Structural changes in wurtzite (Ga,Mn)As nanowire shell during in-situ annealing in a transmission electron microscope

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Introduction

Zinc-blende (ZB) (Ga,Mn)As is a canonical dilute ferromagnetic semiconductor (DFS) with the highest (up to 200 K) Curie Temperature (T_C) among all DFS materials, although still too low for room temperature spintronic applications. However, when (Ga,Mn)As is thermally decomposed, ferromagnetic α-MnAs nanocrystals (NCs) with hexagonal crystal structure are formed within ZB-GaAs (cubic) matrix.

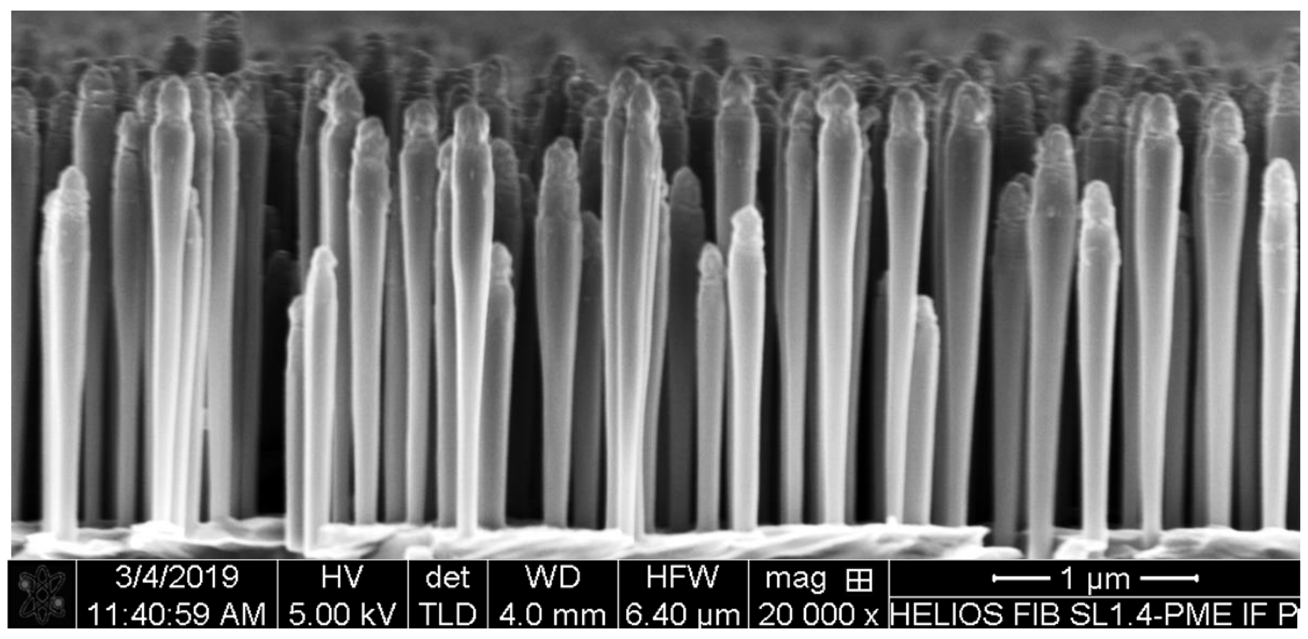
On the other hand, wurtzite (WZ) (Ga,Mn)As, sharing similar symmetry with hexagonal α-MnAs, can be obtained if (Ga,Mn)As is grown as shells on WZ-GaAs nanowire (NW) cores using molecular beam epitaxy (MBE) [1]. We have shown that annealing of the WZ-(Ga,Mn)As results in tensely strained α-MnAs NCs embedded semi-coherently in the WZ-GaAs matrix and stabilizes ferromagnetic α-MnAs phase to above 127 °C [2], in contrast to the bulk α-MnAs with Curie temperature (T_C) = 40 °C.

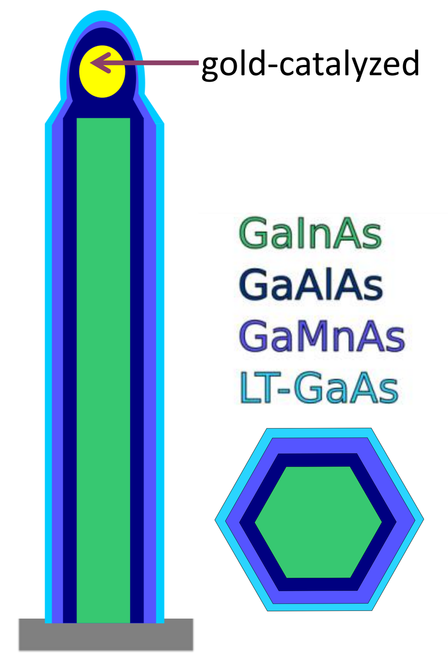
Using scanning transmission electron microscopy (STEM) with in-situ TEM system, the α-MnAs NCs formation can be observed via collecting images at subsequent stages during annealing. Mn atoms start to segregate at temperatures around 300 °C, followed by a phase transition to the MnAs NCs at 350 – 400 °C. At higher temperatures, larger MnAs NCs with visible Moiré patterns are observed.

[1] J. Sadowski, et. al, Nanoscale **9**, 2129 (2017).
[2] A. Kaleta, et. al, Nano Lett. **19**, 7324 (2019) .

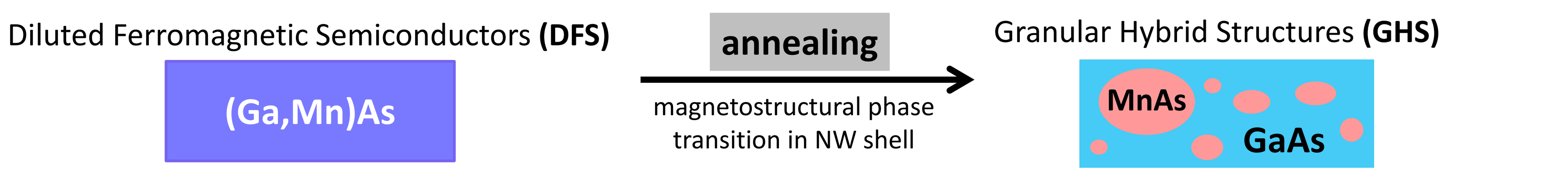
Nanowires Growth – MBE recipe

VLS Axial growth		Epitaxial Radial growth							
CORE		SHELL 1			SHELL 2			SHELL 3	
(Ga,In)As		(Ga,Al)As			(Ga,Mn)As			GaAs	
%In	T [°C]	%Al	d [nm]	T [°C]	%Mn	d [nm]	T [°C]	d [nm]	T [°C]
22	490	50	30	440	6	30	200	4	200

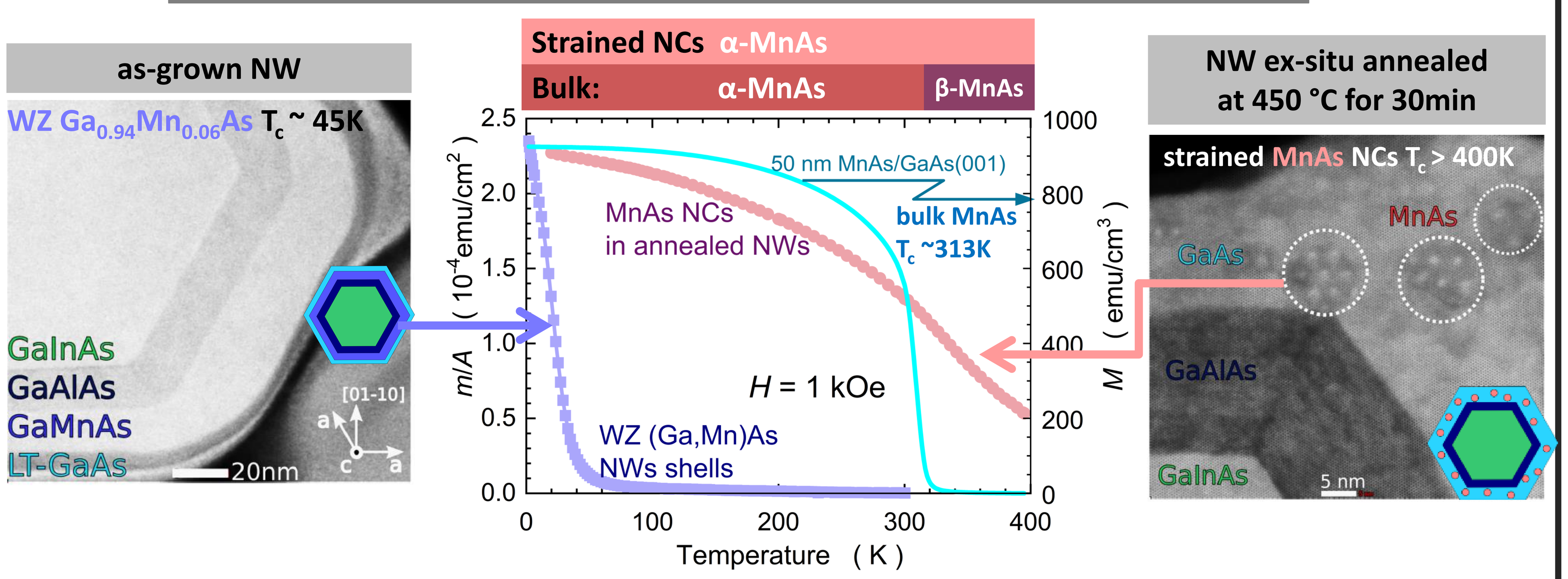




Ex-situ annealing: (Ga,Mn)As phase transition – MnAs NCs precipitation

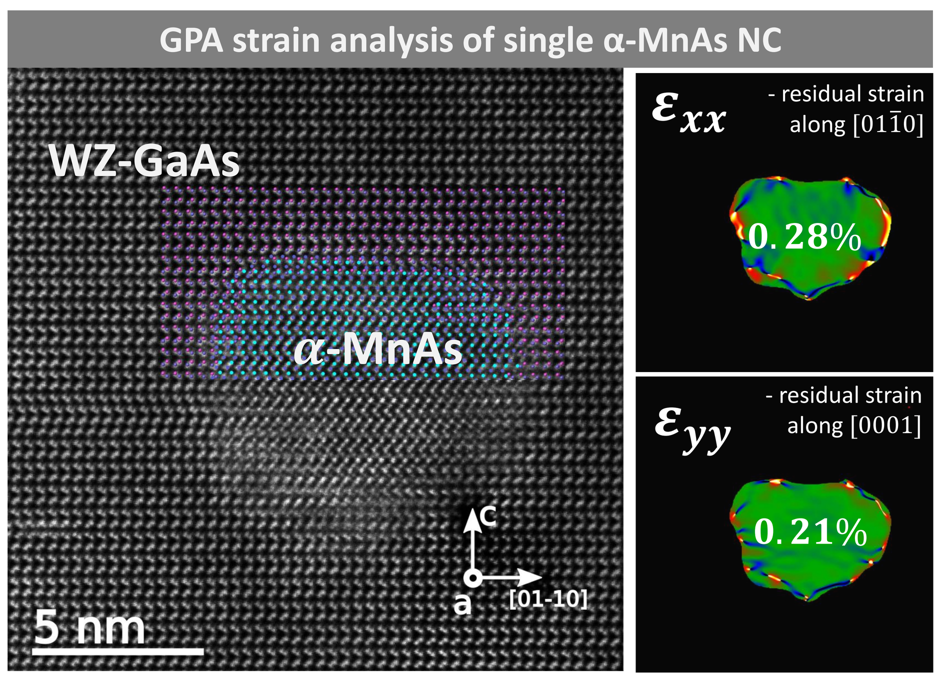


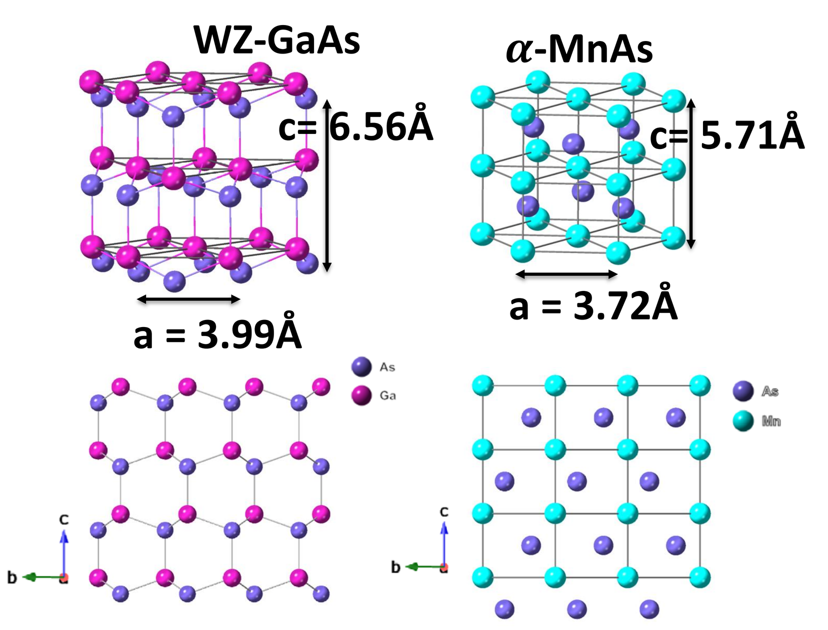
Magnetic properties – Curie temperature increase for strained MnAs!



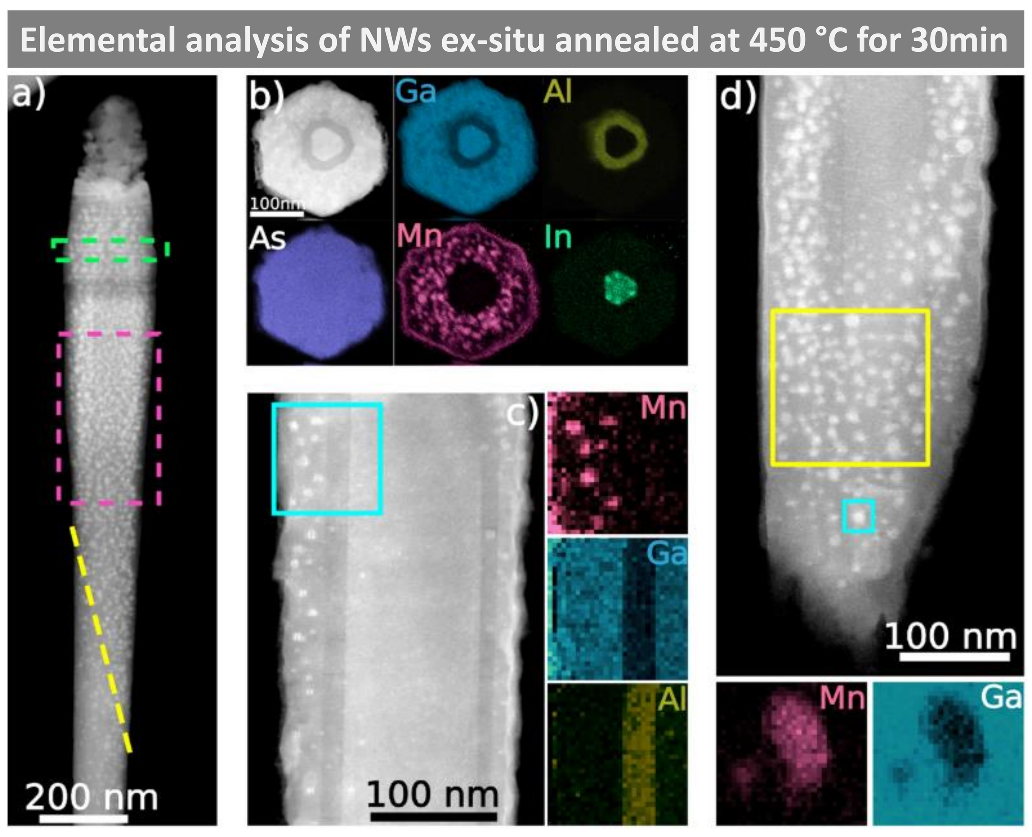
Strain analysis	Structure	System	Space group	$d_{[0001]}$ [Å]	$M_{[0001]}$	$d_{[01\bar{1}0]}$ [Å]	$M_{[01\bar{1}0]}$
reference	WZ-GaAs	wurtzite	P63mc (186)	6.56	-14.2 %	3.45	-7.6%
local	α-MnAs	NiAs-like	P63/mmc (194)	5.71		3.23	

GPA strain analysis of single α-MnAs NC

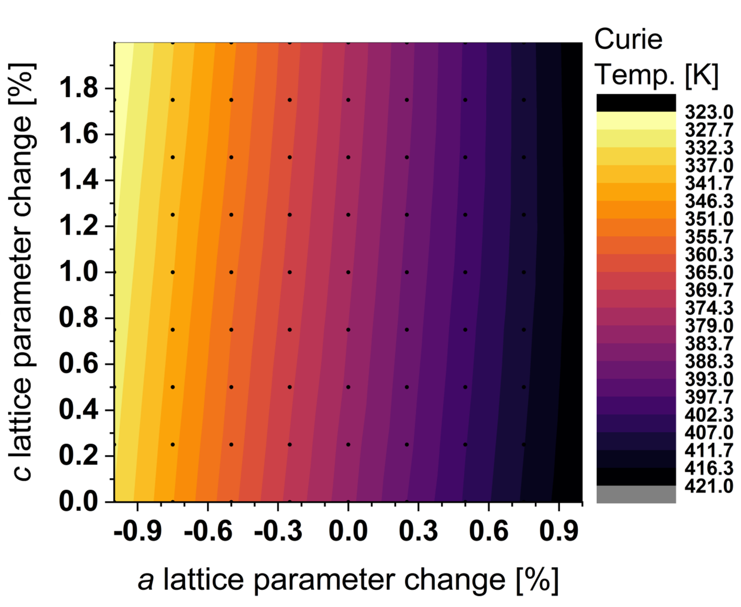




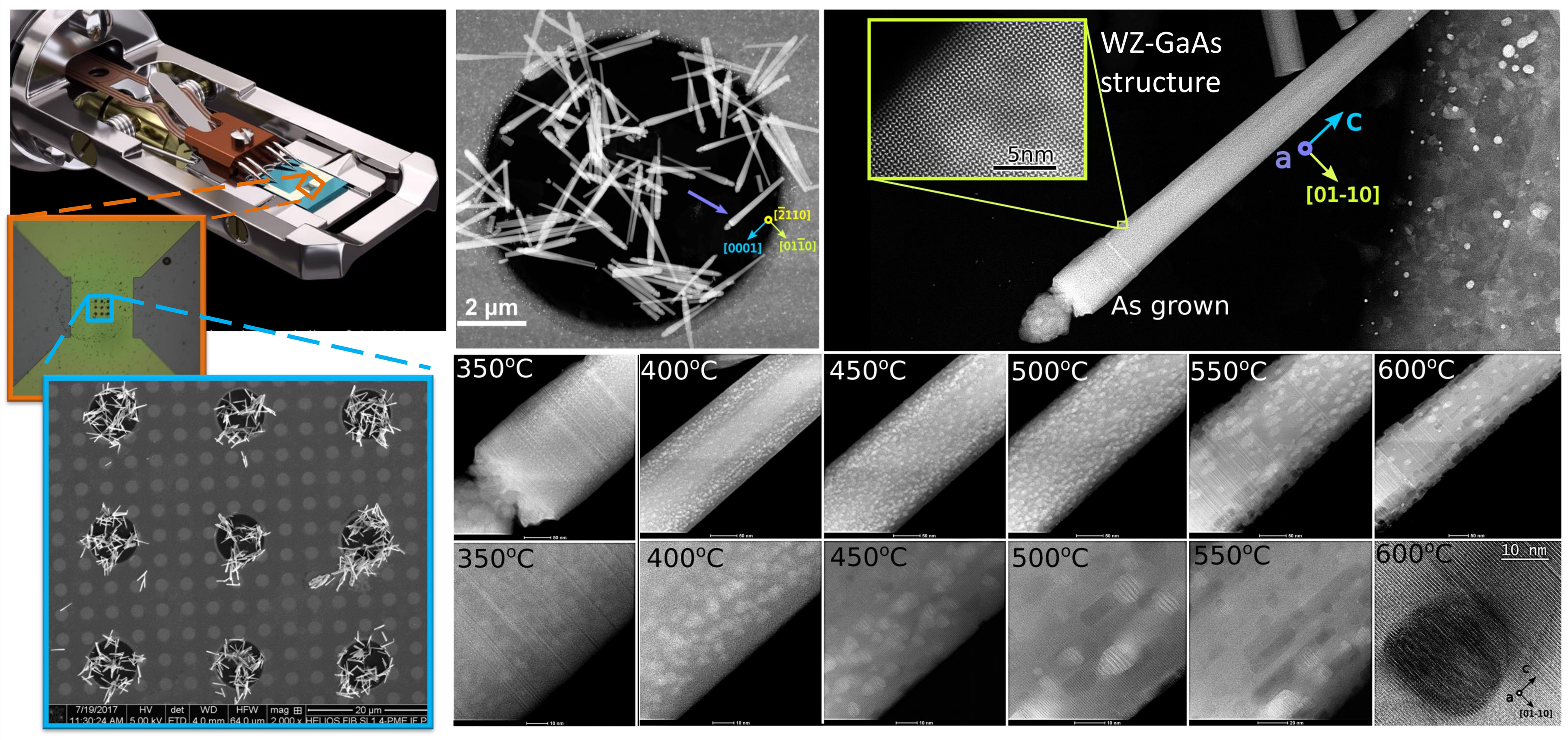
Elemental analysis of NWs ex-situ annealed at 450 °C for 30min



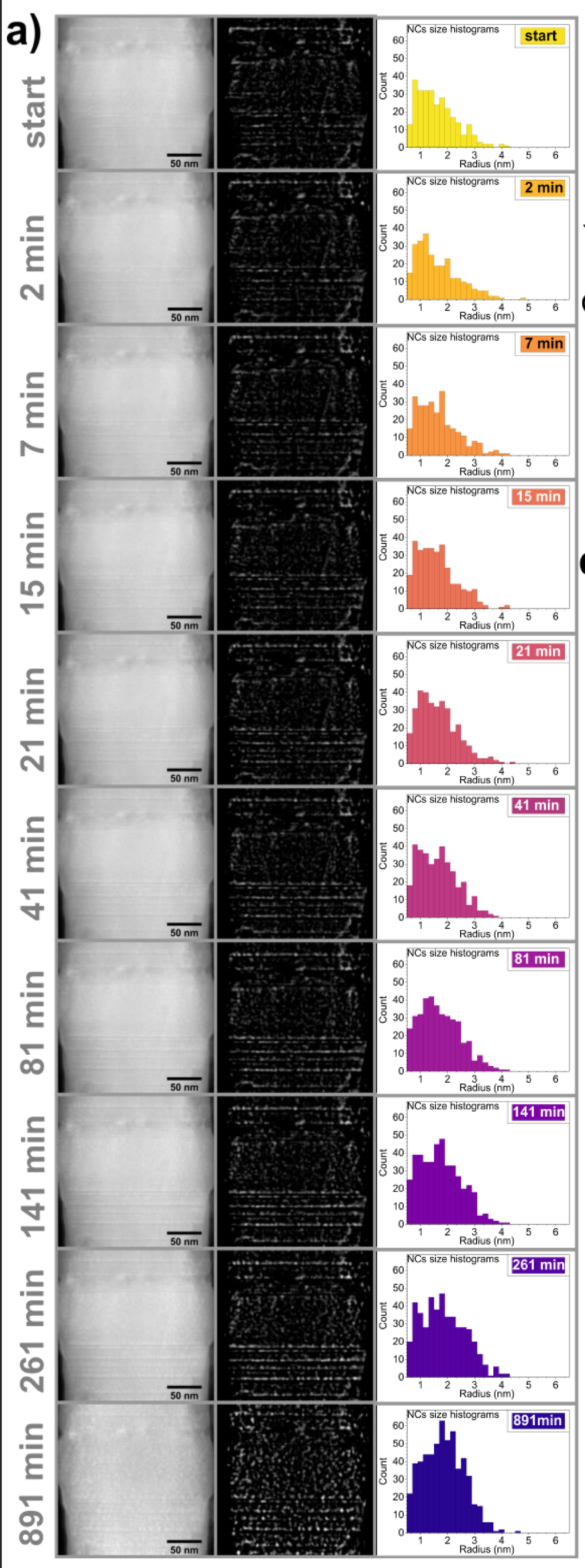
Calculations of Curie temperature changes of bulk α-MnAs with respect to *a* and *c* lattice parameter chnages

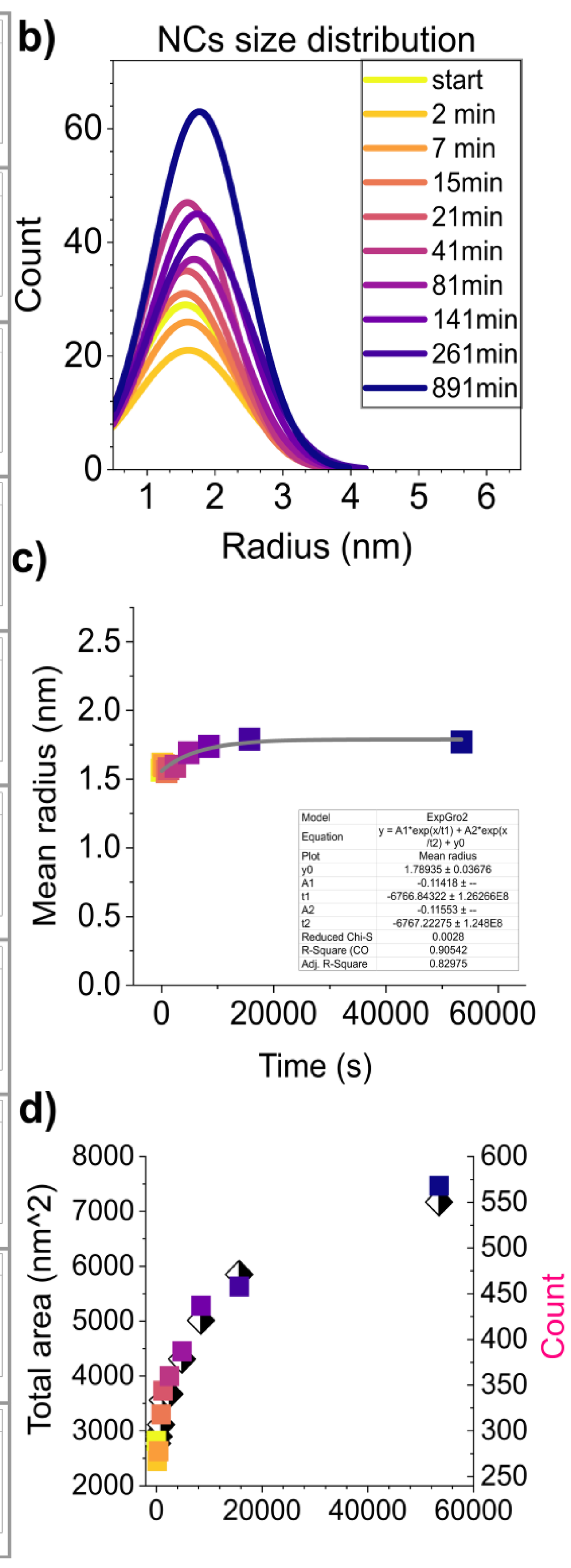


In-situ annealing STEM – tracking Mn segregation

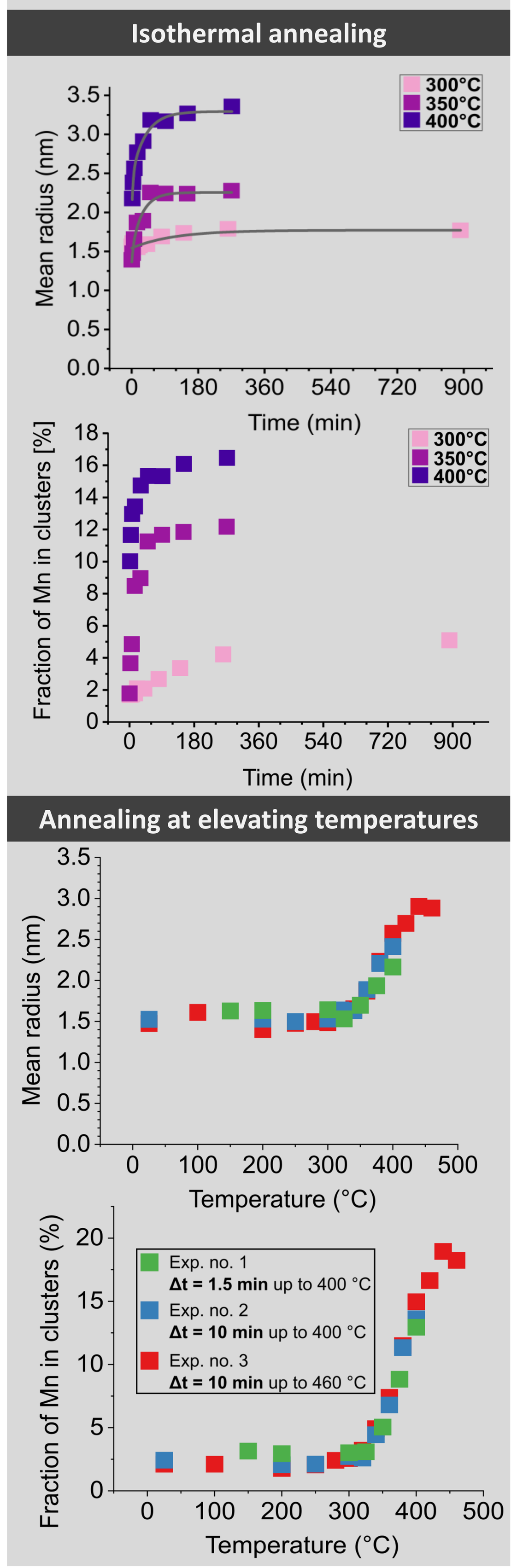


Example of systematic in-situ TEM experiment. Isothermal annealing at 300 °C





Summary of in-situ TEM results



Conclusions

- **WZ-GaAs** matrix exerts tensile strain and **stabilizes α-MnAs ferromagnetic** phase above ~400K
- According to the in-situ experiment analysis, clustering of Mn can be divided into three stages:
  - i. **Nucleation** (~300°C) & growth of WZ-Mn(Ga)As NCLs, coherent & highly-strained with respect to WZ-GaAs.
  - ii. **Phase transformation** (~350°C) WZ-MnAs to α-MnAs (semi-coherent with WZ-GaAs matrix), tensily strained.
  - iii. **Growth via coarsening** (~450°C), i.e. small NCs merging into bigger (coarser) ones.
- Migration of Mn atoms/NCLs/NCs can be additionally **controlled by NW architecture:**
  - i. radially by **(Ga,Al)As shells** acting like diffusion barriers for Mn atoms
  - ii. axially by **ZB-GaAs segments (stacking faults)** perpendicular to nanowire growth axis (WZ c-axis).

Acknowledgments

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