Investigation and characterization of ZnO single crystal microtubes

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Abstract

Morphological, structural, and optical characterization of microwave synthesized ZnO single crystal microtubes were investigated in this work. The structure and morphology of the ZnO microtubes are characterized **using** X-ray diffraction (XRD), single crystal diffraction (SCD), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDX), and transmission electron microscopy (TEM). The results reveal that the as-synthesized ZnO microtube has a highly regular hexagonal cross section and smooth surfaces with an average length of 650-700 μm , an average outer diameter of 50 μm and wall thickness of 1-3 μm , possessing a single crystal wurtzite hexagonal structure. Optical properties of ZnO **single crystal** microtubes were investigated by photoluminescence (PL) and **ultraviolet-visible** (UV-vis) absorption techniques. Room-temperature **PL** spectrum of the microtube reveal a strong UV emission peak at around 375.89 nm and broad and a weak visible emission with a main peak identified at 577 nm, which was assigned to the nearest band-edge emission and the deep-level emission, respectively. The band gap energy of ZnO microtube was found to be 3.27 eV.

Keywords: ZnO; Microtubes; Microwave; Structural properties; Optical properties.

1. Introduction

Zinc oxide (ZnO) is an important functional material possessing semi-conductivity and piezoelectric and pyroelectric properties [1-4]. As a semiconductor, its direct band gap together with a large excitation binding energy, is of great interest in optical industries including blue and UV optical devices, such as light-emitting diodes and laser diodes [5,6].

The synthesis of ZnO with uniform size and various morphologies having micrometer range has been attained considerable focus in recent years [7]. Tubular **structures have** attracted extensive interest due to their potential usage for studying space confined transport phenomena and potential applications in nanotechnology [8]. **Also**, Tubular structures have been fabricated for many compounds with layered structures [9,10]. **Especially, ZnO microtubes become important because a high porosity and a large surface area are required to fulfill the demand of high efficiency and activity in numerous applications [11], like energy harvesting, field emission and optoelectronics compared to other nanoarchitectures. Interest in tailoring ZnO microtubes arises from these facts and is important from the standpoint of both fundamental and applied research [12,13]. Besides, ZnO microtubes are of importance in the fabrication of certain devices, as electrodes can be conveniently attached to the inner and outer surface to give a favorable geometrical arrangement [14].**

Since the high surface area and the special structure of ZnO **microtubes**, they have special magnetic, dielectric, optical, and thermal properties. In order to increase the surface area and further increase the effective reaction area of a photocatalyst, many groups make considerable efforts to synthesize ZnO tube-like particles [15,16].

The kinetics of the ZnO system, the lower energy facets, and the oxidation rates of different surfaces are of the most important factors related to the growth of ZnO tubular structures. The oxidation rates on different crystal surfaces as well as at different temperature regions are distinct. The ZnO surface with lowest energy such as {0 0 0 1} planes (i.e., along c-axis) tends to be more stable and may resist to being oxidized, while the high energy surfaces

such as {1010} (i.e., along the a–b axis) are likely to have a higher oxidation rate [17,18].

In this context, microwave synthesis is a simple and relatively method for the preparation of micro sized crystalline materials very rapidly. Microwave heating in a closed reaction chamber has some advantages over other methods of conventional heating. The reaction rate can be accelerated, yield can be improved and the reaction pathway can be selectively activated or suppressed. Microwave synthesis attains much attention among researchers due to the ultra-purity of the sample synthesized and the simplicity of the basic requirements of the experimental setup [19,20].

In this work ZnO single crystal microtubes have been **successfully** synthesized in a travelling-wave mode microwave system with a higher level of engineering combining hollow and oriented structures which became necessary for providing enhanced and smart functionality that meet the requirements of high technological applications. **The microstructure of the as-grown oriented ZnO single crystals microtubes were investigated. The obtained crystals were characterized by transmission electron microscopy (TEM), field emission scanning electron microscopy (FESEM), energy dispersive X-Ray spectroscopy (EDX), X-ray diffraction (XRD), single crystal diffraction (SCD), photoluminescence (PL), and ultraviolet-visible (UV-vis) absorption.**

2. Experimental

The aqueous PVA solution (2%) was first prepared by dissolving the PVA powder in ultra-pure distilled water and heating it to 80 °C, stirring it for 1 h and then cooling it to **room-temperature**. ZnO powder mixed thoroughly with a PVA solution under constant stirring for 20 min. The obtained homogenous milky white solution was subsequently kept in an oven at 80 °C for 24 h.

The resulting powder was pressed into the form of pellets by applying pressure of 3 MPa and then finally sintered at 750 °C for 2 h.

The prepared ZnO sample was irradiated with microwave radiation by placing inside of a traveling-wave cavity. The power level of the microwave irradiation was adjusted to 1300 W. The ZnO sample was treated with microwave radiation and at a temperature of 1400 °C for about 20

minutes. The synthesis of ZnO microtube was carried out in a traveling-wave mode microwave system with a maximum power of 5000 W and frequency of 2.45 GHz. The details of the traveling-wave mode microwave system have been given in our previous work [21].

The resulting ZnO microstructures were morphological, structural, and optical characterization using **transmission electron microscopy (TEM, JEM2100F, JEOL, Japan), field emission scanning electron microscopy (FESEM, ULTRA plus, Carl Zeiss, Germany), including energy dispersive X-Ray spectroscopy (EDX, X-Max 50, Oxford Instruments, Britain). X-ray diffraction (XRD, X'pert PRO, PANalytical, Holland) was analyzed employing a scanning rate of 0.02 °/s with a 2 θ range of 10°-80°, using copper monochromatized Cu-K α 1 radiation (λ = 0.154 nm) under an accelerating voltage of 40 kV and a current of 40 mA. Single crystal diffraction (SCD) testing was performed, and the data were collected at 298 K on a Bruker Apex-II CCD diffractometer with graphite monochromated Mo-K α radiation under a voltage of 30 kV and current of 15 mA. Processing of the intensity data was conducted using the SANT and SADABS routines, and the structure and refinement were performed using the SHELTL suite of X-ray programs (version 6.10) and the OLEX2 program (version 1.2.6). Room-temperature photoluminescence (PL) was carried out using a Horiba Jobin Yvon HR-800 UV setup with an excitation source of a He-Cd laser with a wavelength of 330 nm and a spectral resolution of 1.03 cm⁻¹. Ultraviolet-visible (UV-vis) absorption was recorded using (Lambda 750 S / PerkinElmer / USA) UV-vis spectrophotometer in the wavelength region of 330–700 nm and a resolution of 0.17–5.00 nm.**

3. Results and discussion

Figure 1 shows the FESEM image of the ZnO single crystal microtube synthesized at 1400 °C for 20 min. The as-synthesized ZnO single crystal microtube has a smooth surface with a length of 650-700 μ m. The front view of the ZnO single crystal microtube shows a tubular structure with an average outer diameter of 50 μ m and wall thickness of 1-3 μ m. The tube has well hexagonal-faceted surface.

The crystallographic structure of ZnO single crystal microtube synthesized is characterized by XRD and SCD, as shown in Fig. 2. The obtained ZnO single crystal microtubes are of wurtzite structure (hexagonal phase, space group P6₃mc (186)) as shown in Fig. 2a, which can be well indexed to the typical wurtzite structure of hexagonal ZnO phase (PDF# 36-1451) and there was no characteristic peaks of impurities observed. It is noted that the relative intensities of the peaks differ from the standard pattern of the bulk material, which should be caused by preferred orientation and distribution of the ZnO crystals [22].

By contrast, our XRD results show that in the microwave reaction growth is along the a-axis. The formation of these microcrystals may be due to the creation of nuclei by the microwave radiation. These nuclei may be composed of zincite, but containing a high density of defects, as it is known from very recent studies [23-25] that defects can strongly affect the surface free energy of the various planes, so that growth along the c-axis will no longer be preferred. Fig. 2b illustrates the obvious polar nature of the ZnO structure reveals that our pure ZnO microtube is a single crystal and the crystal system is hexahedral oriented along a-axis with indices of (100).

TEM analysis was conducted to investigate further characterization of the synthesized ZnO single crystal microtubes, as shown in Fig. 3.

Figure 3a is the TEM image of a tube wall. Fig. 3b is a **selected area** electron diffraction (**SAED**) pattern from the wall of the tube, shows the periodic distribution of lattice points. The sharp spots clearly indicating single crystalline nature of the material which reveals that the tube was single crystalline [26].

Figure 4 shows respectively oxygen (O) and zinc (Zn) element images of a ZnO single crystal microtube with the FESEM picture inserted. The mapping images were obtained by EDX attached with the same FESEM instrument. It is clearly seen, from Fig. 4a, that both Zn and O elements appear in the hexagon with a hole in the center corresponding to the FESEM morphology.

The atomic number and mass of Zn is much higher than those of the O, and as a result, the response of Zn to the detecting X-ray is much stronger than that of O.

Fig. 4b shows the element distribution along the diagonal of a ZnO single crystal microtube that corresponds to the inserted microtube. It can be seen that the Zn signal is almost flat from one side to the other, but the O signal only appears on both sides.

This indicates that the ZnO microtube has a ZnO shell with elemental Zn-rich on the inner wall.

The optical properties of ZnO single crystal microtube were shown in Fig. 5. The room-temperature PL spectrum of the tube is shown in Fig. 5a. **The inset in Fig. 5a shows the ZnO tube during conduct the measurement.** A strong and sharp UV emission at 375.89 nm (3.29 eV), agreeing the near band edge emission originates from the recombination of **the free exciton between the conduction and valence bands through an exciton–exciton collision process** [27-30]. Generally, a visible emission could be observed in the PL spectrum, which comes from the recombination of photo-generated hole with a singly ionized charge state of specific defect [31-34]. However, this kind of emission in our sample can be negligible compared with the very intensive sharp UV emission.

The intensity ratio of the UV **emission** to the visible emission is nothing less than that recorded from the high-quality ZnO microtubes prepared by other research groups using high-temperature CVD or MBE methods [35,36]. It is well known that drastic growth conditions such as high temperature and high pressure, or oxygen-deficient environment usually induces more defects in crystals [37]. But our PL spectrum shows that our high-temperature growth method can produce a low concentration of oxygen defects and high optical quality of single crystal ZnO microtube.

The UV-vis spectrum **of ZnO single crystal microtube is shown in Fig. 5b, which reveals one** prominent absorption band around 378.88 nm (3.27 eV). This peak is attributed to the band gap energy for ZnO due to the jumping of electrons from the valence band to the conduction band of the semiconductor after it absorbs light [38].

In the present synthesis process, microwave irradiation played a crucial role in the rapid

formation of ZnO microtubes. Microwave radiation falling on the ZnO sample contributes both thermal and non-thermal effects for the formation of micro crystallites [39]. The polarization and rapidly changing electromagnetic field of microwave radiation will create anisotropic micro domains of materials. Also, microwave can lead to synthesis of new morphology based ZnO microtubes, as shown in Fig. 6. **By increasing the synthesis time of more than 20 min, down to 40 min at the same synthesis temperature of 1400 °C needed to synthesize ZnO microtubes, ZnO microrods start to grow on the ends of the surfaces walls of the hexagonal ZnO microtube as shown in Fig. 6.**

Figure 7 shows a schematic illustration of possible growth mechanism for ZnO microtubes. It is revealed from Fig.7 that the template for forming the ZnO tube was a hexagonal ZnO rod. At the beginning, ZnO sublimates to provide Zn and O₂ sources at higher temperature zone. Some vapor was absorbed onto the sample. Zn vapor reacted with O₂ forming ZnO seeds along the ZnO sample. The feeding of Zn vapor into favorable nucleation sites of ZnO seeds caused continued growth. ZnO microrods were subsequently formed on the seeds. As a result, the reaction rates of Zn vapor and O₂ at the top edges of the microrod sidewalls were higher than in the central areas of the top surfaces, producing holes in these central areas. With increasing the reaction time, the inner hollow increased correspondingly. Zn vapor and the partial pressure of O₂ were considered to have an approximately uniform distribution around the top and sidewall of a ZnO microrod. Thus, ZnO single crystal microtubes with well-defined crystallographic facets and prismatic hexagon shape could be synthesized uniformly.

4. Conclusions

ZnO single crystal microtubes have been successfully synthesized by microwave heating at an elevated temperature of 1400 °C for 20 minutes with several good features. These products have a hexagonal tubular crystal with smooth surfaces and of nearly uniform wall thickness.

The structural properties (XRD and SCD) of ZnO single crystal microtube indicated the

predominance of a hexagonal phase and growth along (100) direction. TEM and SAED pattern of the sample indicating single crystalline nature of the material which reveals that the tube was single crystalline. The morphology (FESEM) was found to be tubular with an average length of 650-700 μm , an average outer diameter of 50 μm and wall thickness of 1-3 μm . The **EDX** data confirmed the uniform distribution of Zn and O elements across the microtube without any further defect.

The room-temperature PL measurement result indicates that the obtained ZnO microtube has a better UV optical quality at a wavelength of 375.89 nm. Also, the UV-vis spectrum reveals one prominent absorption band around 378.88 nm, making these tubes have technological importance in optical applications.

Acknowledgments

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Figure captions

Fig.1. The FESEM image of microwave synthesized ZnO single crystal microtube.

Fig.2. ZnO single crystal microtube: a. XRD pattern. b. Crystallographic structure.

Fig.3. TEM analysis of ZnO single crystal microtube: a. TEM image of the tube wall. b. Selected area electron diffraction (SAED) from the wall of the tube **with the periodic distribution of lattice points.**

Fig.4. a. EDX mapping images of oxygen and zinc. b. EDX line scanning along the diagonal of a ZnO single crystal microtube.

Fig.5. Optical analysis of ZnO single crystal microtube: a. Room-temperature PL **with inset of the ZnO tube during conduct the measurement.** b. UV-vis absorption.

Fig.6. FESEM image **indicates the possibility for the growth of ZnO microrods on the ends of the surfaces walls of the hexagonal ZnO microtube upon the completion of its growth.**

Fig.7. Schematic diagram of the proposed growth mechanism of ZnO microtube. a. Nucleation of ZnO rod, b. Growth of tower-like ZnO rod. c. Formation of ZnO rod with flat end. d. ZnO microtube formation.

Figures

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Graphical Abstract