Crystal phase selection in semiconductor nanowires

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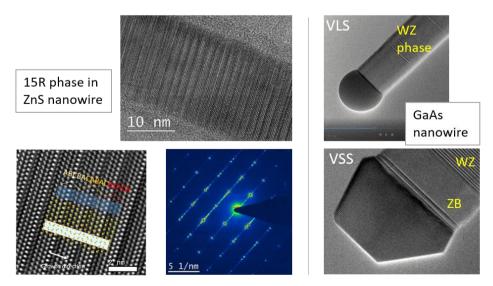
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Unique growth mechanisms involved in semiconductor nanowires (NWs) pave the way to the achievement of new crystallographic phases and remarkable material properties, and hence, studying polytypism in semiconductor NWs arouses a strong interest for the next generation of electronic and photonic applications. Interestingly, in the case of 1D nanostructures, polytypism can occur due to the particular growth mode below a catalyst droplet, that may induce different periodic stacking sequences along the length of the nanowire, giving rise to new phases with distinct properties such as 4H or 6H. In this work, we investigated crystal phases in ZnS NWs as well as in GaAs NWs, comparing two growth mechanisms: VLS mode (vapor-liquid-solid) where the catalyst droplet is liquid, and VSS mode (vapor-solid-solid) where it is solid.

Gold-assisted ZnS NWs were first grown by metalorganic chemical vapor deposition (MOCVD), directly on GaAs (111B) substrate (for a VLS mode), and on ZnS (buffer)/GaAs (111B) (VSS mode in that case). TEM analysis revealed that nanowires grown with liquid catalyst exhibit periodic stacking faults, and the resulting structure was accurately identified as 3 sequences of 5 planes ABCBA-BCACB-CABAC, giving rise to an astonishing 15R crystal structure. In contrast, regarding nanowires grown with solid catalyst on ZnS buffer, a different crystal structure made of pure zinc blende and wurtzite phases was observed.

In a second study, the growth of GaAs NWs has been investigated in real time using NANOMAX facility, a modified FEI environmental transmission electron microscope, where two molecular beam sources have been implemented to supply Ga and As₄ fluxes. Recording movies of the growth, we show again that the physical state of the catalyst droplet changes the crystal phase, from wurtzite (in VLS mode) to zinc blende (VSS).



Crystal phases in semiconductor nanowires investigated by TEM and in situ TEM