



Synthesis of zinc oxide microrods and nano-fibers with dominant exciton emission at room temperature

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ABSTRACT

Employing a simple chemical synthesis method, hexagonal-shaped zinc oxide microrods and zinc oxide nano-fibers were deposited on pyrex-glass and aluminum substrates, respectively. Both kinds of deposits showed zincite crystalline phase with lattice parameters: $a=3.2498 \text{ \AA}$ and $c=5.2066 \text{ \AA}$. Microrods showed very uniform wide and large sizes of around 1 and 10 μm , respectively. Both deposits were homogeneous over all substrate surfaces. Microrods and nano-fibers resulted with good optical quality and with preferential crystalline growth in [1 0 1 0] and [0 0 0 1] directions. The principal optical characteristics for both microrods and nano-fibers were: a) room-temperature photo and cathodo-luminescent spectra with strong exciton emission centered around 390 nm and with FWHMs around 125 and 160 meV, respectively, b) poor photo and cathode-luminescent emissions in the visible region of the electromagnetic spectrum, c) energy band gap of 3.32 eV, d) good emission efficiency supported by the not-required high energy densities to obtain strong exciton emission and e) good ZnO stoichiometry endorsed by photoluminescent results. These characteristics make of these microrods and nano-fibers good for potential photonic applications.

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1. Introduction

Zinc oxide, ZnO, has always been considered one of the most important semiconductors due to its physical and/or chemical properties and the consequent multiple applications that it has, such as: antireflection coatings, transparent conducting films (as electrodes in solar cells), gas sensors, varistors, surface acoustics wave devices and electro- and photo-luminescent devices. Recently ZnO nanostructures have attracted much attention due to their potential applications in field emission displays [1,2] high efficient optoelectronic devices [3–7], UV laser technology at room-temperature [3,8], phosphors [9–11], photo-catalysis [12], electromechanical coupled sensors and transducers [13,14], spintronics [15,16], super-hydrophobicity and super-hydrophilicity surfaces [17,18], cosmetics [19], etc.

ZnO is a direct band-gap semiconductor with wide band-gap energy ($\sim 3.37 \text{ eV}$) at room temperature and a very large exciton

binding energy of about 59 meV, which allows for more efficient excitonic emission at higher temperatures [20–22] better than other very important semiconductors such as: GaSb, Ge, GaAs, ZnTe, Si, ZnSe, GaP, GaN, CdS and ZnS with exciton binding energies of: 1.6, 4.15, 4.2, 12, 14.7, 17, 21.5, 25, 28 and 40 meV, respectively. This makes ZnO suitable for short wavelength optoelectronic devices based on excitonic effects that work at room temperature and above. The large ZnO exciton binding energy makes this material an attractive candidate for room-temperature lasing [3,23]; in addition ZnO in low dimensional nanostructured forms offers the possibility of further improving lasing conditions due to quantum confinement effects [3,23].

Typical photoluminescent (PL) emission spectrum for zinc oxide shows an emission peak in the near UV region and a broad band in the visible region. Recent studies on ZnO are focused to obtain strong ultraviolet emission and minimize the emission in the visible region in order to increase the optical quality of the ZnO for future applications as a lasing material [24–27]. The near-band-edge (UV-PL peak) is commonly observed in the range 370–390 nm, which corresponds to energies in a range 3.2–3.35 eV [24–28]; this is believed to result from an excitonic type recombination where free exciton process is dominant. The typical visible emission in ZnO

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is in the blue–green–orange region, which results due to deep energy levels in the forbidden band gap, resulting from structural defects in the crystal lattice [24–27,29–32]. These structural defects act as traps for carriers, and have been mainly attributed to surface defect levels associated with oxygen vacancies, oxygen interstitial, antisite oxygen O_{zn} , zinc vacancies and/or zinc interstitials in the ZnO crystal lattice [29–33].

Up to now, the origin of the visible emission is highly controversial and with numerous hypotheses [32,34], this has been attributed to surface defects as was mentioned before but the nature of these defects is still not fully understood [32,34]. Detailed investigations on the properties of ZnO are required in order to have functional ZnO devices.

The aim of the present manuscript is to evaluate a simple chemical synthesis method to obtain zinc oxide microstructures and/or nanostructures that have predominant ultraviolet emission over visible emission. These ZnO structures could have good possibilities of room-temperature lasing applications. The results show that the synthesis method is appropriate to produce ZnO microrods and nano-fibers structures with predominant ultraviolet emission over visible emission.

Employing the wet chemical synthesis method, rod shaped structures with dimensions of microns and fiber structures with dimensions of nanometers were synthesized. Both structures presented photo- and cathode-luminescence emission spectra without significant contribution in the visible region of the electromagnetic spectrum. The blue–green–orange emission was not present even though emission is very common in ZnO prepared by chemical methods [35]. Precursor materials and the method employed here minimize the structural defects, which maximize the emission centered in the range 370–390 nm associated to exciton processes.

2. Experimental procedures

Zinc oxide deposits were obtained by wet chemical synthesis method [36]. The precursor solution was zinc acetate hydrate 99.99%, Aldrich, (0.032 M) and hexamethylenetetramine 99% and Aldrich (0.032 M) in deionized water (18 M Ω cm). The zinc oxide was grown on aluminum and pyrex-glass substrates. The substrates with 1.0×1.0 cm² dimensions were immersed in 100 ml of precursor solution at 90 °C for 15 h. Subsequently the deposited zinc oxide was washed with deionized water several times to eliminate residual salts. A Leica Cambridge Stereoscan 440 Scanning Electron Microscope (SEM) equipped with a beryllium window X-ray detector was employed to obtain the morphology of the samples, and their chemical composition (by Energy Dispersive Spectroscopy, EDS). Crystalline structure was analyzed by X-ray diffraction (XRD) using a Broker-axs D8-advance with $CuK\alpha$ radiation at 1.5426 Å. Identification of hexagonal phase and indexing of the peaks for the XRD patterns were carried out using XRD-PDF cards provided by ICDD with associated numbers: 00-036-1451 for zinc oxide, 00-004-0831 for zinc and 00-004-0787 for aluminum. Photoluminescence excitation and emission spectra at room temperature, T_{room} , were

recorded using a spectrofluorometer SPEX Fluoro-Max-P. Lamp intensity correction is performed automatically by this instrument that measures the excitation light intensity with an additional photomultiplier tube and performs the correction accordingly before displaying the data. A 10 ns Nd:YAG pulsed laser model Quanta-Ray of Spectra Physics was employed as excitation source to obtain T_{room} and 18 K PL spectra of the samples. A filter was used to reject the 532 and 1064 nm laser lines. The emission spectra were recorded using a conventional setup. The sample was placed in a mobile holder for aligning purpose, which was inside a compressed-helium cryostat of Air Products. The emission was collected perpendicular to the pumping signal. A monochromator, model SpectroPro 2500i of Acton Research Corporation, was used to scan the emission spectrum and then measured using a photomultiplier tube, model R-930 of Hamamatsu, connected to a PC through a Lock-in amplifier, model SR530 of Stanford Research Systems. Both slits of the monochromator were placed at 100 μ m. A luminoscope, model ELM-2; MCA of Relion Corporation was employed to obtain Cathodo-Luminescence (CL) measurements; these were obtained in a stainless steel vacuum chamber equipped with a cold cathode electron gun. Samples were placed inside the vacuum chamber and evacuated to 10^{-2} Torr. The emitted light from the sample was coupled to an optical fiber bundle leading to a spectrofluorometer SPEX Fluoro-Max-P. CL spectra were recorded at room temperature. The accelerating voltage of the electron beam was 10 kV and the applied current was kept constant at 0.3 mA. The spot size of the electron beam on the sample surface was approximately 3 mm in diameter. Diffuse reflectance measurements in a range 200–800 nm were carried out by employing an UV–vis–NIR spectrophotometer, model Cary 5000 of VARIAN.

3. Results and discussion

Fig. 1 shows SEM micrographs that are representatives of the surface morphology for zinc oxide deposited on pyrex-glass (ZnO_{glass}) and aluminum substrates (ZnO_{Al}). Fig. 1a, b, and c shows how ZnO_{glass} was conformed by overlapping ZnO microrods. These figures show ZnO microstructures with evident hexagonal crystalline structure and the preference of the material to grow in a well formed rod shape. It is notable that the preferred growth of ZnO is along the *c*-axis [0001] direction. In Fig. 1a, three different microstructures can be observed principally: 1) well formed rods (R_W), 2) Two rods with single intersection (R_{SI}) and 3) Multiple rods with single intersection (R_{MI}); these characteristics possibly result from certain differences in the growing processes of the material properly influenced by the local chemical and/or thermodynamic environment, but not by the substrate nature. From Fig. 1b it is possible to observe uniformity in diameters and lengths for R_W , R_{SI} and R_{MI} microstructures and a remarkable predominant existence of R_W over the other two types of microstructures. Diameter and length average values were lower than 1 and 10 μ m, respectively. A random inspection over all substrate areas shows how this was uniformly covered by these kinds of microstructures, analogous to the area showed in Fig. 1c. SEM micrographs presented in Fig. 1d

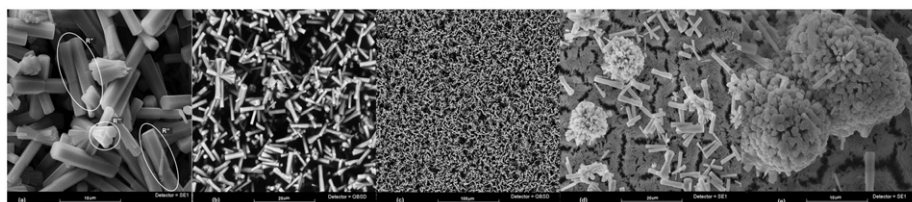


Fig. 1. SEM micrographs that present different magnifications of ZnO_{glass} (a, b and c) and ZnO_{Al} (d and e) samples. R_W —well formed rod, R_{SI} —two rods with single intersection, R_{MI} —microrods with multiple intersections.

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