Three-dimensional hetero-epitaxial assembly of single-crystalline wurtzite structured ZnO/ZnS core/shell nanorods array

X Huang¹, M Wang¹, M Willinger², LD Shao², DS Su³ and XM Meng¹

1. Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, P. R. China.
2. Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Berlin, Germany.
3. Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, Shenyang, P. R. China.

Email address: xinghuang@fhi-berlin.mpg.de; xmmeng@mail.ipc.ac.cn
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Component-modulated semiconductor heterostructures, such as superlattices,[¹] core/shell,[²] and biaxial nanostructures,[³,⁴] with integrated multifunctionality of disparate components, are increasingly important in the assembly of nanoscale photonic and electronic devices. Extensive investigations on synthesis and manufacturing of heterostructures have been carried out for dimension-related applications by controlling shapes, structures and components.[¹-⁵] ZnO and ZnS, as important wide-gap II–VI semiconductors with band-gaps of 3.37 and 3.67 eV, have been intensively studied owing to their excellent optoelectronic properties.[⁶,⁷] Recently, ZnO/ZnS heterostructures have attracted theoretical and experimental interests for showing superior optoelectronic properties to their individual materials.[⁸-¹¹] However, the investigations on ZnO/ZnS heterostructure system are mainly related to the polycrystalline nature of ZnS nanoparticles covered on the ZnO or crystallographic inconsistency in terms of orientation between ZnO and ZnS crystals. Controllable approaches have not been achieved so far for systematically controlled assembly of ZnO/ZnS heterostructures with corresponding components possessed the same structure and crystallographic orientations. Especially for three-dimensional hetero-epitaxial growth, their large lattice mismatch along the interface and high sensitivity to synthetic conditions are great obstructions.[³,⁴]

In this work, we report the first time on array of ZnO/ZnS core/shell nanorods composed of single crystalline wurtzite (WZ) structured ZnS that uniformly and compactly grows on ZnO rods with a crystallographic epitaxial relationship synthesized via a simple two-step thermal evaporation method. And single crystalline WZ structured ZnS nanotubes array is also innovatively synthesized by etching away the inner ZnO cores. The morphologies, compositions, and crystal structures of hetero-epitaxial core/shell ZnO/ZnS nanorods and ZnS nanotubes array are systematically studied. A growth mechanism is proposed based on the structural analyses. The optical properties are also investigated and discussed in detail. Using the hetero-epitaxial growth of ZnS shell on ZnO core as an example, we demonstrate the possibility of a rational and facile way for establishing three-dimensional hetero-epitaxial nanostructures from materials with intrinsic large lattice mismatch.

References

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Figure 1. (a) Low-magnification cross section view TEM image of the of ZnO/ZnS core/shell nanorod; (b) STEM-EDX elemental mapping of the core/shell nanorod; clearly, O and S elements are concentrated at the middle core and hexagonal shell regions, respectively, while Zn elements are dispersed throughout the whole particle; (c) HRTEM image of cross section of core/shell nanorod viewed along the [0001] direction, indicating an epitaxial relationship of (01-10)ZnO//(01-10)ZnS and [0001]ZnO//[0001]ZnS.