Among these methods, thermal evaporation is considered to be one of the important methods employed to synthesize ZnO because of its unique features, namely, catalyst-free growth, simple, cost-effectiveness, and easily controlled growth parameters, such as growth rate, distribution on the substrate, and film thickness. In addition, thermal evaporation presents a wide range of nanostructures with various morphologies and with different shapes and sizes [14], such as nanobelts [15], nanosheets [16], nanocombs [17], nanoscrews [18], nanonails [19], and tetrapods [20].

Recently, ZnO tetrapods (ZnO-Ts) exhibited potential applications, as novel multiterminal devices. The structure of ZnO-Ts is unique, which makes them appear as 3D geometry with four legs pointing along approximately 109.5° angle with each other [21]. The difference between the angles of the legs of tetrapods and its perfect geometry is caused by compensating the stresses generated as a result of dislocations in the core of the seed ZnO particles [22]. The legs of tetrapods can sometimes reach up to several micrometers in length, and its hexagonal crystal structure along the *c*-axis has alternate Zn^{2+} and O^{2-} stacking planes [23]. The junctions of the legs of tetrapods show diverse dimensions, such as nanorod–nanowire junction, nanorod–nanoneedle junction, and nanoleaf–nanowire junction [24]. The diversity of synthesized ZnO-Ts, with different size ranges, morphologies, and properties makes them important for various applications. Several reports showed that single ZnO-Ts gas sensing and UV radiation devices have the advantages of low-power consumption, miniaturization, and cost-efficiency [25,26]. In general, the controlled synthesis of nanostructures with regard to their size and shape has been of significant interest and has led to novel applications that can be investigated depending on their structural properties, which can be controlled through the conditions and parameters that are used in the synthesis of nanostructures [27]. Many conditions can have a significant effect on the controlled synthesis of nanostructures using thermal evaporation method, such as growth temperature, substrate, gas flow rate, source material, and glancing angle deposition (GLAD).

GLAD stands out among the conventional physical vapor

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deposition techniques because it is able to generate a wide range of morphologies of the nanostructures that can only be tailored with a change in the direction of the incident particle flux [28]. GLAD is an angle deposition technique where the substrate direction is manipulated during the growth of nanostructures and has been used in experiments as mobile or fixed substrate [29]. First reported in 1959, the deposition of thin films using different inclination angles and fixed or mobile substrate was successfully conducted with numerous materials and has been increasingly investigated and developed various applications, such as in sensor, optical, and energy devices [30,31]. Researchers realized that they can develop the structural, optical, and electrical properties of nanostructures by controlling the substrate direction, as it enables the fabrication of a unique functional nanostructure [32,33]. In a common (GLAD) system, a uniform growth flux is obtained by evaporation techniques, such as sputtering, electron-beam evaporation, laser beam ablation, and thermal evaporation. The growth flux approaches the fixed substrate at an angle referred to as the incident angle or the deposition angle (θ°). The shadowing effect is the predominant mechanism controlling the morphology, distribution, and size of 3D nanostructures in GLAD without substrate motion [34].

In the present study, the growth of ZnO-Ts with various morphologies and sizes on glass substrates is presented for the first time by using thermal evaporation method without metal catalyst or seed layer. In addition, controlling the morphological, structural, and optical properties of ZnO-Ts was conducted using three-step directions of glass substrate toward the gas flow. The objective of study is to use a low-cost substrate in the synthesis of ZnO-Ts with different morphologies and sizes, and to determine the optimized parameters for the control of high crystal quality, uniform shape and size of tetrapods, which will serve as a basis for further research on the growth of ZnO-Ts on a cost-effective glass substrate.

The crystal structure, surface morphology, and optical properties of the grown ZnO-Ts were investigated by using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), UV–Vis spectrophotometry, and Photoluminescence (PL).

2. Experimental details

Fig. 1(a) shows the schematic of the growth process of ZnO-Ts on a catalyst-free glass substrate by thermal evaporation method. Prior to the growth process, the glass substrate was treated by organic cleaning with acetone, ethanol, and deionized water to remove any undesirable impurities on the substrate, according to the literature [35]. Three-step directions of glass substrate placed in a horizontal two-zone tube furnace with inclination angles of 0°, 45°, and 90° toward the gas flow are clearly shown in Fig. 1(b). High-purity Zn powder (99.99%; Aldrich Chemical Company, Inc, Milwaukee, WI, USA) was used as the first source material, which was placed in a quartz boat. This boat with Zn powder was inserted into the center of the furnace using a quartz tube with a diameter of 4 cm, a length of 70 cm, and a reaction zone of 40 cm. The source material (Zn powder) in the first zone was gradually heated from room temperature to 650 °C at a rate of 10 °C/ min. Meanwhile, the temperature of the substrate zone (second zone) was 425 °C. High-purity Ar gas (99.99%) employed as carrier gas was fed into the system at a rate of approximately 30 sccm. High-purity O_2 gas (99.99%) employed as second source material was fed into the reaction zone at a rate of approximately 5 sccm after the temperature reached 650 °C. Pumping of O_2 gas into the system continued for 60 min A white material formed on the glass substrate after evaporation was completed. Then, quartz tube was allowed to cool down naturally.

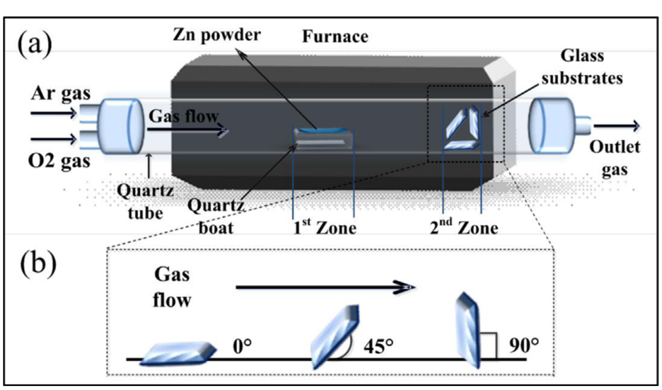

Fig. 1. Schematic of the set-up used for the growth of ZnO-Ts by thermal evaporation method.

Morphological observations of ZnO-Ts were conducted using a FESEM model (FEI/Nova Nano SEM450) with energy-dispersive X-ray spectroscopy. Structural analysis was conducted using an X-ray diffractometer (PANalytical X'Pert PRO) equipped with Cu-Kα radiation (λ=1.5418 Å). The absorption curves were obtained using a spectrophotometer. A Varian Cary system 5000 UV–vis–NIR spectrophotometer was used to obtain the optical transmission spectra. PL spectroscopy of the ZnO-Ts films was conducted at room temperature using a PL spectroscopy system (HR 800 UV system; Jobin Yvon-, Edison, NJ, USA) with He–Cd laser operating at 325 nm. The thickness of the ZnO-Ts films was determined using optical reflectometer (Filmetrics F20).

3. Results and discussion

3.1. Morphological study

The morphologies of the catalyst-free growth of ZnO-Ts on glass substrates via thermal evaporation method with substrate inclination angles of 0°, 45°, and 90° were recorded by FESEM. Fig. 2 shows the high-magnification and low-magnification images of ZnO-Ts with various morphologies and sizes. Fig. 2(a_1) and (a_2) reveal that the ZnO-Ts grown at a substrate inclination angle of 0° with gas flow have uniform dimensions and consist of four straight needle–shaped legs with the top aspheric and the bottom enlarged. The tetrahedrally arranged legs were connected at the center, forming a tetrapod structure. The length and diameter of one tetrapod are approximately 0.9–1.2 μm and 75 nm, respectively. The legs of the tetrapod have a nanorod–nanowire type structure with a substrate inclination angle of 45°, as shown in Fig 2(b_1) and (b_2). The nanowires grew from the ends of the nanorods; therefore, this structure is called a rod–wire junction, which is similar to the result reported by Chen et al. [24] and Roy et al. [36]. The rods have a length of approximately 0.6μm, and a diameter of 60 nm. The nanowires that grew from the ends of the legs of the tetrapods short (less than 1 μm). Notably, observed the appearance of another tetrapod structure in the same sample. It can be seen that wires are grown from the nucleus which resembles a leaf; therefore we call this structure a leaf–wire junction. Fig. 2(c_1) and (c_2) shows that tetrapods were fabricated more successfully at an inclination angle of 90° than at other inclination angles. It can be seen that the ZnO-Ts have grown with large-scale uniformity over large surface areas on glass substrate. Moreover, the film appears more systematically and consistently. Four uniform legs can be clearly observed in the tetrapod. These legs were connected to a central nucleus and have a nanoneedle–nanowire type structure. Therefore, this structure is called a needle–wire junction. The nanorods have a length of approximately 2.1–2.6 μm and a