In Situ Observation of GaAs Nanowire Growth :
Focus on the Crystal Phase Dependence on the Physical State of the Catalyst

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The unique growth mechanisms involved in semiconductor nanowires (NWs) pave the way to the achievement of non-standard crystallographic phases (i.e. phases of higher energy) and, consequently, enable the modification of the material properties. Indeed, in the case of 1D nanostructures, polytypism is observed due to the particular growth mode below a catalyst droplet, that may induce different stacking sequences of (111) cubic planes or (0001) hexagonal planes along the length of the nanowire. The control of the nucleation at the catalyst/nanowire interface can give rise to cubic or hexagonal phases, as well as high order polytypes such as 4H or 6H. Hence, crystal-phase heterostructures alternating different phases in the same material, e.g. crystal-phase quantum dots with perfectly abrupt interfaces, could be fabricated by an accurate control the catalyzed-growth conditions (temperature, droplet contact angles, source fluxes…). This arouses a strong interest for the next generation of electronic and photonic devices.

In this study, the fabrication 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 As_4 fluxes towards a heated SiC membrane. Gold-gallium alloy droplets were formed to act as catalysts. In particular, we distinguished and compared two growth mechanisms : VLS mode (vapor-liquid-solid) where the catalyst droplet is liquid, and VSS mode (vapor-solid-solid) where it is solid. In such *in situ* observations, not only the construction, plane by plane, of the GaAs crystal structure is followed, but also the phase and composition of the $Au_{1-x}Ga_x$ catalyst can be determined in the case of VSS mode. That enables to precise where the catalyzed growth takes place in the Au-Ga phase diagram. Commonly in the literature, the VSS growth is achieved by lowering the SiC membrane temperature (i.e. crossing the Au-Ga liquidus line vertically). Interestingly in this work, when the growth occurs close to the $AuGa_2$ solidification point, we show that the physical state of the catalyst (liquid, solid, or mixed) can be also tuned by varying the Ga composition in the droplet (i.e. crossing the Au-Ga liquidus line horizontally). This was achieved by opening the As flux which involved a consumption of the Ga in the catalyst, or closing it in order to refill the droplet with Ga. As a result, playing with the As flux at constant temperature, we demonstrate that we can master a growth cycle which alternates cubic and hexagonal phase GaAs segments, as illustrated in figure 1. These studies help to understand the growth mechanisms for a better control of crystal-phase heterostructures in semiconductor nanowires.

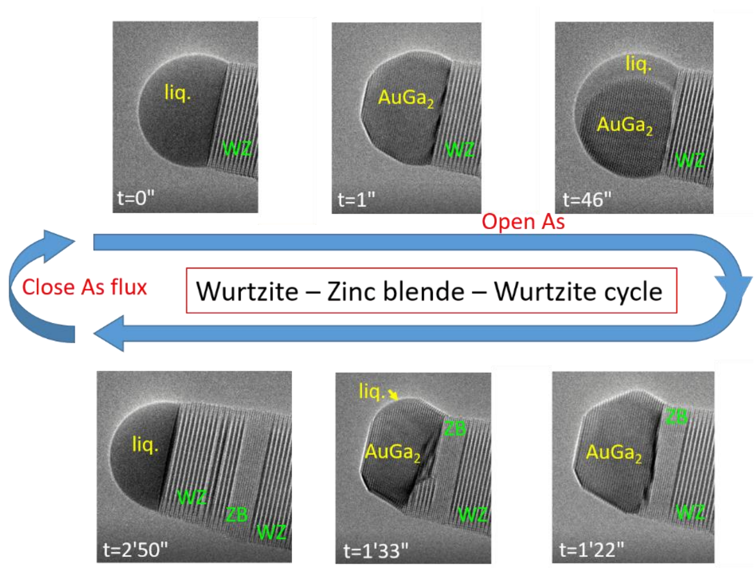

Fig.1. Transmission electron microscopy images from in situ observations, illustrating the growth of hexagonal or cubic phase GaAs NW.