

One-dimensional ZnS nanocrystals grown by VLS-mechanism

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Zinc sulfide is an important IIB-VI semiconductor with a wide bandgap of 3.7 eV at 293 K. It has several useful properties, such as piezoelectricity, luminescence and a high transmittance in the visible which makes it an important material for optoelectronics [1]. By “vapor-liquid-solid (VLS) mechanism” [2], ZnS has been synthesized in different morphologies like nanowires, nanobelts and nanosaws [3-5]. In this contribution we present some first results on Au-catalyzed growth of 1-D ZnS nanostructures by a simple thermal evaporation method. The crystal structure and the formation of stacking faults are revealed by TEM investigations. The studies were conducted on Philips CM30 and Philips CM300 FEG/UT electron microscopes.

ZnS nanostructures were synthesized with high purity ZnS powder as starting material heated to 1000°C and transported by Ar carrier gas to the substrate which consists of fused silica coated with Au particles. The optimum deposition temperature for a unique growth of the nanocrystals is 870°C. The ZnS structures show a characteristic belt-like morphology each with a Au droplet on the top which proves the VLS-mechanism as the dominating growth process (see Fig.1). The length of the structures amounts to several hundreds micrometers whereas the diameter is 100-500 nm.

ZnS exists in two modifications, cubic sphalerite (space group $F\bar{4}3m$) and hexagonal wurtzite (space group $P6_3mc$). Due to the small difference in Gibbs free energy the phase transformation appears easily and is very sensitive to the reaction parameters. Sphalerite and wurtzite differ in the stacking sequence along the c axis: ABAB (wurtzite) and ABCABC (sphalerite). Electron diffraction shows that the ZnS nanobelts generally have the wurtzite structure. As can be seen in Fig.2 $[10\bar{1}0]$ is the growth direction and the polar c axis is perpendicular to it. This leads to a different growth mechanism on the cation-terminated, chemically active (0001) surface (“vapor-solid” (VS) mechanism). During the formation of the (0001) planes a change in stacking sequence results in a phase transformation from wurtzite to sphalerite. Fig.2 shows that the ZnS nanobelts consist of three differently oriented parts: Beside the typical wurtzite reflections one can observe two sphalerite domains in twin orientation. On the left in the HRTEM image (Fig.3) the (0001) and $(10\bar{1}0)$ planes are resolved and the corresponding lattice plane spacing could be determined to 620 pm for kinematically forbidden (0001) and 330 pm for $(10\bar{1}0)$, respectively. After change of the stacking sequence to the cubic one, the $[0001]$ direction in wurtzite becomes $\langle 111 \rangle$ in sphalerite and there two $\{111\}$ -type lattice planes with lattice plane spacing of 315 pm can be observed.

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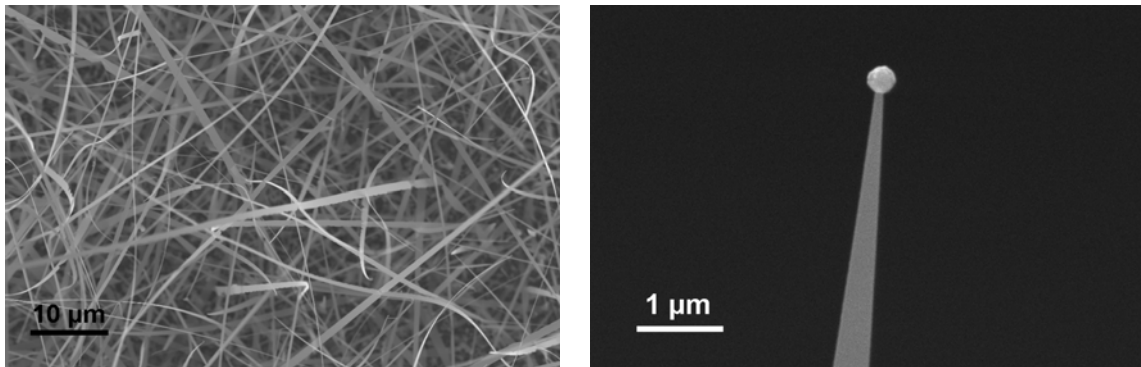


Figure 1. SEM images of ZnS nanobelts synthesized at 870°C.

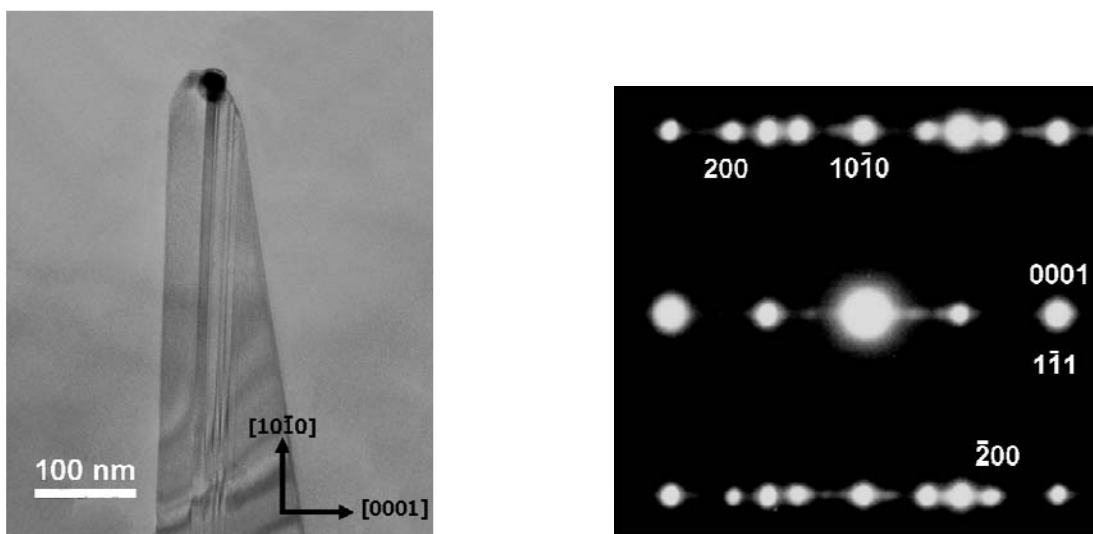


Figure 2. Bright field image and corresponding diffraction pattern in $[2\bar{1}\bar{1}0]_w \parallel [011]_s$ of ZnS with twinned sphalerite.

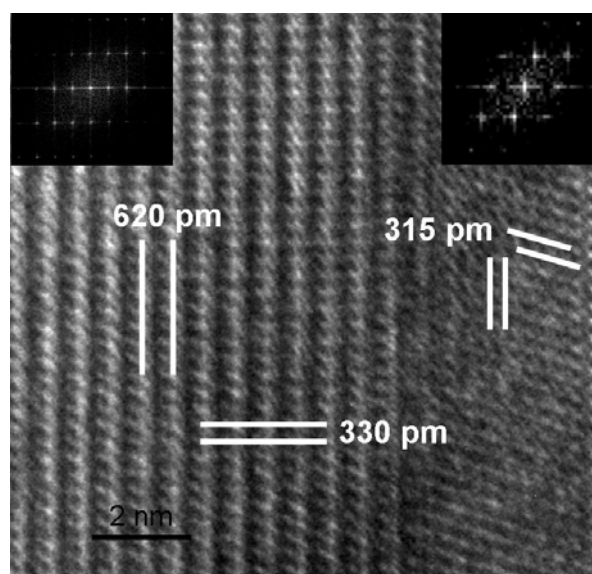


Figure 3. HRTEM image of interface region wurtzite / sphalerite of a ZnS nanobelt. Crystal orientations: $[2\bar{1}\bar{1}0]_w \parallel [011]_s$, insets are corresponding FFTs.