Thin Solid Films xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Electrodeposited ZnO morphology transformations under the influence of SeO_2 additive: Rods, disks, nanosheets network

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ARTICLE INFO

Keywords:
Zinc oxide
Rods
Disks
Nanosheets network
Electrodeposition
Additive
SeO_2
Platelets

ABSTRACT

In this study various morphologies of ZnO including rods, disks, and nanosheets network were synthesised by electrodeposition method. The influence of the SeO_2 additive concentration on morphological, structural, and optical properties of ZnO was studied by using scanning electron microscopy, X-ray diffractometry (XRD), energy-dispersive X-ray analysis (EDX), optical (UV–Vis) and photoluminescence (PL) spectroscopy methods. The formation of the disk-like ZnO structure with a diameter of ca. 300–500 nm and thickness ca. 80–100 nm was observed when 0.03 mmol/L of SeO_2 was added to the solution. Further increase of dopant concentration up to 0.2 mmol/L in the solution yielded a highly-porous network structure composed of thin nanosheets with a wall thickness of ca. 20 nm. According to the XRD results, all structures were composed of ZnO, rod-like crystals were strongly c-axis oriented, whereas disks and nanosheets network structures were a-axis oriented. EDX analysis revealed that Se was present in the disks and nanosheets structures. PL study of the rod sample showed UV emission at ~370 nm, whereas the disks and nanosheets network showed intense deep-level emission band centred at ~540 nm. The disks and nanosheets exhibited total transmittance of ~80–90% in the region of 380–780 nm, whereas transmittance of the rods was increasing from 5% to 50% in this region. According to haze factor calculations, samples possessed scattering ability of 20% for disks, 45% for sheets and ca. 50% for rods. The probable mechanism for the formation of ZnO structures was discussed in detail.

1. Introduction

Zinc oxide has been recognized as one of the most important semiconductor materials for optoelectronics, solar cells, detector, LED, piezoelectricity, gas sensing, photocatalytic applications etc. ZnO has been an object of intensive research, particularly in its low-dimensional structures [1–3].

ZnO possesses a hexagonal wurtzite crystal structure and its typical crystal is enclosed by two polar non-stable planes (0001), and six nonpolar, low-energy, stable, side-faceted planes (10$\bar{1}$0), (01$\bar{1}$0) etc. Intrinsically, due to the higher energy of the top (0001) crystal surface than other planes, the ZnO crystals have a strong tendency to grow along the [0001] direction or the c-axis orientation. C-axis directional growth results in one-dimensional or nanowire [4], nanotube [5], nanoflowers [6], nanorod-like elongated structures with a low exposed surface area of (0001) plane and larger areas of side facets (10$\bar{1}$0), (01$\bar{1}$0). However, much research effort has been recently devoted to the synthesis of two-dimensional (2D) ZnO including nanosheets, nanowalls, nanoplates, nanodisks, and nanoflakes [7,8]. In general, these structures tend to grow along the [0110] direction or the a-axis and its own dominantly exposed (0001) crystal facet. 2D or a-axis oriented growth is achieved mainly by the promotion of the growth direction [0110] and the suppression of the growth direction [0001]. Furthermore, selective adsorption of certain molecules (surfactants) along the (0001) plane or high deposition temperatures of 650–700 °C retard the longitudinal growth [8]. It is reported that the (0001) plane is more reactive and energetically favourable for the chemisorption of oxygen species, which enhance the sensing properties [7]. The (0001) planes are side facets of disks and nanosheets-like morphologies (nearly perpendicular to the substrate) having higher surface area than the surface area of (0001) plane of rods. ZnO nanodisks reportedly exhibited excellent gas sensing performances [9]. In addition to high reactivity of (0001) plane, 2D ZnO structures show high photocatalytic activity by itself due to the high surface area [10]. Moreover, nanodisks have a smaller effective volume and better mechanical stability than nanorods. It makes them attractive for applications in information storage, transducers, light emitters, and sensors [11]. Thus, size and shape controlled synthesis for nanostructures is essential for nanoscience and

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https://doi.org/10.1016/j.tsf.2017.12.004
Received 16 June 2017; Received in revised form 1 December 2017; Accepted 7 December 2017

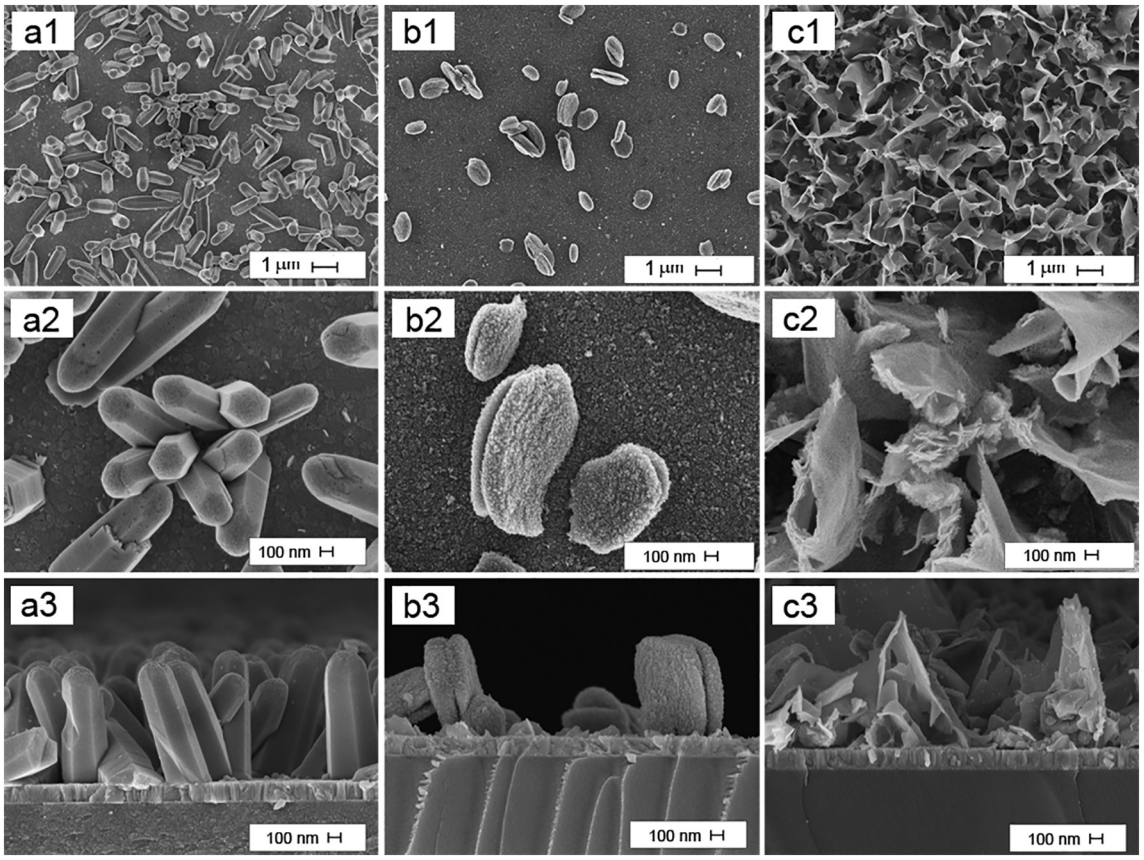

Fig. 1. SEM images of the ZnO a) rods; b) disks; c) nanosheets network.

nanotechnology, as chemical and physical properties of nanostructures could be affected by their morphologies [12].

ZnO nanostructured layers have been fabricated by various deposition techniques such as spray pyrolysis [13,14], electrodeposition [15], pulsed-laser deposition [16], chemical bath deposition [17], chemical vapor deposition [18], vapor–liquid–solid technique [19], etc. Among them, electrodeposition is a low-cost and non-vacuum technique suitable for large-area deposition [20]. It has been shown that electrodeposition is capable of producing high-quality materials for electronic device applications when materials are grown with accurate conditions [21].

In this paper, we report an easy way to synthesize 2D ZnO nanostructures including disks and network of nanosheets by the facile electrodeposition method. We show that the morphology of ZnO can be transformed from rod-like to disk and highly-porous nanosheets network by adding different amount of SeO_2 to the $ZnCl_2$ precursor solution. To date, there are only a few reports about the influence of SeO_2 additive on the properties of electrodeposited layers [22,23]. It is reported that small amount of SeO_2 added to the precursors ($CdCl_2$ and $Na_2S_2O_3$) led to the formation of compact CdS film instead of discontinuous island structure that is usually produced without additives [22]. Selenious acid additive suppresses undesired parallel reaction of hydrogen evolution during manganese electrodeposition process [23]. In the literature, there is no studies covering the effects of SeO_2 additive in solution on the formation and properties of ZnO layers produced using the electrochemical method. Herein, the influence of the SeO_2 additive on ZnO morphology, structure, composition and optical properties are studied, and possible formation mechanism is proposed.

2. Experimental details

2.1. Synthesis details

Electrodeposition of ZnO rods was carried out potentiostatically in a three-electrode glass cell, where the indium tin oxide (ITO)/glass was used as a working electrode, whereas a silver/silver chloride/3 M KCl (Ag/AgCl/KCl) and a platinum (Pt) wire were used as reference and counter electrodes, respectively. ITO/glass substrates with an ITO thickness of 150 nm were purchased from Zentrum Sonnenenergie and Wasserstoff Forschung (ZSW). The concentration of $ZnCl_2$ (Sigma-Aldrich), was fixed to 0.2 mmol/L, pH ~5, concentration of supporting electrolyte was maintained to 0.1 mol/L KCl and 50 mL of solution was utilized for all depositions. In order to study the effect of additives on ZnO morphology evolution, various amounts of SeO_2 aqueous solution were taken. Molar ratios of Zn:Se as 1:0, 1:0.15 and 1:1 with corresponding concentrations of SeO_2 c = 0 mmol/L, c = 0.03 mmol/L and c = 0.2 mmol/L were taken.

The growth temperature was kept at 80 °C using a temperature-controlled circulating bath. Deposition time was fixed to 1 h. Electrochemical deposition was done under − 1.0 V potential versus the reference electrode using the Radiometer Analytical potentiostat PGP201.

2.2. Characterization

X-ray powder diffraction (XRD) was used to examine the crystal's structure, phase composition, and crystallite orientation. The XRD patterns of the samples were recorded on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5406 A, at 40 kV and at 40 mA) using a silicon strip detector D/teX Ultra. Surface morphologies and cross-sections of the deposited layers were examined by scanning