**Structural transformation of wurtzite (Ga,Mn)As nanowires shells under in-situ TEM annealing experiment**

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For over two decades, scientists have been intensively searching for new spintronic materials combining semiconducting and magnetic properties at room temperature. The studies on dilute ferromagnetic semiconductors (DFS), which most prominent representative is (Ga,Mn)As, have shown so far, that this material grown in the form of thin epitaxial layers reaches remarkably high Curie temperature ~ up to 190K (Tc) as for DSF material, but still too low for applications. However, its potential can be used after a thermal treatment resulting in hybrid material - the semiconducting matrix (Ga,Mn)As with intermetallic MnAs nanoprecipitates. The detailed works on this thermodynamical transition show that in the zinc-blende (ZB) (Ga,Mn)As matrix different types of crystallographic phases can appear including favourable hexagonal alpha-MnAs (ferromagnetic<40ºC).

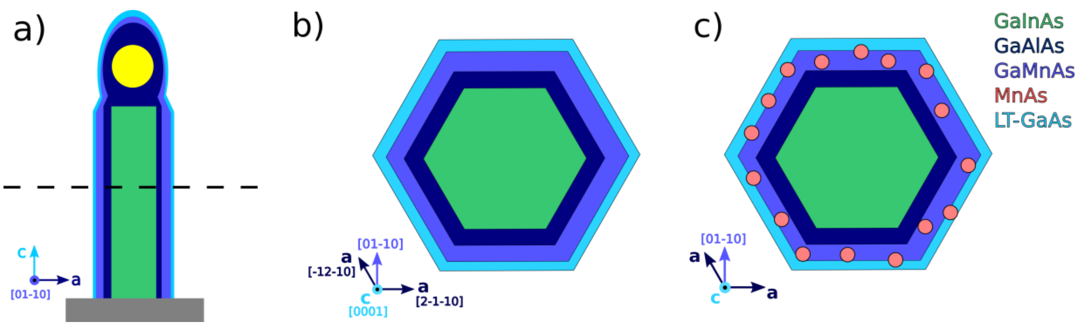


**Fig. 1 a)** Schematic model of core-shell NW grown in MBE. Cross-sections cut along dashed line of: **b)** as grown NW, **c)** post-annealed NW with visible precipitations.

In our previous studies [1], we proved that it is possible to obtain (Ga,Mn)As in **hexagonal - wurtzite** (WZ) structure as a form of cylindrical epitaxial shell around WZ GaInAs core of the nanowire (NW) in molecular beam epitaxy process. Firstly, the WZ GaInAs cores are grown by vapour-liquid-solid process using Au catalytic droplets, then after temperature reduction - WZ shells, including (Ga,Mn)As, are axially grown on the side walls of the NWs coherently to the core *(Fig.1ab, Fig.2)*. Ex-situ post-annealing of such NWs revealed that above 450ºC in (Ga,Mn)As shells, hexagonal MnAs nanoprecipitates arise coherently in the WZ matrix *(Fig.1c)*.

In this research, we want to determine how the formation of MnAs precipitates occurs in the WZ core-shell $Ga_{0.78}In_{0.22}As/Ga_{0.5}Al_{0.5}As/Ga_{0.94}Mn_{0.06}As$/LT-GaAs NWs *(Fig.2)* and compare it with the kinetics and thermodynamics of the phase transition in ZB GaAs/(Ga,Mn)As epitaxial layers. In the experiment, the NWs were placed on the heating chips covered with holey carbon film. During measurement performed in transmission electron microscope (operating at 300kV), the NWs were oriented to perfect zone-axis in double tilt holder. Our study shows that structural changes in WZ NWs start from Mn atoms segregation in WZ lattice at temperatures around 300ºC *(Fig.2ab)* and are followed by phase transition to hexagonal MnAs precipitates semi-coherent with WZ-(Ga,Mn)As matrix over 400ºC *(Fig.2cdef)*. At higher temperatures, the precipitates have the same orientation as the matrix (i.e. [0001]GaAs || [0001]MnAs) and we observe their growth with visible Moiré pattern and additional voids creation *(Fig.2gh)*. The decomposition of NWs occurs above 550ºC *(Fig.2ijkl)*.

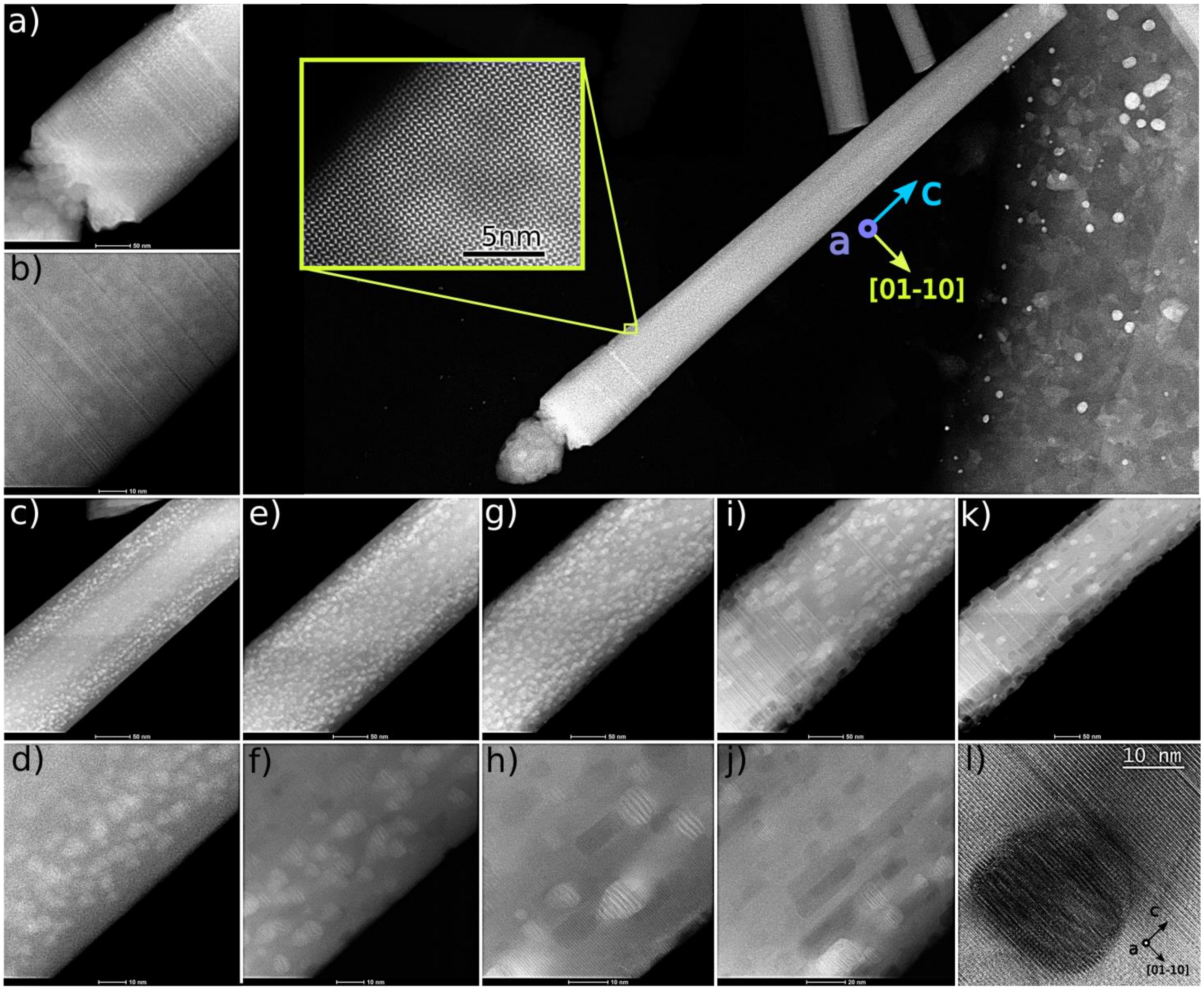


**Fig. 2** Scanning Transmission Electron Microscopy (STEM) images of the typical as-grown WZ NW (left top) placed on the heating chip and its structural changes while in-situ annealing measurements in: **a,b)** 350°C **c,d)** 400°C **e,f)** 450 °C **g,h)** 500°C **i,j)** 550°C **k)** over 600°C **l)** HRTEM image of one MnAs nanoprecipitate. Annealing was performed in double tilt heating holder and phase transformation was observed in perfect zone-axis.

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References:

[1] J. Sadowski, S. Kret, A. Siusys, T. Wojciechowski, K. Gas, F. Islam, C. M. Canali and M. Sawicki, Nanoscale **9**, 2129 (2017)