

Growth of ZnO Nanostructures by Wet Oxidation of Zn Thin Film Deposited on Heat-Resistant Flexible Substrates at Low Temperature

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Abstract—Coral-like ZnO nanostructures were successfully grown onto heat-resistant flexible substrates by the oxidation of Zn thin films. At a relatively low temperature (100°C), Zn thin film was oxidized using a horizontal furnace under the flow of water vapour. The obtained results revealed well-defined aggregates of ZnO nanostructures grown on the flexible films. XRD patterns exhibited a strong and sharp diffraction along the (002) plane suggesting a well-crystallized ZnO phase. Field emission scanning electron microscopy observations showed high-density ZnO nanostructures aggregated in coral-like shape. The present study introduced a cost-effective and simple approach to grow high-quality ZnO nanostructures with controlled shape and size, offering a promising candidate for nano-based devices such as fast-response photodiodes and gas sensors.

Keywords: ZnO, nanostructures, low temperature, wet oxidation

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1. INTRODUCTION

Zinc oxide (ZnO) material has attractive properties, such as a broad direct band gap (3.37 eV) at room temperature and high binding energy of free excitation (60 meV), being in addition transparent conductive metal oxide with important piezoelectric characteristics [1, 2]. Accordingly, ZnO offers potential applications in various electronic and optoelectronic devices. Various preparation techniques have been reported to produce ZnO films with variety of nanostructures (NSs) such as thermal evaporation [3], hydrothermal processing [4], chemical vapour deposition [5], metal-organic [6], and carbothermal reduction. The synthesis of Zn nanoparticles followed by thermal oxidation process is considered as an effective technique to grow ZnO nanowires (NWs) [7]. This process can be achieved through two approaches; namely, wet and dry oxidations. In addition, it offers outstanding features compared to other techniques such as low preparation cost and simplicity of deposition onto different substrates including polymeric materials, without the need of catalysts.

Numerous studies have been carried out to grow ZnO NSs by oxidation of Zn films [8–10]. Zn metal was successfully transformed into ZnO nanoparticles by the oxidation process through arc discharge in air at

relatively low temperatures (250, 300, and 350°C) at different periods of time [11]. ZnO nano-wires (NWs) had been shaped by the annealing of Zn NWs at 500°C for 1 h; the NWs were synthesized by the heating of ZnO and graphite mixture [12]. ZnO nano-needles (NNs) were selectively grown from Zn metal microstructures by thermal oxidation for 4 hours in the temperature range of 250–400°C [13]. Nevertheless, there is still a need for further researches on the preparation of ZnO NSs by wet oxidation from zinc thin films prepared by different deposition techniques. In this study, the growth of ZnO NSs onto flexible substrates at low temperature will be addressed using wet oxidation technique of sputtered Zn metal thin films.

2. EXPERIMENTAL DETAILS

ZnO NSs were grown on heat-resistant flexible substrates (long-term temperature of 260°C) by the oxidation of Zn metallic thin films prepared by sputtering technique. The preparation of ZnO NSs can be summarized in the following steps: (1) first, the substrates were cleaned by isopropyl alcohol solution in ultrasonic bath at 60°C for 15 min; (2) Zn metal thin layer (100-nm thickness) was deposited as a seed layer on the cleaned substrates using high-purity Zn target

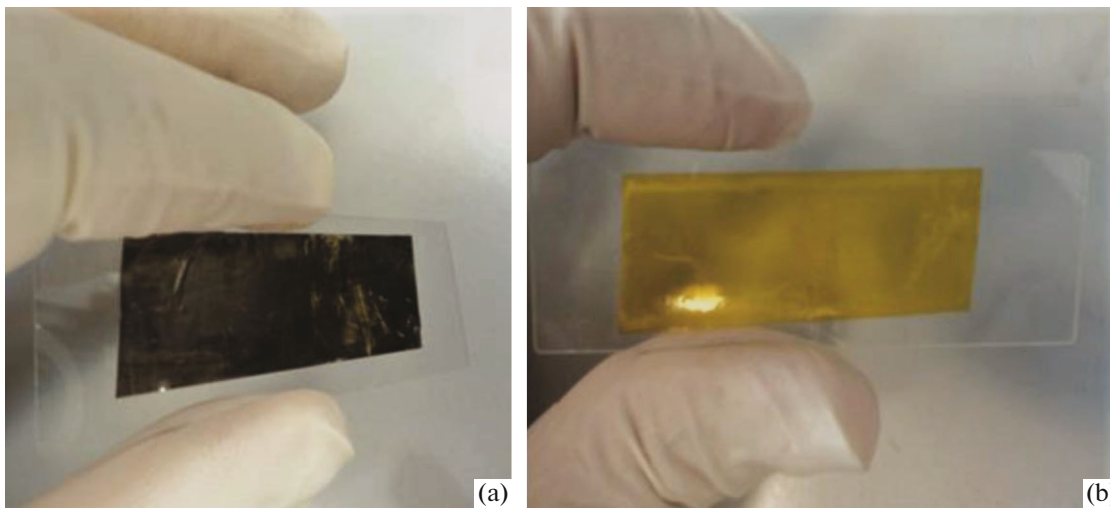


Fig. 1. (a) uniform sputtered Zn film before wet oxidation process, (b) substrate after wet oxidation process coated by ZnO NSs.

(Aldrich 99.99% purity) by radio frequency magnetron sputtering system under argon pressure of 5.5 mTorr and sputtering power of 150 W; (3) ZnO NSs were then grown onto Zn seed-layer/films using a horizontal furnace at 100°C for about 5 h under the flow of water vapour. The grown layer was then cleaned by deionized (DI) water.

Surface morphology was investigated by field emission scanning electron microscopy (FESEM) using FEI/Nova NanoSEM 450 equipped with energy dispersive X-ray (EDX) for chemical composition analysis. The crystal structure was checked by X-ray diffraction (XRD) using PANalytical X'Pert PROMRD-PW3040. Photoluminescence (PL) and Raman spectroscopy helium-cadmium (He–Cd) laser of wavelength 325 nm were used as excitation source to evaluate the optical properties, crystal quality and the presence of defects/impurities in ZnO NS.

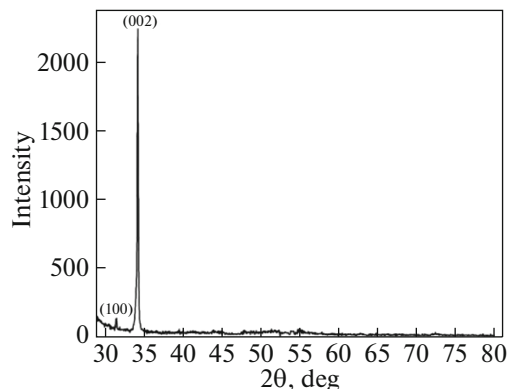


Fig. 2. XRD patterns of ZnO NSs grown onto flexible films at 100°C.

3. RESULTS AND DISCUSSION

3.1. Growth Mechanism of ZnO NSs

ZnO NSs growth onto flexible substrates by wet oxidation of Zn metal thin film occurs as follows. The preparation steps involve the attraction and absorption of water molecules onto Zn layered structure. Water molecules breakup to release hydrogen and result in the oxidation of Zn thereby the formation of ZnO NSs. This approach facilitates the formation of nucleation sites existing on the surface of the platelet-like microstructure to be oxidized within Zn grains. ZnO NSs start to grow from the formed nucleation sites and dispersed in water vapour flow [14]. Interestingly, the introduction of water vapour to the oxidizing environment can significantly reduce the oxidation temperature by hastening the oxidation reaction. The separation of H₂O molecules is faster than break-up of oxygen molecules at elevated temperature, which enabled the growth of ZnO NSs at moderated temperatures.

3.2. XRD Analysis of ZnO NSs

Figure 1 illustrates a typical XRD pattern of the grown ZnO NSs. The pattern exhibits high intense diffraction peaks with a dominant peak along the (002) plane. The diffraction peaks correspond to the hexagonal (wurtzite) crystal structure of ZnO compound [15], in agreement with JCPDS card no. 36-1451. A very sharp and narrow dominant peak suggests high crystallinity and good quality of prepared ZnO NSs [16].

The crystallite size (D) was estimated using the Debye–Scherrer formula:

$$D = \frac{0.90\lambda}{\beta \cos \theta}, \quad (1)$$

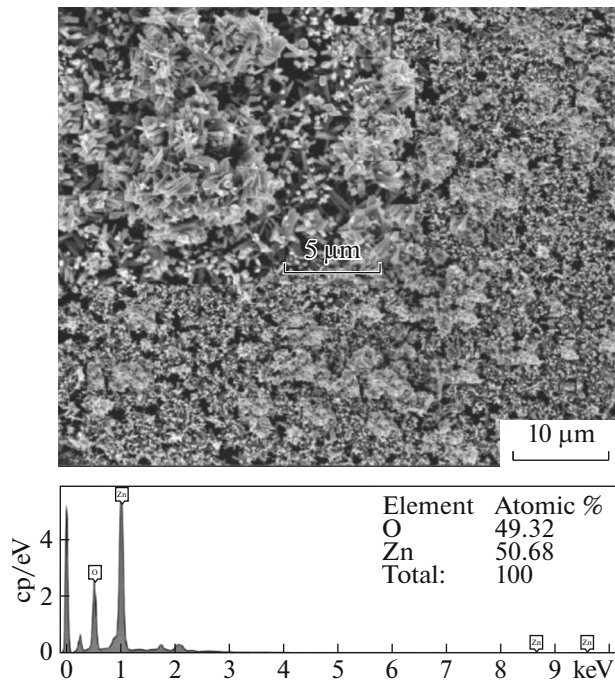


Fig. 3. FESEM images with different magnifications of ZnO nano coral-like aggregates grown onto flexible film along with the EDX spectrum.

where λ is the X-rays wavelength and β is the full width at half maximum (FWHM) in radians. The calculated average crystallite size of the prepared ZnO NSs was found to be 14.3 nm.

The value of strain along Z-axis (ϵ_c) has been determined using Eq. (2) [17]:

$$\epsilon_c = \frac{c - c_0}{c_0} \times 100, \quad (2)$$

where c and c_0 are the lattice constant of the fabricated ZnO NSs and the standard lattice constant for unstained ZnO, respectively. The calculated strain was found to be -0.0331% , indicating a compressive lattice strain. The low obtained value confirms the high quality of crystal structure of ZnO NSs.

3.3. Morphological Observations

A top view of the prepared ZnO NSs is shown in Fig. 3.

The magnified image reveals quasi-aligned nano coral-like aggregates with high density, distributed along different directions, which can be attributed to the flow of the water vapour through the oxidation tube. The EDX spectrum of the grown ZnO NSs indicates the presence of Zn and O elements, with a chemical composition close to the stoichiometry, see in-set table. The atomic ratio Zn/O is near to unity, suggesting that the wet oxidation technique could produce high rate of oxidation to convert Zn into ZnO due to the enhanced diffusion of O atoms of water molecule through the sputtered Zn film.

3.4. Photoluminescence Analysis

The crystal quality of the synthesized ZnO NSs has been evaluated using PL measurement. The room-

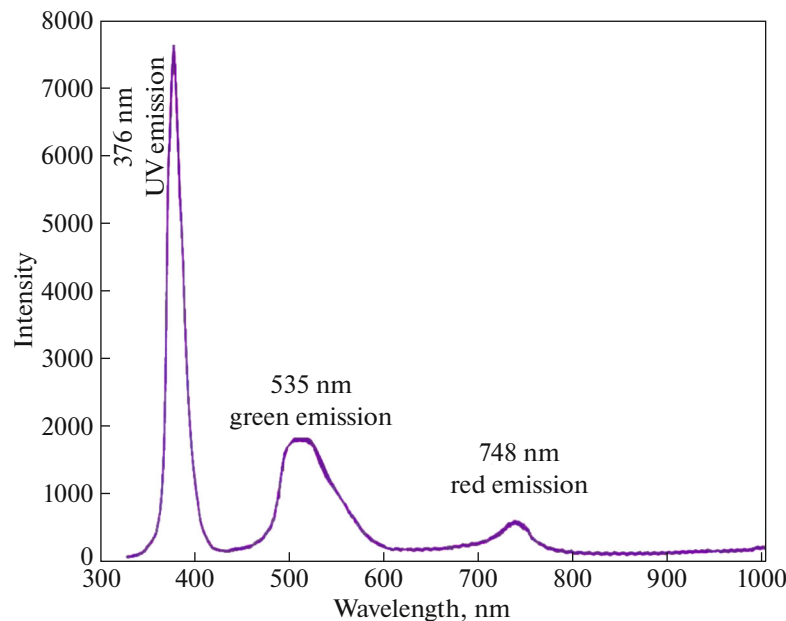


Fig. 4. Room-temperature PL spectrum of ZnO NSs.

temperature PL spectrum shown in Fig. 4 exhibits a sharp UV emission along with broad peaks in the visible light region.

The sharp peak centered at 380 nm is typical characteristic of the near-band-edge emission of ZnO wurtzite structure, resulting from the recombination of free excitons [18]. Whereas, the two broad (green and red bands) emission peaks located at 535 and 748 nm are commonly referred to as deep-level or trap-state emission. The red transition has been usually attributed to the singly ionized oxygen vacancy within ZnO crystal lattice, and the green emission results from the radioactive recombination of a photo-generated hole with an electron occupying the oxygen vacancy [19–21].

However, broad emission band of 500–700 nm in ZnO PL spectra is usually observed in the literature and attributed to the defect level induced by the defects of oxygen vacancies and Zn interstitials or their complexes [22]. The high UV peak intensity compared to the weak bands in the visible region indicates that the as-grown ZnO NSs are of high-crystal quality with minimum structural defects [23, 24].

4. CONCLUSIONS

Nanostructured ZnO film was successfully grown onto heat-resistant flexible substrate at a relatively low temperature of 100°C. Structural analysis confirmed the formation of nanocrystalline ZnO wurtzite phase. Besides, morphological observation revealed high-density coral-like aggregates randomly distributed over the entire film surface, which was attributed to the flow of the water vapour through the oxidation tube. Moreover, the sharp UV emission at 380 nm as revealed by PL measurement suggests high crystalline quality of ZnO nanostructures. The present study introduced a simple and cost-effective approach to grow ZnO nanostructures onto flexible substrates, which would be a remarkable candidate for nano-based electronic devices such as photodiodes and gas sensors.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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