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Synthesis, structural and optical characterization of ZnO crystals grown in the presence of silver

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ABSTRACT

Zinc oxide microcrystals grown at atmospheric pressure by the *laser assisted flow deposition* method were characterized by morphological, structural and optical techniques. A set of samples with 0, 0.8, 2.0, 3.0 and 5.0 mol% nominal $AgNO_3$ content were studied in order to analyse the influence of silver amount on the near band edge recombination. A detailed study of the samples' photoluminescence evidence that at room temperature the free exciton recombination occurs at ~3.334 eV for crystals grown in the presence of silver instead of the broad peak observed at ~3.28 eV for the undoped ones.

1. Introduction

ZnO has been one of the most studied materials in the last decades, either as bulk material, epilayers and nanostructures. This direct wide band gap semiconductor (E_g ~3.438 eV at 4 K [1]) is seen as a promising candidate for several technological applications covering an entire range of purposes from electronics, optoelectronics, energy and medical surveys [2–8]. The near band edge recombination of undoped and doped bulk material, epilayers and nanostructures have been extensively studied [9–25]. Nowadays, it is well established that ZnO has a free exciton (FX) binding energy of 60 meV [13,14,16–18,21,24,25]. The most debated optical centres in ZnO structures are the 3.31 eV line [15,26,27] and the broad green, orange and red bands [17]. Among other optical phenomena, the room temperature (RT) peak position of the FX recombination has been explored in less extent. Usually, in high optical quality ZnO samples the RT peak position located at ~3.28 eV is attributed to an overlap of the FX recombination with its LO-phonon replica [16,21,24] or to the 3.31 eV line assigned to stacking faults in the basal plane [15].

The aim of the present study is to clarify the nature of the RT ultraviolet emission band. Therefore a detailed photoluminescence (PL) studies was carried out in ZnO microcrystals grown by *laser assisted flow deposition*. By comparing the results obtained for ZnO samples grown with and without $AgNO_3$ the nature of the observed ultraviolet emission is discussed.

2. Experimental details

The laser assisted flow deposition was used to grow the ZnO crystals. This technique is based on a modified laser floating zone growth chamber (Fig. 1a) which comprises a 200 W CO_2 laser (Spectron) coupled to a reflective optical set-up producing a circular crown-shaped laser beam. This crown-shaped beam is focused at the tip of extruded rods prepared by mixing the commercial ZnO (AnalaR, 99.7%) and $AgNO_3$ powders (MERCK, 99.8%) with polyvinyl alcohol (0.1 g/ml, Merck). This mixture was further extruded into cylindrical rods with diameters of 1.75 mm. Different nominal concentrations of $AgNO_3$ were used: 0.8, 2.0, 3.0 and 5.0 mol%. The Si {001} substrates are placed on a sample holder attached to the upper spindle of the LFZ system, above the feed rod, Fig. 1b. The laser beam is focus radially on the tip of the precursor leading to the ZnO evaporation. This process occurs during 3 min keeping the laser power at 25 W. The generated gases are so transferred to the low temperature regions, promoting the reaction of zinc with oxygen to form ZnO [28]. Fig. 1c shows the ZnO crystals grown at the top of the feed rod precursor.

The morphology of ZnO crystals was characterized by scanning electron microscopy, SEM (Hitachi SU-70) with a operating voltage of 25 kV and the crystalline structure was investigated by performing θ–2θ scans by X-ray diffraction (XRD) using a PANalytical X'Pert PRO apparatus (Cu Kα radiation, λ = 1.54056 Å).

Steady state PL measurements were carried out between 14 K and RT using the 325 nm He–Cd laser line as excitation source. The emitted light was dispersed by a Spex1704 monochromator (1 m, 1200 mm^{-1}) and detected with a cooled Hamamatsu R928 photomultiplier.

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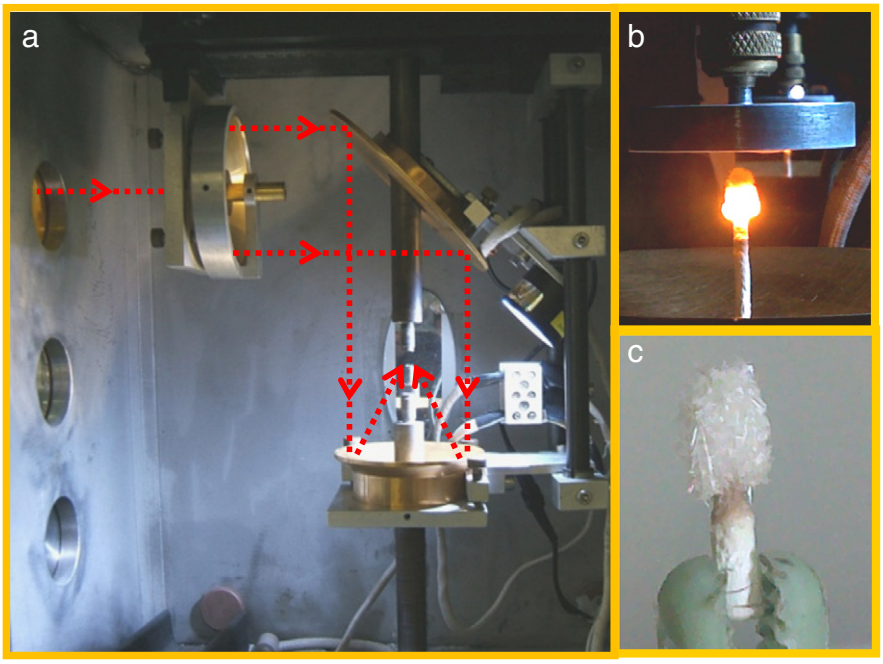

Fig. 1. Scheme of the laser optical path inside the chamber before hitting the feed rod (a); close-up of the growth region, the laser incidence area being clearly shown (b); ZnO crystals formed at the feed rod tip (c).

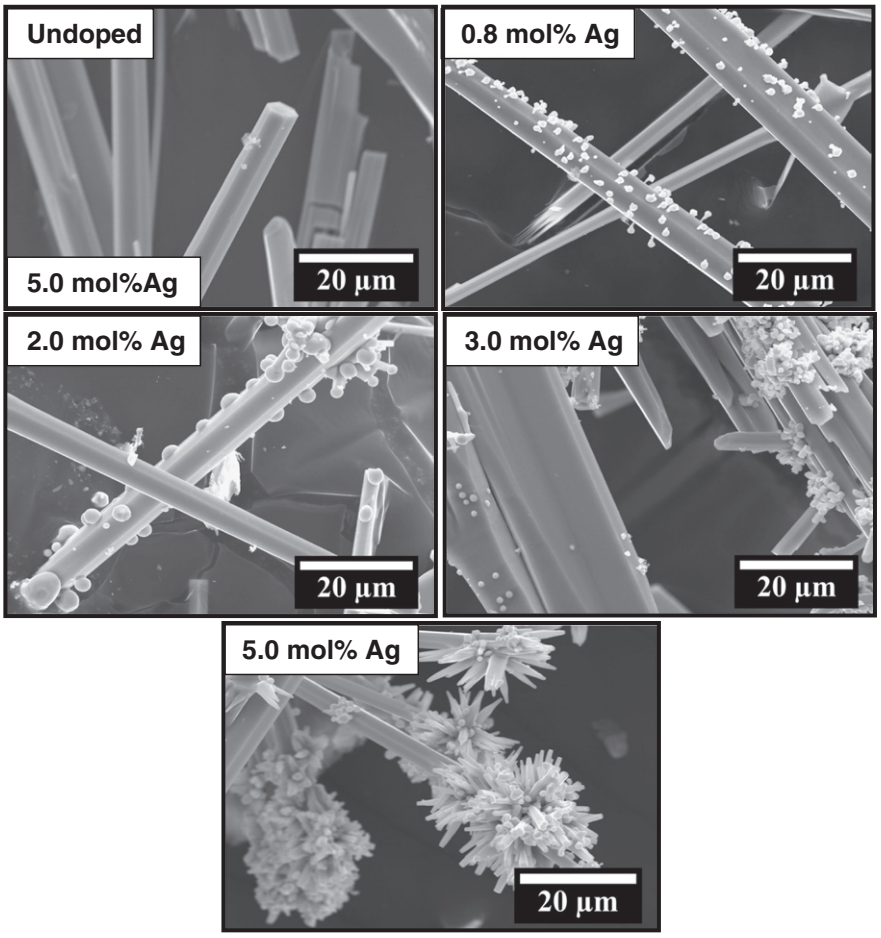

Fig. 2. SEM micrographs of the ZnO crystals grown with different nominal silver contents showing randomly oriented ZnO hexagonal rods with spherical droplets deposited over the surface of the rods. For higher Ag nominal concentration a re-nucleation growth is observed.