Electron microscopy study of Bi doped ZnO and Zn-In-O nanowires and nanobelts grown by a thermal method

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In the frame of the increasing activity on nanoscale electronic and optical devices a high number of doped and undoped ZnO elongated nanostructures, such as wires, rods or needles, have been reported in the last years, including few works on Bi or In doped nanostructures. It has been suggested [1] that Bi doped nanowires have potential applications as nanovaristors. In doped ZnO is a good transparent conductor which can show better transparency and similar conductivity than Indium-Tin –Oxide or ITO. The compound Zn-In-O is also of interest as transparent conductor and other applications. In this work, Bi doped ZnO and ZnInO elongated nano- and microstructures have been grown by thermal treating of compacted mixtures of ZnO-Bi_2O_3 or ZnO-In_2O_3 powders, respectively. Growth was performed by a vapor-solid (VS) method, which has been found to be efficient to grow nanostructures of different semiconductor oxides, including ZnO doped nanowires [2][3]. Samples were prepared by milling the corresponding mixtures in a centrifugal ball mill. The final powders were compacted under a compressive load to form disk shaped samples and were annealed under argon flow at 1350º C for 15 hours and 950ºC for 10 hours. The structures were characterized by XRD, SEM, CL-SEM, EDS and TEM. In addition, electrical resistance measurements of single Bi doped ZnO wires have been performed.

The obtained Bi doped ZnO structures have mainly needle or rod shape with typical Bi content in the range 0.15-0.35 %.at. Figure 1 shows an arrangement of oriented Bi doped structures. Occasionally, large aggregates of rods become the core of hierarchical structures. HRTEM images of the thinner wires show lattice fringes perpendicular to the growth direction, whose analysis show that the nanowire growth direction is (101). CL spectra show a red shift of the near band gap luminescence emission in the Bi doped structures, relative to the undoped material. However, EDS and CL measurements do not enable a quantitative correlation between the amount of the shift and the Bi content. I-V curves of single Bi doped rods, show a non-linear behavior, the influence of the presence of Bi on this effect is being investigated.

XRD and EDS measurements indicate that the structures grown from the ZnO-In_2O_3 mixture belong to the $Zn_4In_2O_7$ phase. Large hexagonal plates and nanobelts are the main structures grown (Figure 2). Most of the belts have been found to grow at the edges of the plates. The main CL bands in the belts appear in the red and near infrared range. TEM of the belts show a modulated structure of the plane fringes.

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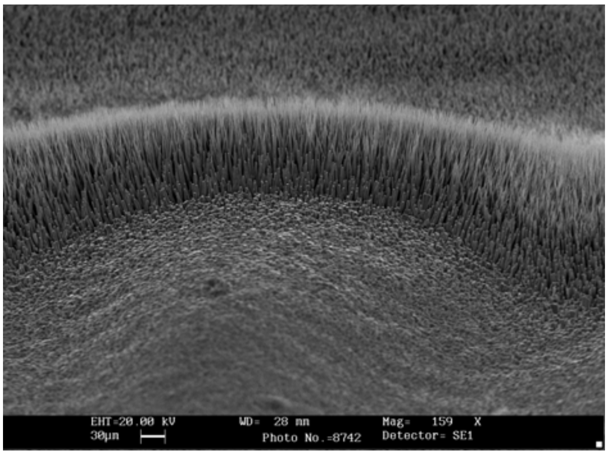

Figure 1. Bi doped ZnO structures. Structures grown on regions closer to the gas inlet during the annealing, are longer and their cross section decreases along the growth axis so that they terminate in needle shape. Tips of the needles have dimensions of tens on nanometers.

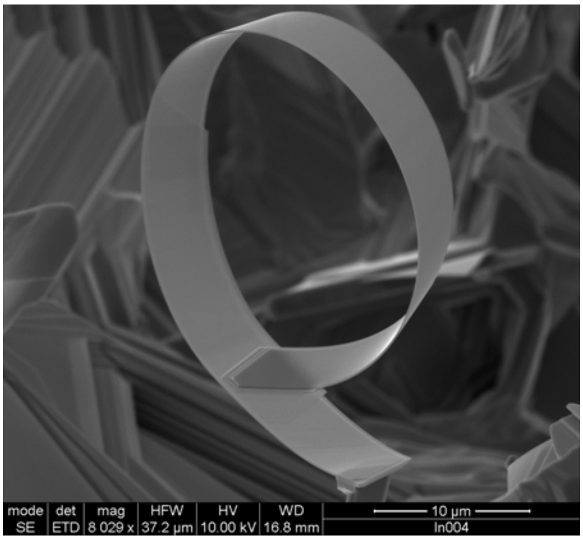

Figure 2. Zn-In-O nanobelts. The edges of large hexagonal plates have been found to be the nucleation sites for the growth of the nanobelts.

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