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Highlights of 15R crystal phase in Au-catalyzed ZnS nanowires

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Unique growth mechanisms involved in semiconductor nanowires (NWs) pave the way to the achievement of new crystallographic phases and remarkable material properties. Interestingly, in the case of 1D nanostructures, polytypism can arise due to the particular growth mode below a catalyst droplet, that may induce stacking faults along the length of the NWs. Moreover, these stacking faults can be correlated and form ordered arrays, until giving rise to new phases (polytypes) with distinct properties [1,2]. Hence, 4H, 6H, 8H, and 10H (so-called high order polytypes) can been observed in NWs [3]. Hence, studying polytypism in semiconductor NWs arouses a strong interest for the next generation of electronic and photonic applications. In this framework, ZnS is an important II-VI semiconductor which has a wide range of optoelectronic applications including luminescent devices, infrared windows, and UV-photodetectors.

In this work, Au-assisted ZnS NWs were grown by MOCVD, directly on GaAs (111B) substrate (VLS, vapor-liquid-solid mode), and on ZnS (buffer)/GaAs (111B) (VSS, vapor-solid-solid mode). The idea is to provide a change in the growth mechanism *via* the physical state of catalyst droplet (liquid or solid) and hence, study the induced polytypism in ZnS NWs. ZnS NWs with length up to 1.4 µm and diameter in the range 10–34 nm was successfully achieved. The obtained morphologies and densities of the NWs has been systematically inspected by scanning electron microscopy (SEM) directly on the substrate. Transmission Electron Microscopy has been also used to investigate the crystallographic structures and compositions of both catalysts and NWs. NWs grown directly on GaAs (VLS mode) induced periodic stacking faults, and the resulting structure was accurately identified as 3 sequences of 5 planes ABCBA-BCACB-CABAC (refer Figure 1), giving rise to an astonishing 15R crystal structure [4]. This structure is highlighted for the first time in ZnS nanowires. Additional conventional TEM has been performed to identify the signature of the 15R phase and its peculiar pattern (*i.e.* a 5th order superstructure). Additionally, we modeled this 15R structure and plotted its formation probability in the framework of the classical nucleation theory and axial-next-nearest-neighbour-Ising model (ANNNI).

Interestingly, in contrast with the VLS case, in nanowires grown on ZnS buffer (i.e. VSS mode, with solid catalyst), a different crystal structure made of pure ZB and WZ phases was observed.

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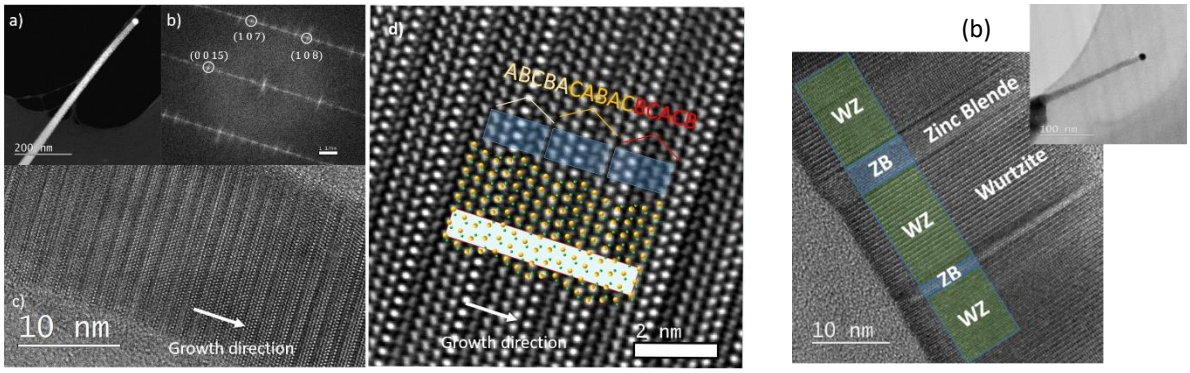

Figure 1: HRTEM image of ZnS nanowires grown by a) VLS process, HRTEM image of NW with 15R stacking sequence, and b) VSS process, pure ZB/WZ phases.