TEM and CL Investigations of Doped ZnO Nanostructures

Y. Ortega[1,2], Ch. Dieker[1], P. Fernández[2], J. Piqueras[2], W. Jäger[1]

1. Microanalysis of Materials, Christian-Albrechts-University of Kiel, 24143 Kiel, Germany
2. Dept. Materials Physics, University Complutense of Madrid, 28040, Madrid, Spain

yov@tf.uni-kiel.de
Keywords: vapour-solid growth, ZnO nanostructures, SEM, CL, TEM

Advanced imaging and spectroscopic techniques of electron microscopy play a crucial role in characterizing the microstructure and the structure-property relationships of nanostructured materials and interfaces. Doped ZnO nanostructures of different morphologies were grown by catalyst-free vapour solid growth at 1280 °C for times < 20 h using the different precursors $ZnS+SnO_2$, $ZnS+Al_2O_3$, and $ZnO+Eu_2O_3$. The morphology and the cathodoluminescence from nanostructures were investigated in a SEM equipped with a CL spectrometer [1]. Investigations of the structure and of the interface phenomena for a variety of rod-like nanostructures were performed by bright-field, dark-field, and high-resolution TEM imaging and combined with composition analyses by EDX in a TECNAI F30 at 300 kV [2].

Fig. 1a shows an example of a SEM image of larger rod-like ZnO nanostructures with hexagonal cross-sections. The CL investigations reveal locally varying emission intensities with a maximum intensity from the core region of the ZnO nanostructures (Fig. 1b). The broad emission band in the CL spectra (Fig.1c) suggests the presence of defects. For Sn- and Al-doping the rod-like nanostructures are characterized by distinct core and shell regions, with the core regions frequently containing either voids or other defects. Void formation appears to be absent for rod-like Eu-doped ZnO nanostructures. Fig. 2 shows a single nanorod structure with a hollow core next to a core region enriched in Sn. In addition, the surfaces are decorated by nanocrystals. The spatially resolved EDX measurement clearly indicates the presence of Sn in this region (as opposed to the adjacent hollow region). Small amounts of S are also detected (the Cu signal results from the TEM support grid). For the case of Al-doping, Fig. 3a shows an example of a nanostructure with a band of defects in the core region and nanocrystals that are attached to the protruding surface regions of the rod. The high-resolution lattice image (Fig. 3b) is taken from a near-tip region of a rod-like Eu-doped ZnO nanostructure. The analysis reveals that the lattice distances are consistent with the ZnO wurtzite structure. The growth direction of this particular rod is the [001] direction.

Concluding, the most prominent morphological and structural observations will be discussed in terms of a model which accounts for the growth and interface phenomena observed by TEM. For Sn-doped ZnO nanostructures, the comparison between TEM and CL investigations suggests that the spatial and spectral distribution of CL intensity can be correlated with the presence of defects in a core-shell arrangement in different regions of the nanostructures.

1 Y. Ortega, P. Fernández, J. Piqueras, J. Crystal Growth 311, 3231 (2009).
2 Y. Ortega, Ch. Dieker, P. Fernández, J. Piqueras, W. Jäger, to be submitted (2009).
Y. Ortega., P. Fernández., and J. Piqueras acknowledge funding by MEC (project MAT2006-01259).

DOI: 10.3217/978-3-85125-062-6-587 , © Verlag der TU Graz 2009

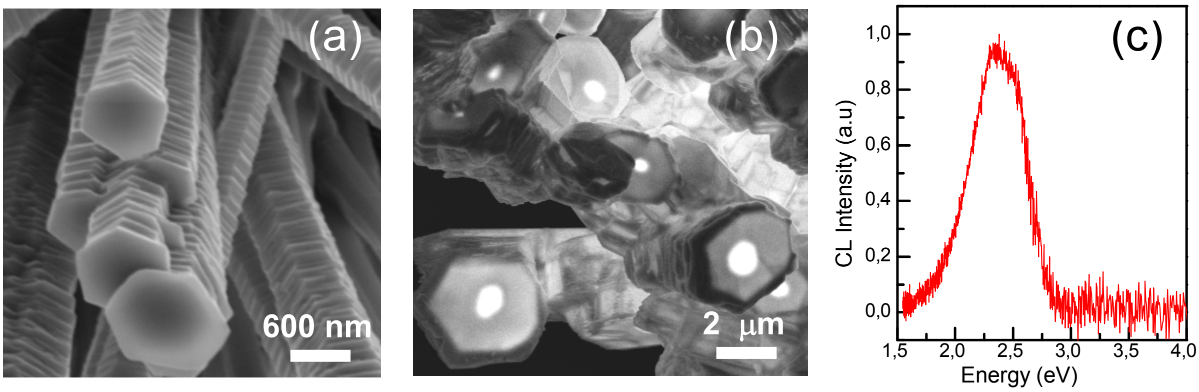

Figure 1. (a) Secondary-electron SEM image of larger Sn-doped ZnO nanostructures. (b) Inhomogeneous CL emission from hexagonal faces. (c) CL spectrum taken from core region with highest intensity shows a broad emission band related to electronic states of defects.

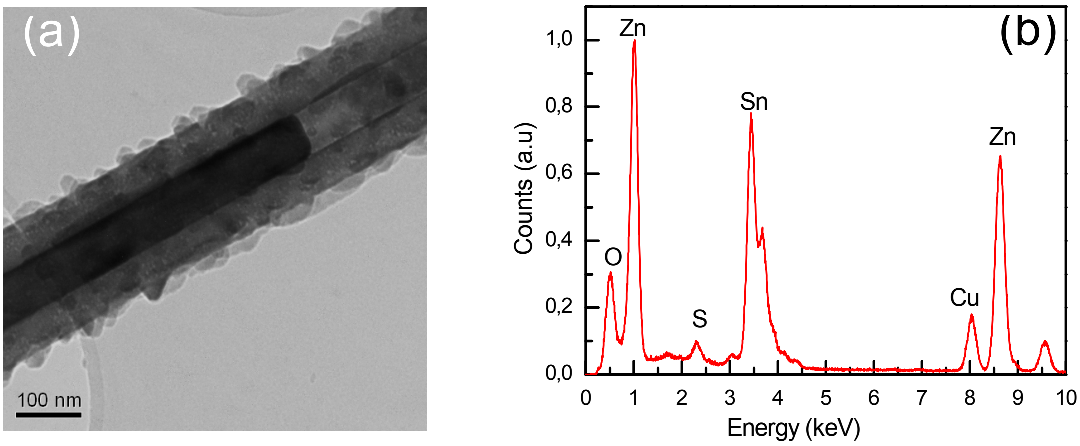

Figure 2. (a) Bright-field TEM micrograph of single Sn-doped ZnO nanorod showing hollow core regions, regions consisting of Sn-rich material, and surface nanocrystals. (b) Spatially resolved EDX spectrum displaying the presence of Sn and of traces of S in the core region.

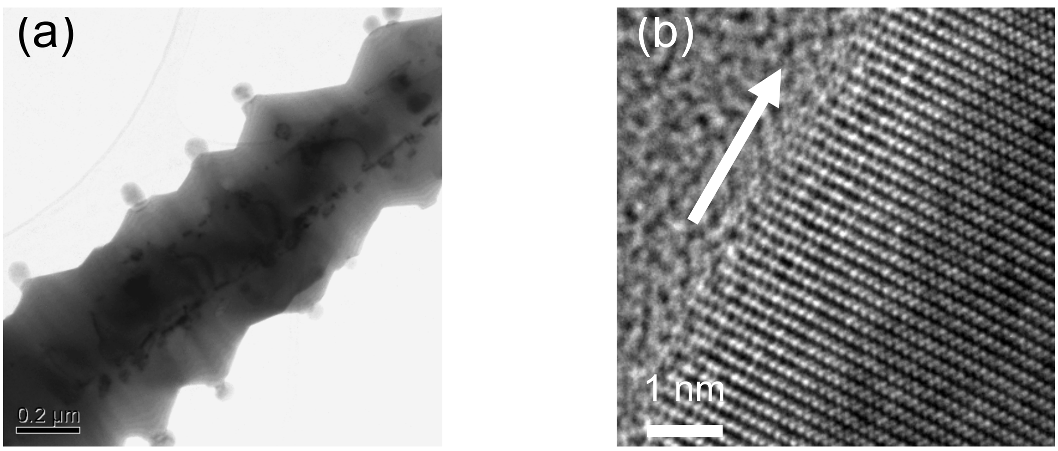

Figure 3. (a) Al-doped ZnO nanostructure with defects and surface nanocrystals. Bright-field TEM micrograph. (b) High-resolution lattice image of Eu-doped rod-like nanostructure. The (0002) lattice plane distance along the growth direction (arrow) amounts to 0.26 nm.

W. Grogger, F. Hofer, P. Pölt (Eds.): MC2009, Vol. 3: Materials Science,
DOI: 10.3217/978-3-85125-062-6-587 , © Verlag der TU Graz 2009