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Photoluminescence of nanocoral ZnO films

M.A. Borysiewicz [a,*], M. Wzorek [a], T. Wojciechowski [b], T. Wojtowicz [b], E. Kamińska [a], A. Piotrowska [a]

[a] Institute of Electron Technology, Al. Lotników 32/46, Warsaw 02-668, Poland
[b] Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, Warsaw 02-668, Poland

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ABSTRACT

Photoluminescence studies of nanocoral ZnO nanostructures, fabricated using magnetron sputter deposition of porous Zn films with subsequent oxidation by RTP annealing at 400–800 °C is presented. Structural characterization of the films performed using electron microscopy techniques show the nanocoral morphology of the films with individual coral branches constituting of bunched single crystal ZnO grains of 30–100 nm in dimensions. High resolution images confirm the high quality of individual grains. The features in the photoluminescence spectra are identified using temperature-dependent and power-dependent measurements, with rich features observed in the excitonic region at 5 K, as well as zinc vacancy lines and surface-state recombination lines being present. It is found, that the spectra significantly depend on the annealing temperatures of the samples, with the spectra acquired for the sample annealed at 800 °C exhibiting stronger excitonic emission by 2 orders of magnitude than any other features, thus proving the highest structural quality of the nanostructures.

1. Introduction

Nanostructured ZnO has received a considerable amount of attention recently due to the wide band gap (3.4 eV) and high exciton binding energy of the material (60 meV), as well as the possibility of achieving developed surfaces of nanostructures including nanorods, nanowires, nanosheets, nanofibers and 3D hierarchically complex architectures [1–7] which are beneficial for absorption-based applications in sensors and photovoltaics. In particular, Ko et al. fabricated hierarchical nanoforest structures for dye sensitized solar cells [8] and Wang presented a selection of ZnO forms including nanowires, nanotubes, nanobelts, nanohelixes, nanocombs, nanorings, nanopropellers, nanosprings and nanoshells for nanoscale photonics, optoelectronics, piezoelectricity, and sensing applications [9]. Furthermore, porous ZnO was developed via nanotube membranes [10] or dynamic template assisted electrodeposition [11]. However, most of the above results were obtained using solution-based methods as well as using hydrothermal and powder sublimation growth.

Recently, the first ZnO nanostructures fabricated using porous Zn sputter deposition with post deposition oxidation annealing have been independently demonstrated by Zainelabdin [12], Lamberti [13] and our group [14]. These structures are unique in that they are fabricated using a vacuum-based technique offering a higher level of process stability and purity control than in the case of solution-based methods, which typically require reliable high throughput operation in wet conditions, as well as unprecedented scalability enabling its use in modern industrial coating applications, such as architectural or automotive glass coatings. This compatibility makes this technique preferential for future large-scale applications. First applications of these materials were demonstrated in photovoltaic cells [13] and alcohol and gas sensors [15] as well as in biochemical sensors [16]. This report focuses on the photoluminescence of the structures starting with a discussion of a selected spectrum measured as a function of temperature and excitation power, and then discusses the influence of process parameters during porous Zn deposition as well as the temperature during oxidation on the features in the spectra, allowing conclusions to be drawn about the structures themselves.

2. Experimental details

Nanocoral ZnO thin films on silicon (1 0 0) substrates were fabricated using a room temperature, DC reactive magnetron sputter deposition process for porous Zn, with subsequent RTP oxidation step in 6N oxygen flowing at 400–800 °C. The details of the procedure are given in our previous communication [14]. From previous experiments we know that the highest working gas pressure under which porous Zn films grow using reactive magnetron sputtering was 3 mTorr. Therefore, the films studied were grown at 3 mTorr and 1.5 mTorr. The morphology of the

* Corresponding author. Tel.: +48 225487875.
E-mail address: mbory@ite.waw.pl (M.A. Borysiewicz).

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resulting film is presented in cross-section and plan-view Scanning Electron Microscope (SEM) images acquired using a Zeiss Auriga. Transmission Electron Microscope (TEM) and high-resolution (HR) TEM images of individual crystallites of the nanocoral ZnO were taken using a JEOL JEM-2100 HRTEM. The photoluminescence of nanocoral ZnO was studied under He–Cd laser excitation at 325 nm wavelength. Excitation power density and temperature dependent photoluminescence spectra were acquired in a closed-cycle pumped He Oxford cryostat in the temperature range 5–300 K. The emitted light was guided to an Andor Solis Shamrock 500 spectrometer with 600 lines/mm and 2400 lines/mm diffraction gratings.

3. Results and discussion

3.1. General characterization of the films

The morphology of the resulting film is presented in cross-section and plan-view SEM images in Fig. 1. The comparison to a coral reef structure is evident with polycrystalline coral dendrites constituting the film. The microstructure of the films is polycrystalline ZnO as reported earlier [14] with no Zn crystallites. Therein it was also shown that the morphology and microstructure exhibit no significant dependences on the Zn deposition conditions nor oxidation temperatures used, with the only observable effect in the lowering of FWHM of the XRD pattern peaks with increasing temperature, evidencing an improvement in the crystallite quality.

Conventional and high resolution (HR) TEM images are presented in Fig. 2. Based on the images it can be stated, that the corals are composed of smaller crystallites of around 50 nm and

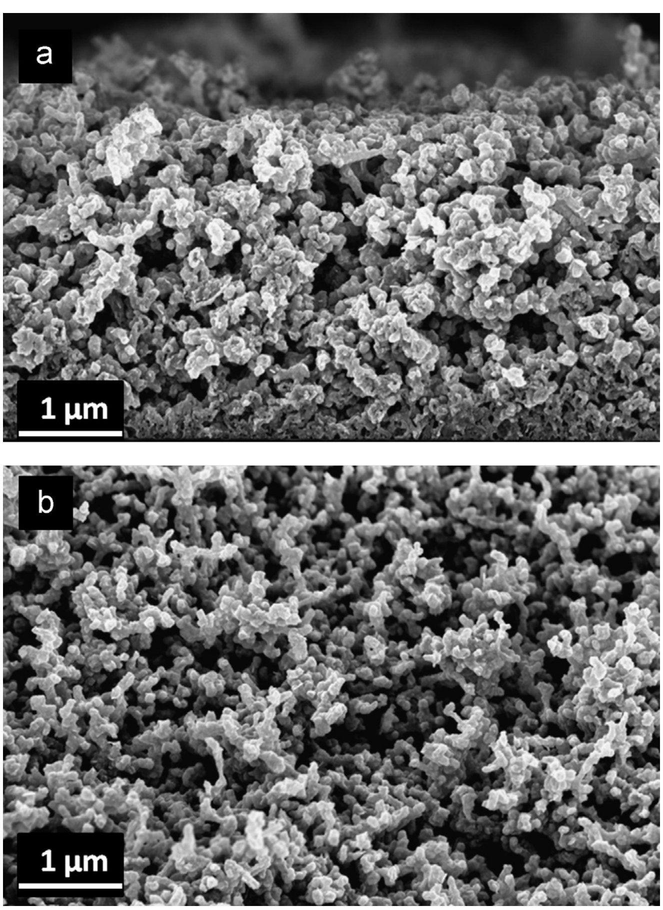

Fig. 1. Nanocoral ZnO morphology in cross-section (a) and plan view (b).

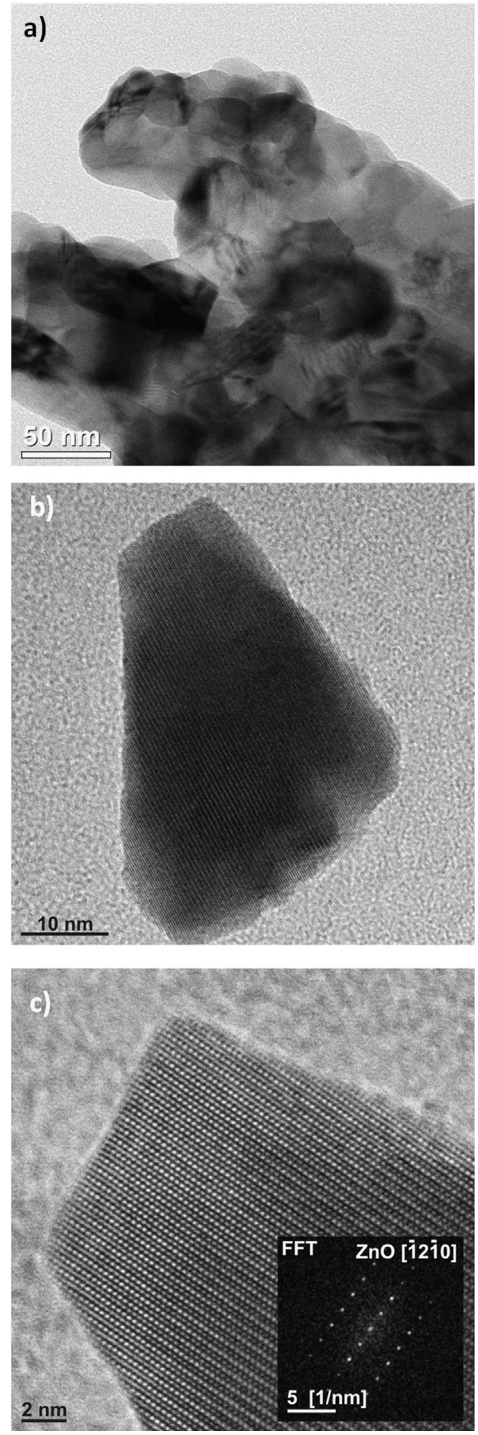

Fig. 2. TEM image of a single coral branch (a) and of an individual crystallite (b) with HR-TEM image of the crystallite showing perfect ordering and Fast Fourier Transform analysis (FFT) image in the inset (c).

less in diameter. The HRTEM image presented in Fig. 2(c) shows that a good atomic ordering in the nanocrystals is present with no significant defects visible. Fast Fourier Transform (FFT) analysis of this image confirms that it is ZnO yielding lattice constants c=5.16 Å and a=3.27 Å, which are slightly smaller than the bulk lattice constants of 5.2062 Å and 3.2495 Å, respectively [17].

The film fabricated by depositing porous Zn at 1.5 mTorr and subsequent oxidation at 600 °C will be the one used for the general discussion of the photoluminescence spectra with individual line identification. The discussion of the influence of