Bulk nanocomposite made of ZnO lamellae embedded in the ZnWO₄ matrix: growth from the melt

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ABSTRACT
Zinc oxide (ZnO) nanostructures exhibiting high exciton binding energy and efficient radiative recombination, even at the room temperature, are of increasing interest due to their prospective exploitation in optoelectronic and laser applications. However, attempts to synthesize well-ordered structures through simple and fast process have faced many difficulties. Here, we demonstrate a novel manufacturing method of ZnO lamellae embedded in a crystalline wide band gap dielectric matrix of the zinc tungstate, ZnWO₄. The manufacturing method is based on a directional solidification of a eutectic composite, directly from the melt, resulting in a nanostructured bulk material. Electron microscopy studies revealed clear phase separation between the ZnO and ZnWO₄ phases, and cathodoluminescence confirmed exciton emission at room temperature and thus high quality and crystallinity of the ZnO lamellae, without defect emission. Hence, utilization of directional solidification of eutectics may enable cost-efficient manufacturing of bulk nanostructured ZnO composites and their use in optical devices.

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Introduction

Zinc oxide has received much attention in recent years because it exhibits a wide range of favorable properties. The lack of a center of symmetry and large electromechanical coupling give rise to strong piezoelectric and pyroelectric properties and the resulting use of ZnO in mechanical actuators and piezoelectric sensors [1]. Moreover, ZnO is a wide band gap (3.37 eV) semiconductor that is suitable for short wavelength optoelectronic applications, and its high exciton binding energy (60 meV) can ensure efficient excitonic emission at room temperature [2]. ZnO is also biocompatible, biodegradable, and bio-safe for medical and environmental application and shows good photocatalytic activity [3]. Hence, ZnO may be considered for an extensive range of applications such as energy storage, sensors, cosmetic products, optoelectronic and electronic devices, among others [4]. Recently, ZnO nanostructures have received broad attention due to their unique properties [5]. In particular, they have been widely used for sensing applications because of their high sensitivity to the chemical environment. ZnO nanowires have the advantage of a high surface area and have demonstrated high sensitivity, even at the room temperature, whereas ZnO thin film gas sensors often need to be operated at elevated temperatures [6]. Lasing in ZnO nanowire arrays grown by a variety of methods has been observed by different research groups, and single nanowire light-emitting diode was presented as well [7]. Moreover, well-aligned single-crystalline nanowires were proposed for use as high-aspect-ratio probes for atomic force microscopy (AFM) [7]. Recently, ZnO nanostructured films have been also used in dye-sensitized solar cells as an electrode material [6].

High-quality crystals can, in principle, be grown from the melt. However, despite several trials [8], it is not really possible, since ZnO decomposes into atomic components below the melting point, 1975 °C, at atmospheric pressure [9]. However, this can be overcome with a eutectic transition, where from a one-phase melt a two-solid-phases composite material is crystallized at much lower melting temperature than its constituent phases, enabling growth of phases like the ZnO.

Directional solidification of eutectics has been considered as a promising method to fabricate bulk, highly crystalline and self-organized nano-/microstructures out of various materials combinations, with a plethora of geometrical motifs, controllable structure refinement and sharp interfaces [10].
Recently, directional solidification of eutectics was utilized for energy materials such as solid-oxide fuel cells [11, 12] and electrodes for hydrogen generation [13, 14], and optical materials such as photonic crystals [15, 16]; THz polaritonic materials [17, 18]; metamaterials [19–23] and nanoplasmonic materials [24–26]. It has been also shown that eutectic composites could exhibit unusual geometries when properly engineered [27–29], in addition to being grown as bulk materials [30] even on the industrial scale and also printed [31].

In this work, we utilize the eutectic directional solidification for manufacturing of well-ordered ZnO layers directly from the melt. The ZnO ca. 250-nm-thick layers are embedded in the ZnWO₄ matrix forming a bulk ZnO-ZnWO₄ material. The growth of the composite by the micro-pulling down method is presented. The optical response of the obtained nanostructured ZnO composites was assessed by cathodoluminescence studies.

Materials and methods

Crystal growth

ZnO-ZnWO₄ eutectic rods were grown by the micro-pulling down method using Cyberstar commercial equipment. This method utilizes a metallic crucible with a shaper at the bottom and a centrally placed nozzle (Fig. 1a). Starting charge material is placed in the crucible which is then mounted in the furnace. The raw materials are molten in the crucible; the melt exudes through the nozzle and wets the bottom of the shaper. The molten material is kept by the surface tension, liquid viscosity and cohesion forces between the liquid and the crucible. Then, the molten material is touched with the seed crystal, and the seed with the growing rod is pulled down. The growth atmosphere was nitrogen, and a SrLaGaO₄ crystal was used as a seed [32]. The growing process was controlled by adjustment of power and pulling rate. In this case, to obtain good quality with homogeneous distribution of ZnO precipitates in the whole volume of the rod, an iridium crucible (Heraeus Holding GmbH) with a rectangular die 3 × 5 mm and a slit of 1 × 3 mm was used. A picture of the crucible and its cross-sectional scheme are shown in Fig. 1b, c.

High-purity ZnO (99.9999%) and WO₃ (99.999%) oxide powders were mixed with ethanol in an agate mortar and dried at 350 °C, and then, the charge material was loaded into a crucible and heated up.

The growth processes were monitored by CCD camera, and the temperature was measured using a Raytek MM2MH pyrometer. The emissivity of the iridium crucible used during the growth was determined experimentally and was equal to 0.46 for the 1.6 µm spectral range and the temperature range of 900 to 1200 °C. The measured area was 1 mm in diameter and was located on the wall of the crucible as close as possible to the growth zone. Figure 1e shows the crystallization front, growing fiber and the temperature measurement area.

The process was controlled manually by changing the pulling rate and output power of generator at the initial stage of growth in order to obtain a crystallization front as thin as possible and parallel to the surface of the shaper. After stable thermodynamic conditions of the growth were obtained, only the output power of the generator was changed to control the parameters of the crystallization front and the pulling rate was kept constant. Figure 1f shows the temperature recorded during the process. The rapid rise of temperature after 30 min of the heating procedure was related to the change in emissivity of the crucible, as molten material began to climb on the walls of the crucible during seeding process. Then, the thermodynamic conditions were stabilized and the growth started. The temperature was raised from 1170 °C to the melting point of ZnO-ZnWO₄ eutectic 1190 ± 20 °C [33]. The increase in temperature around the 7th hour was due to re-climbing of molten material on the wall of crucible. However, it did not affect the growth of the eutectic rod and its quality. After a period of stable growth, the temperature was increased to detach the eutectic fiber from the bottom of the crucible, and cooling was started. The as-grown ZnO-ZnWO₄ eutectic rod is presented in Fig. 1g.

Phase and micro/nanostructure characterization

The crystallographic structure and phase content of the ZnO-ZnWO₄ eutectic were analyzed by powder X-ray diffraction (XRD) using a Siemens D500 diffractometer equipped with a semiconductor Si/Li detector and KαCu radiation. The diffraction patterns were measured in 2θ/2θ scanning mode with a step of
0.02° and counting time of 10 s/step. The experimental data were analyzed by Rietveld refinement using the R. A. Young DBWS-9807 program package. Microstructure characterization was carried out with scanning electron microscope (SEM) Auriga® CrossBeam® Workstation (Carl Zeiss) equipped with an energy-dispersive spectroscopy detector (EDS) for chemical composition analysis. This dual beam workstation was also used for focused ion beam SEM (FIB-SEM) tomography. Serial FIB cross sections in situ milling was performed by Ga-ion beam. For each slice, SEM images (image size 1024 × 768 pixels, 24 bit grayscale) were taken. The crystal orientation relationship between the two phases and interface planes were determined using a transmission electron microscope (TEM) FEI Tecnai F20ST, FEG 200 keV.

Cathodoluminescence

Cathodoluminescence (CL) measurements were taken with SEM (CamScan CS3200 with a LaB6 cathode) at the Centre of Optoelectronics, the University of Southampton. The electron beam was focused onto the sample via a parabolic mirror mounted directly above it. The mirror collected the light emitted from the sample and directed it out of the SEM chamber to a Horiba spectrometer with a liquid-nitrogen-cooled CCD detector. The covered spectral range was 250–1000 nm using 1024 channels. During the CL spectra measurement, beam current of probe varied between areas of interest; therefore, recorded spectra were normalized.
Results and discussion

In order to demonstrate the possibility of utilizing directional solidification of eutectics for manufacturing ZnO nanostructured materials in a bulk form directly from the melt, we have grown rods with the eutectic composition of 65 mol% ZnO and 35 mol% of WO₃, marked on the WO₃-ZnO phase diagram in Fig. 1d [33]. According to Shchenev et al., the ZnO-WO₃ equilibrium phase diagram encloses only one ternary compound ZnWO₄ and two eutectic invariant points [33]. The ZnO-ZnWO₄ eutectic at 65 mol% of ZnO and 35 mol% of WO₃ molar ratio allows the solidification of ZnO as one of the component phases. The melting temperature at the eutectic point is about 1187 °C, which is much lower than the melting point of ZnO (1975 °C) [4] and WO₃ (1473 °C) [33]. The melting point is low enough to allow the coexistence of solid and liquid phases of ZnO and, under these conditions, the material does not decompose. Eutectic rods were obtained with a pulling rate of 0.1 and 0.5 mm/min. At the initial stage of growth, when the thermodynamic conditions were not stable, large ZnO inclusions (400 × 40 μm) could be observed within the eutectic rod core as shown in the SEM image (Fig. 1h). After stabilization of eutectic growth conditions, large inclusions of ZnO were not observed.

The XRD demonstrated two phases in the obtained rods, Fig. 2a. The diffraction peaks match well the standard diffraction pattern of wurtzite ZnO phase (JCPDS-04-015-4060) and wolframite ZnWO₄ phase (JCPDS-04-009-8448) with no evidence of any extra phases within the XRD detection limits. The lattice parameters deduced by Rietveld refinement of the XRD profile of ZnO-ZnWO₄ eutectic are \( a = 3.25 \) Å and \( c = 5.21 \) Å for ZnO and \( a = 4.69 \) Å, \( b = 5.72 \) Å, \( c = 4.93 \) Å, \( \beta = 90.64^\circ \) for ZnWO₄ and match well the previously reported values [34, 35]. The plane orthogonal to the growth direction was determined directly from bulk crystal samples. They correspond to (1010) \( (2\theta = 32^\circ) \) and (1120) \( (2\theta = 56^\circ) \) for the ZnO and (001) \( (2\theta \sim 36^\circ \) and \( 2\theta \sim 72^\circ) \) and (013) \( (2\theta \sim 57^\circ) \) for ZnWO₄, the last one giving rise to a weaker diffraction signal.

The SEM images and EDS studies Fig. 2b, c revealed a eutectic micro/nanostructure consisting of ZnO lamellae/layers embedded in the ZnWO₄ matrix in the entire volume of the eutectic rods regardless of the thermodynamic conditions of growth, Fig. 3a–c. In the whole volume of sample, eutectic grains as big as \( 100 \times 100 \) μm² and more were observed. Within one grain, ZnO lamellae were parallel to each other and their thickness was approx. 250 nm.

In order to reconstruct the microstructure of ZnO-ZnWO₄ eutectic in three dimensions (3D), the FIB-SEM technique was used. In this technique, the sample is sequentially milled using an ion beam perpendicular to the specimen while imaging the newly exposed surface using an electron beam. A thorough analysis of sectional micrographs perpendicular to the growth axis recorded using FIB-SEM technique confirms that the ZnO-ZnWO₄ eutectic crystallizes in the broken-lamellar structure, Fig. 3d [36]. The characteristic feature of the eutectic with broken-lamellar structure is the small volume ratio of the lamellar phase to the matrix phase. The minor ZnO phase appears as broken lamellae in the 2D microstructure, but FIB-SEM shows that the ZnO phase is continuous and occurs as perforated plates with holes filled with ZnWO₄ matrix phase. This broken lamellar type microstructure obviously represents a structure dictated by a long-range force favoring lamellar morphologies. However, a short-range force (instability perhaps) clearly exists which “breaks” the lamellae [37]. As suggested by Beghi, the relatively large interlamellar spacings and thin lamellae observed in low-volume-fraction eutectics require large diffusion distances. Therefore, it seems quite possible that thermally induced local irregularities in the solute concentration or diffusional flow in the melt could produce the irregular “breaks” as seen in two dimensions or “holes” in three dimensions [38].

The ZnO-ZnWO₄ eutectics have been further studied using high-resolution TEM (HRTEM). The thin foil was extracted from a plane containing the growth axis. In order to study the crystal orientation relationship between the ZnO and ZnWO₄ and to define the interface planes, diffraction studies were performed (Fig. 4). Figure 4a shows a selected area electron diffraction (SAED) pattern of the ZnWO₄. When the thin foil is perpendicular to the electron beam, no simple zone axis can be obtained for the matrix. Only the [001]* reciprocal direction can be imaged, indicating that the (001) plane of the ZnWO₄ matrix is perpendicular to the surface of the FIB foil. With a few degrees tilt, the foil is oriented in [100] zone axis, Fig. 4a with the 001 reflection obtained by
double diffraction (dd). For the same tilt angles, the ZnO lamella does not show a simple zone axis but the [0001]* reciprocal direction for ZnO (Fig. 4b). Figure 4c depicts diffraction patterns recorded at the interface, to superpose the two patterns. The (0002) planes of ZnO are parallel to the (020) planes of ZnWO4 as their inter-planar distances are compatible (d020. ∗ 0.286 nm for ZnWO4 and d0002. ∗ 0.260 nm for ZnO). The HRTEM image of the interface between (010) ZnWO4 and (0002) ZnO is shown in Fig. 4d. Based on the TEM observation, the orientation relationship for the ZnO lamellae and ZnWO4 matrix is defined as [1100] ZnO almost // [100] ZnWO4 (less than 5° mismatch) and planes (0001) ZnO // (010) ZnWO4.

Figure 5a shows the CL spectra acquired for ZnO-ZnWO4. The spectra consist of two emission peaks at about ∼ 371 and ∼ 498 nm. The peak at 371 nm (UV luminescence) is attributed to near band edge (NBE) emission [39], which originates from the recombination of free-excitons through an exciton-exciton collision process in ZnO. The other peak ∼ 498 nm is usually attributed by intrinsic tungstate emission. The WO6 octahedra and a slight deviation from perfect order in the crystal structure are responsible for blue light emission band of ZnWO4 [40]. Only UV luminescence (∼ 373 nm) was observed for ZnO lamellae, whereas the ZnWO4 matrix exhibited a broad band emission centered at 498 nm. The study of luminescence properties of ZnO-ZnWO4 eutectic component phases independently reveals that the blue/green luminescence originates only from the ZnWO4 phase. No green and blue luminescence has been detected in ZnO. In contrast to our ZnO-ZnWO4 eutectic composite, the photoluminescence (PL) studies on (ZnO)1-x-(ZnWO4)x (x = 0, 0.1,0.2,0.3,0.5,0.7, 0.9, 1) nanocomposite prepared by precipitation method revealed...
Figure 3 Broken-lamellar micro-/nanostructure of the ZnO–ZnWO₄ eutectic composite. a SEM image for the eutectic rod grown with the pulling rate p.r. = 0.5 mm/min, b eutectic grains (p.r. = 0.1 mm/min), c High-magnification image of the eutectic micro-/nanostructure observed in stable thermodynamic conditions, outside the core zone; ZnO layers (av. ~ 240 nm thick) embedded in the ZnWO₄ matrix (p.r. = 0.1 mm/min). d FIB-SEM images of the sections perpendicular to the growth axis and reconstructed 3D model confirming the broken-lamellar character of the micro/nanostructure. e A scheme of the broken-lamellar structure.

Figure 4 Crystal orientation relationship between the ZnO and ZnWO₄ phases as investigated by transmission electron microscopy. Selected area diffraction pattern of a the ZnWO₄ matrix, b the ZnO lamella, and c the eutectic composite. d HRTEM image of the (010)ₜ₎ₕₕₖₜₖRelativeLayout of the (010)ₜₕₕₖₜₖ (0002)ₕₕₚₜₚ interface region.
mainly broad blue-green emission band in the range of 440–550 nm and the PL intensity of ZnO was insignificant compared with that of ZnWO$_4$ [41]. Figure 5b, c shows CL intensity and SEM images taken at 371 nm which corresponds to NBE emission in ZnO. The strong excitonic emission, with negligible emission in the visible range in ZnO lamellae, indicates the good optical quality of these nanostructures. Although the actual recombination mechanisms for visible emission in ZnO are still not fully understood, the absence of the visible defect-related deep level (DL) emission reveals a lower density of such defects in ZnO lamellae within the obtained eutectic composite [42].

Conclusions

A new eutectic with 65 mol% ZnO and 35 mol% WO$_3$ composition has been grown, and its structural and optical properties have been studied. The presence of only two phases, ZnO and ZnWO$_4$, has been confirmed by XRD and SEM. The ZnO-ZnWO$_4$ eutectic tends to grow with a broken-lamellar structure, with the ZnO phase forming perforated nanolamellae embedded in the ZnWO$_4$ matrix. Growth of ZnO-ZnWO$_4$ eutectic is an excellent platform for achieving ZnO nanostructures with high crystal quality and low density of defects as assessed by cathodoluminescence. Such a bulk yet nanostructured ZnO material exhibiting ZnO lamellae/layers could work as optoelectronic elements which can be cut from the volumetric material and polished. Potential applications could include filters [43], polaritonic lasers [44], efficient second harmonic generators [45], ultraviolet photodetectors and optical switches [46].

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Author’s contribution

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Declarations

Conflict of interest  The authors declare that they have no conflict of interest.
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