In situ studies of high-purity mono- and bimetallic nanostructures in experiment and simulation

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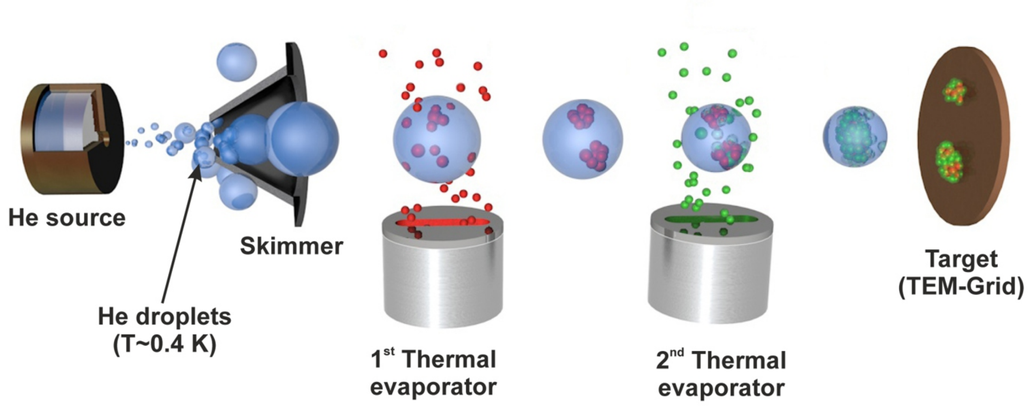
Introduction

- We performed in situ TEM heating experiments of metallic nano structures and interfaces
- Study of surface and interface diffusion processes between different metals on an atomic scale
- Demo system: Nanostructures synthesised in superfluid helium droplets
- Application: Metallic interface systems
- Computational modelling of temperature- and beam induced diffusion processes

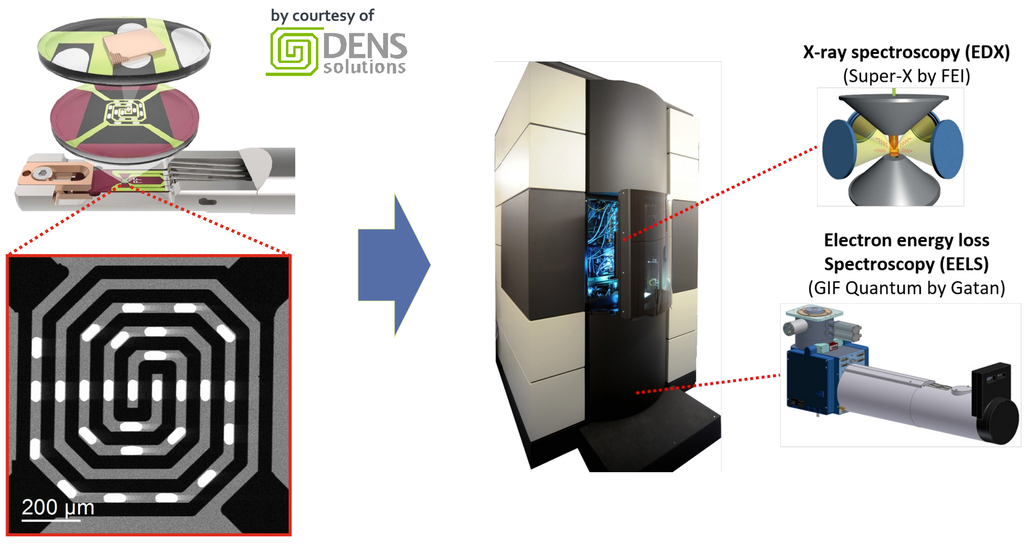
Methods

Synthesis of metallic nanostructures:



+ High purity structures (UHV, no surfactants) [1,2]
+ With variable morphologies
+ Can be deposited on any surface

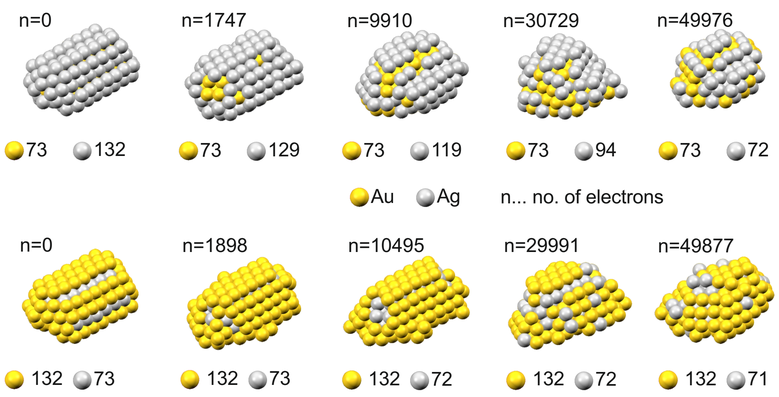
TEM in situ analysis:



- DENS Wildfire D6 holder with FEI Titan^3 G2 60-300
- Precise and fast temperature control up to 1300 °C
- Allows to utilize resolution and high analytical capability of the microscope

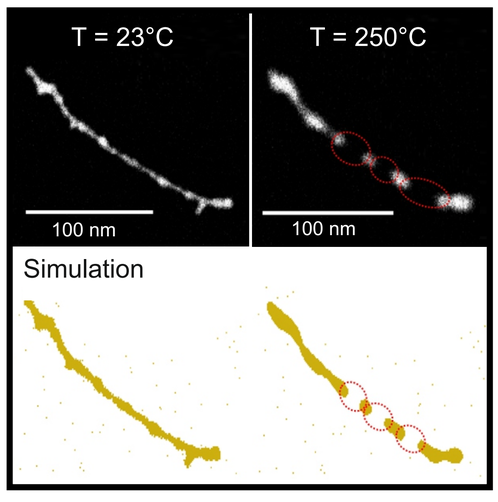
Beam damage simulations with molecular dynamics:

- Beam induced displacements and sputtering on metallic nanostructures dominated by “elastic” interactions of the nuclei with the electrons [3]
- Exemplary on AuAg clusters:



Results

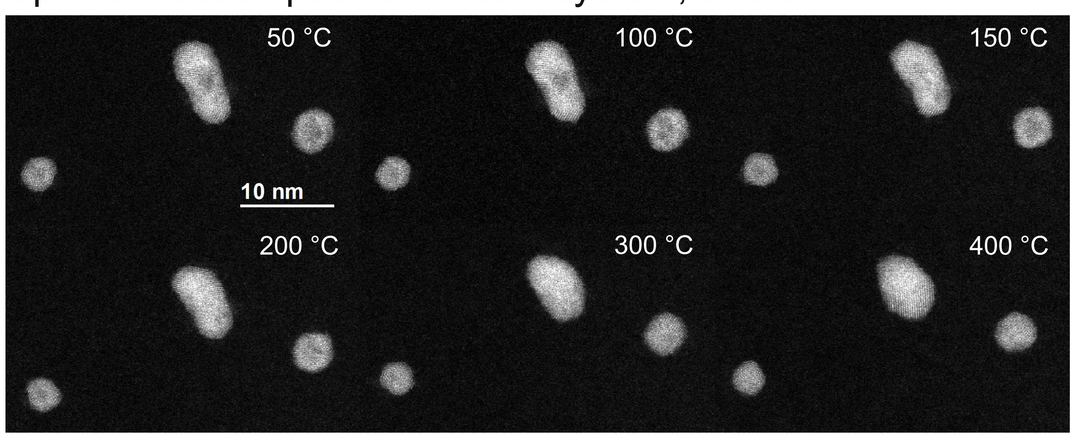
Rayleigh breakup of Au nanowires:



- Rayleigh breakup is well known in fluids
- Occurs in solids on the nanoscale
- Breakup of metallic nanostructures far below melting temperatures
- Mediated by surface diffusion
- Simulation with a cellular automaton (no. of nearest neighbours maximised) [4]

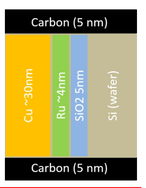
Alloying of Ni-Au core-shell clusters:

Au-Ni phase diagram exhibits large miscibility gap:
Spinodal decomposition in bulk system; cluster?

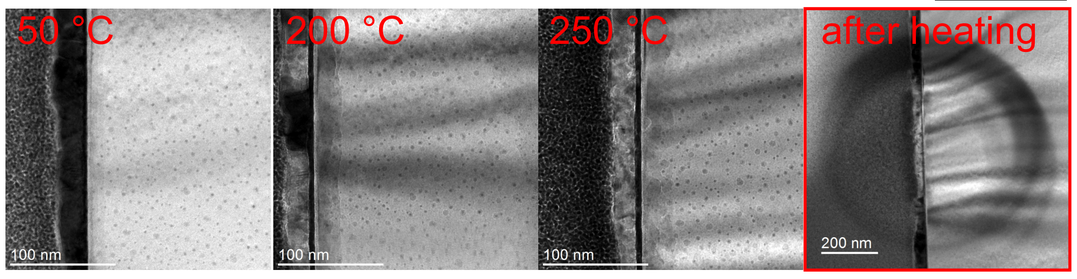


- Morphology change
- Irreversible alloying at higher temperatures
- Larger particles alloy easier than smaller

Cu diffusion “through” Ru barrier layer:



- FIB preparation of Cu/Ru/SiO_2/Si layer stack
- Inhibition of surface diffusion with 5 nm carbon layer



- Heating from RT to 250 °C with 3 K/min
- Diffusion of Cu into Si: formation of copper silicide
- Transformation only occurs in electron irradiated areas
- Influence of the electron beam must be considered

References/ Literature

[1] Volk, A. et al. The impact of doping rates on the morphologies of silver and gold nanowires grown in helium nanodroplets. Phys Chem Chem Phys 18, 1451–459 (2016).
[2] Gomez, L. F., Loginov, E. & Vilesov, A. F. Traces of Vortices in Superfluid Helium Droplets. Phys. Rev. Lett. 108 (2012).
[3] Egerton, R. Mechanisms of radiation damage in beam-sensitive specimens, for TEM accelerating voltages between 10 and 300 kV. Microsc. Res. Tech. 75, 1550–556 (2012).
[4] Schnedlitz, M. et al. Thermally induced breakup of metallic nanowires. Experiment and theory. Phys Chem Chem Phys (2017).

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