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Electron Microscopy Investigations of Doped ZnS Nanostructures

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Zinc sulfide (ZnS), a semiconductor compound of the II-VI group, has a wide bandgap energy at room temperature. The bandgap energy is structure dependent, about 3.72 eV for cubic ZnS blende, and about 3.77 eV for hexagonal wurtzite blende. Due to its intrinsic properties ZnS is a promising material for photonic, optical, and electronic devices [1]. One-dimensional ZnS nanostructures can be synthesized by various techniques including thermal evaporation, laser ablation, arc discharge, self-assembly methods, and chemical synthesis techniques. Pending on the synthesis method ZnS nanostructures with various crystal structures and morphologies can be obtained. The ZnS nanostructures shows superior chemical and thermal stability compared with another better known wide bandgap semiconductor, ZnO. Therefore, ZnS nanostructures are more suitable for visible-blind ultraviolet (UV) devices such as sensors and photodetectors.

In the present work severa one-dimensional ZnS nanostructures have been produced by vapor solid growth on various substrates. One sample was pure ZnS grown on a gold film deposited on a silicon substrate. Two copper doped ZnS were growth on two different substrates. All samples show strong photoluminescence in the visible light region. The morphology, chemical composition, and crystallographic structure of the obtained samples were investigated using electron microscopy techniques. Morphological and chemical composition investigation was done in a JEOL JSM-7600F field emission scanning electron microscope. Atomic resolution investigation and electron crystallography was performed in a JEOL 2100 scanning/transmission electron microscope. TEM samples have been prepared by ultrasonic separation of ZnS nanostructures in hexane.
Figure 1, shows there distinct ZnS nanostructure morphologies observed in the present investigation. Figure 1(a) shows self-organization of a dendritic structure made of ordered arrays of ZnS nanoplates. Similar structures have been previously reported under different nomenclature such as nanosaws and/or nanocomb structures [2]. Figure 1(b) is a typical ZnS nanobelt or nanosheet structure, and the ZnS structures in Figure 1(c) have a rod-type morphology. The ZnS rods in Figure 1(c) are not electron transparent, since their thickness is of the order of hundreds on nanometers. Therefore, only the samples in Figures 1(a) and 1(b) have been prepared for TEM investigation. Figure 2(a) shows dark field scanning transmission electron micrograph of a copper doped ZnS nanobelt. The XEDS spectrum in Figure 2(b) proves the presence of cooper in ZnS material. Aluminum peak is due the TEM grid material. Figure 3 shows a high resolution TEM micrograph of a relative large area of a ZnS nanobelt. The nanobelt has a uniform crystalline structure with linear imperfections oriented along the longitudinal axis of the structure. These linear imperfection might be responsible for the strong photoluminescence shown by the copper doped ZnS nanostructures, similar to the photoluminescence effect in the case of ZnO thin films. Several independent studies of ZnO thin films suggested that the 3.317 eV emission line in these materials is due to a free conduction-band electron to neutral acceptor bound hole (e, A^0) transition, originating from the basal-plane linear defects in which acceptors are preset [3]. A similar mechanism might be responsible for the strong photoluminescence effect in ZnS nanostructures. However, more experimental work is needed to explain the photoluminescence mechanism in ZnS nanostructures.

References:

[1] X. Fang *et al.*, Critical Reviews in Solid State and Materials Sciences **34** (2009), p 190.
[2] D. Moore and Z. Wang, Journal of Materials Chemistry **16** (2006), p. 3898.
[3] S. Yang *et al.*, Applied Physics Letters **100** (2012), 101907.
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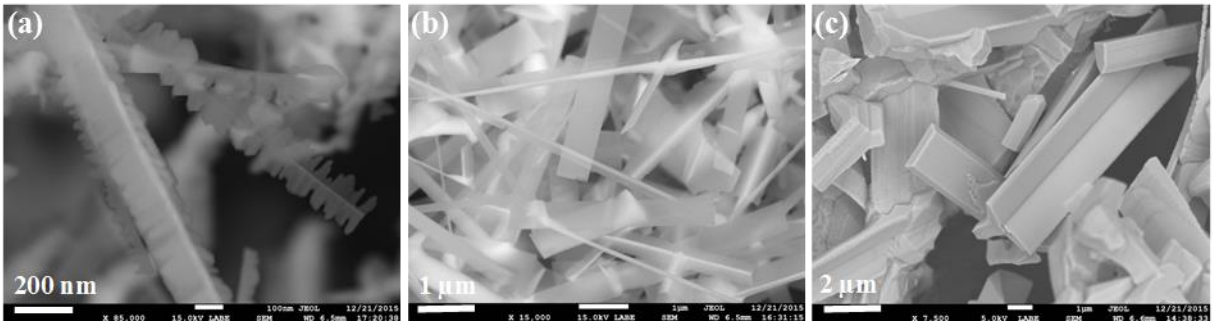

Figure 1. SEM micrographs of ZnS nanostructures: (a) dendritic-type structure; (b) nanobelt; (c) nanorods.

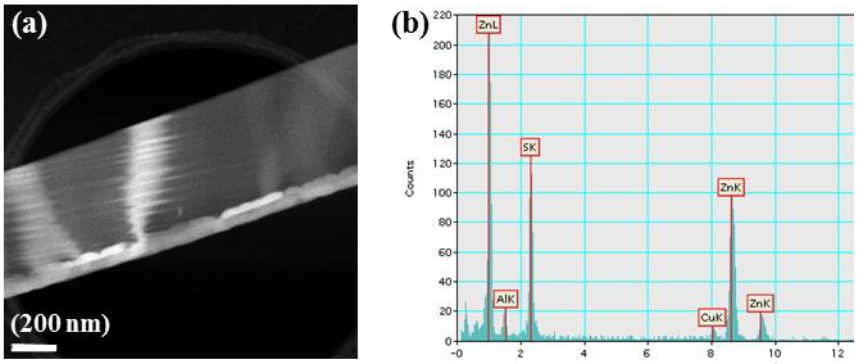

Figure 2. (a) DF STEM micrograph of a ZnS nanobelt; (b) XEDS spectrum from the structure in (a).

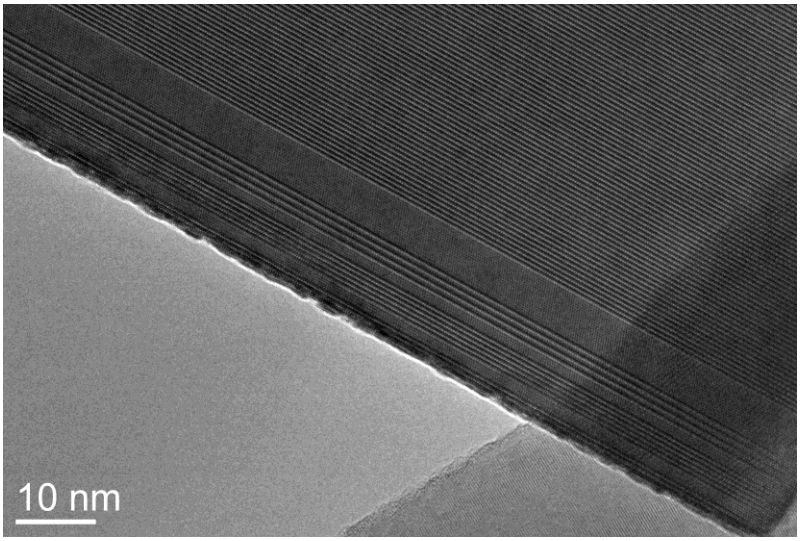

Figure 3. HRTEM micrograph of a ZnS nanobelt.

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