In situ growth and phase engineering of manganese arsenide nanostructures in environmental TEM

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Background incl. aims

For magnetic materials, in situ synthesis offers an additional advantage by enabling the exploration of the magneto-structural relationship. Understanding magneto-structural phase transitions is crucial for the development of materials such as those used for magnetocaloric applications. One such material is MnAs, in bulk known for the ferromagnetic transition around 315K coupled with a structural transition from hexagonal (α-MnAs) to orthorhombic (β-MnAs). However, experimental studies of MnAs nanoparticles have shown discrepancies where the ferromagnetic transition occurs even in the absence of the structural transition.

Nanomaterial synthesis is usually done ex-situ, which can sometimes be tedious and time-inefficient, especially when exploring new or metastable materials. An environmental TEM (ETEM) specifically designed for exploring new material systems, allows for simultaneous exploration of synthesis parameters while observing the changing nanostructures with atomic resolution. Parameters can be fine-tuned, and even metastable material systems and crystal structures have been synthesized this way, showing promise for exploring not only new material systems but also those that have previously been discarded.

In this study, we focus on transition metal pnictides, particularly MnAs, due to their promising applications in spintronics, magnetic refrigeration, and data storage devices. During the preliminary work, the goal is to explore the diffusion behaviour of manganese, how to control the growth rate of MnAs and explore the various structural phase transitions, laying the groundwork for a deeper understanding of magnetic transition metal pnictides. In the long term, we would like to integrate Lorentz imaging techniques to also explore the magnetic properties. This way, material growth could be paired with atomic resolution imaging, chemical analysis, and even information about magnetic domains, and pave the way for a new approach to fundamental studies and phase engineering of magnetic nanomaterials.

Methods

MnO_2 nanoparticles were prepared via spark ablation and sputtered directly onto a MEMS chip for further work in the Hitachi HF-3300S 300kV ETEM. In the ETEM, arsine (AsH_3) was used as the precursor gas to facilitate the growth of MnAs nanostructures. Various parameters, including temperature, gas flow, and electron beam effects, were explored to map the parameter space of this material system and optimize the stability of both MnO_2 and MnAs. For analysis, HRTEM, FFT, SE and Z-contrast in STEM mode, and both TEM- and STEM-EDX were performed during the experiments.

Results

It was observed that AsH_3 diluted with H_2 during electron beam irradiation causes MnAs to form outside of the MnO_2 particles. Together with the oxide reducing in size and eventually disappearing, this might indicate that the manganese atoms diffuse out of the oxide particles to crystallize into MnAs. This effect seems to be correlated with electron dose and is not observed in STEM mode. The fact that MnAs only form under a strong electron beam can be advantageous in the exploration of the parameter space, as no changes were observed for the non-exposed oxide particles. However, using manganese oxide particles instead of pure manganese also introduces some limitations. At lower temperatures, around 200°C, the stability of the MnO_2 nanoparticles under the electron beam was compromised, even without any AsH_3 supplied. However, at higher temperatures, around 400°C, the MnO_2 particles were observed to be more stable and thus preferable for control of the diffusion of manganese into MnAs.

Conclusion

MnAs was successfully synthesized from MnO_2-particles under AsH_3 atmosphere using an in situ ETEM due to what seems like an electron beam-activated process. These preliminary findings demonstrate the feasibility of synthesizing stable MnAs nanostructures in the ETEM environment and underscore the potential of this approach for exploring transition metal pnictides and similar material systems. The results show that this method is promising for future studies of magneto-structural relationships in transition metal pnictides, especially if magnetic imaging techniques are well integrated into the system. Additionally, the results are laying the foundation for further investigations into phase engineering and combinations with semiconducting III-V nanowires, such as GaAs and InAs, which already have been greatly explored in this system.

Keywords:

ETEM MnAs in-situ

Reference:

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