

## Following the crystallisation of GeTe nano particles using in-situ HRTEM techniques

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GeTe is a chalcogenide phase-change material (PCM) that is successfully applied in optical storage disks based on its rapid and reversible transformation between crystalline and amorphous phases. The ever-present demand for better and better performing memory devices has pushed researchers into investigating the properties of PCMs at the nanoscale, assuming that the smaller the dimension of the material the faster its phase transitions. However, at ultimate dimensions, researchers face additional challenges, such as nanosize effects and only few techniques that are capable of both spatially and temperature resolved investigation of single NPs. Here, we take on this major challenge by following in-situ thermal annealing and with atomic resolution the crystallization of single GeTe nanoparticles (NPs) utilizing a probe and image aberration-corrected FEI Titan Ultimate and a probe aberration-corrected FEI Themis equipped with Super-X energy-dispersive X-ray spectroscopy (EDX) detection system.

This talk focuses on the in-situ crystallization of amorphous, surfactant-free, spatially separated, and highly monodisperse approximately 8-nm GeTe NPs. Such GeTe NPs may become the key to the next generation of PCM memory devices. Stable samples were prepared using a gas-aggregation cluster source method and a temperature calibrated e-chip for high-resolution transmission electron microscopy (HRTEM) imaging. To observe accurately the amorphous-to-crystalline transformation of single NPs inside the TEM, we used a computer-controlled heating setup with a temperature resolution of 0.1 °C. Using HRTEM with atomic resolution and (selected area) electron diffraction, we evidenced the transformation of the NPs. We found that the crystallization temperature for GeTe NPs ranges from 200 °C up to 290 °C with, at a given temperature, a slow phase transition kinetics. These observations are consistent with optical measurement on NP layers. Using EDX, we quantified the chemical composition of the NPs before, during and after the annealing. We found that the chemical composition of the NPs can be heterogeneous, providing clues to some aspects of the crystallisation mechanism. We also looked closely at the compositional and structural similarities/differences between spatially isolated NPs and NPs that were touching each other, suggesting what might trigger the crystallization.

This talk will not only provide fundamental insights in the crystallization mechanism of GeTe NPs but also will highlight that in-situ microscopy is an indispensable and powerful tool for characterising materials at ultimate dimension.

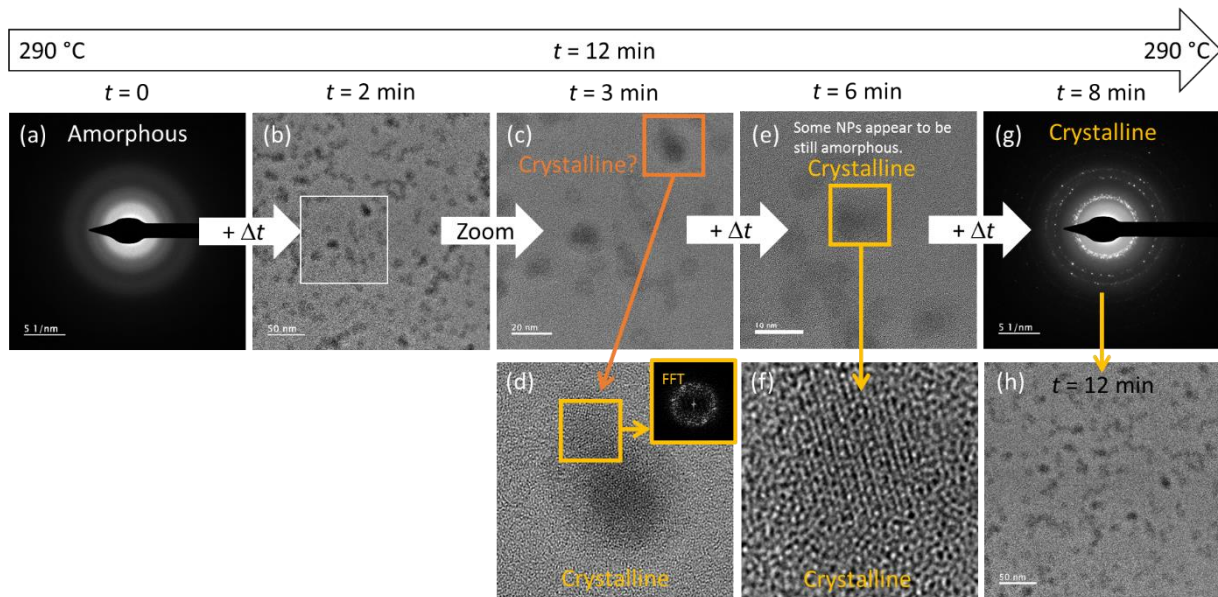


Figure 1: Crystallization of GeTe nanoparticles (NPs) at 290 °C during in-situ annealing inside the TEM. (a) Right after 290 °C were reached, the diffuse rings in the electron diffraction (ED) indicate that the majority of the NPs were amorphous. (b,c,d) After 2-3 min at 290 °C, ordered structures became visible in imaging mode. (e) After 6 min at 290 °C, crystalline NPs were present. Some particles appeared to be still amorphous, indicating that the phase transition kinetics of GeTe NPs was slow at this given temperature. (g,h) After 8-12 min at 290 °C, the spots in the ED pattern of the region of interest indicate that the majority of the NPs was crystalline.

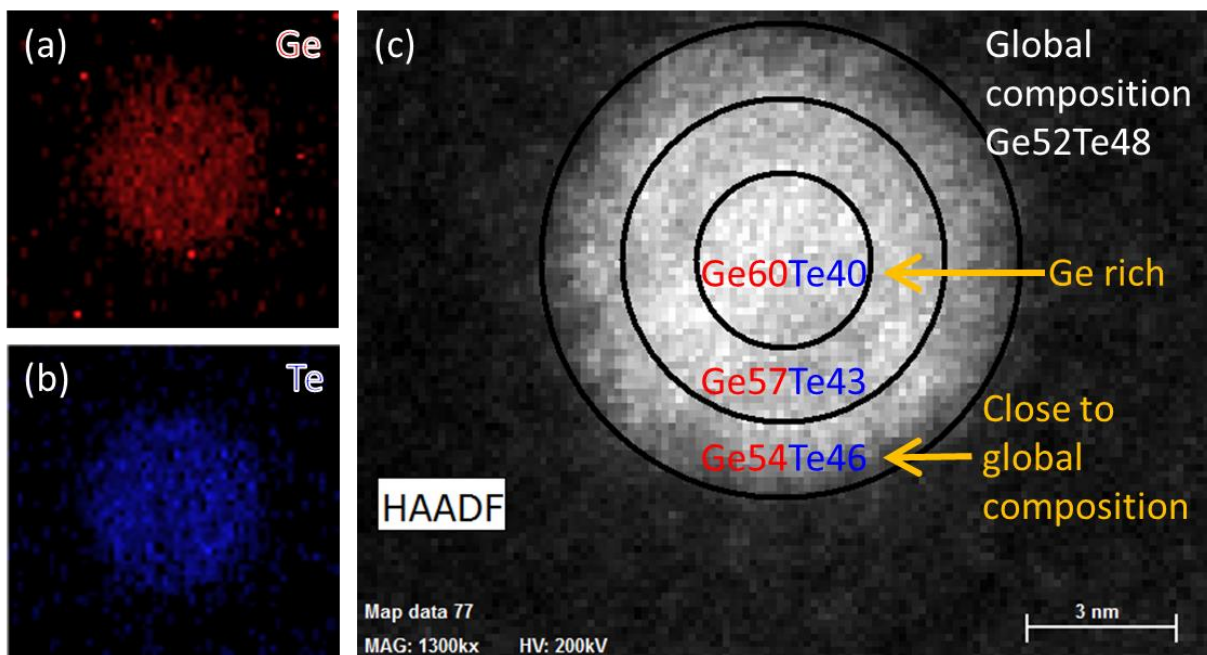


Figure 2: Energy-dispersive X-ray spectroscopy (EDX) of an amorphous 9-nm GeTe NP at room temperature before annealing. (a,b) Qualitative elemental EDX maps of Ge and Te. (c) Quantification of the elemental distribution of Ge and Te within the NP using the Cliff-Lorimer method. The NP was globally composed of 52 at.% of Ge and 48 at.% of Te (Ge<sub>52</sub>Te<sub>48</sub>), consistent with the composition of the target used in the synthesis of the NP. Within the NP, the concentrations of Ge and Te varied: the closer to the core, the higher the Ge concentration and the lower the Te concentration.