

In-situ synthesis of thin kesterite films using high voltage TEM

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A promising route for the synthesis of kesterite solar cell absorber layers consists in the annealing of thin layers in vapours resulting in alloys of kesterites, a route that has recently also been used for the synthesis of van der Waals materials. This straightforward annealing procedure includes several structural transformations of the absorber thin film layer such as phase transformations, diffusion processes and grain growth. The disentanglement of these different processes is difficult and TEM analysis is essential to understand the structural changes during the annealing of those materials. The best approach to follow the structural changes during the synthesis process of such kesterite materials is to carry out the related annealing steps in situ in the TEM. Since the layers have a certain thickness and the annealing must be carried out in a Se atmosphere, the high voltage TEM (HVTEM) is an appropriate method for this type of in situ annealing which we carry out in this work.

Methods

For the TEM in-situ synthesis of kesterite structures of $\text{Cu}_2\text{ZnSnSe}_4$, we used the JEOL-1000K RS HVTEM at Nagoya University. The starting materials are $\text{Cu}_2\text{ZnSnS}_4$ and $\text{AgCu}_2\text{ZnSnS}_4$, which are annealed in a Se atmosphere to obtain a $\text{Cu}_2\text{ZnSnS}_x\text{Se}_{4-x}$ phase with as high as possible Se content. The temperature is increased in steps of 50-100 °C up to 500 °C while the Se-enriched carrier gas streams along the sample surface. At each temperature ramp, the sample is analysed by electron diffraction, TEM and STEM imaging as well as by EELS spectroscopy. In addition, the TEM is equipped with a highly sensitive mass spectrometer, which enables us to analyse the gases coming from the sample during annealing.

Results

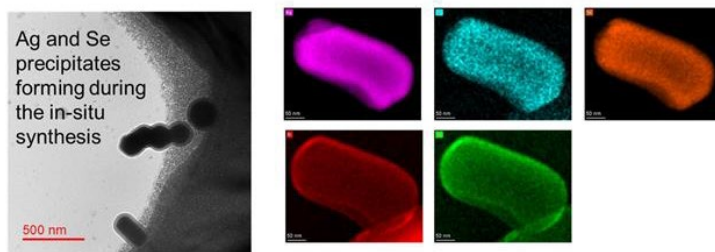
We started the synthesis either from the metallic stacks or from $\text{Cu}_2\text{ZnSnS}_4$ which are exposed to Se vapours. Though the analysis of the metallic stacks has promising results, the thickness increase of about a factor of 2 during the selenisation process made the sample so thick that it was difficult to analyse nanometric changes in the sample happening during the synthesis process. This situation changed by using thin $\text{Cu}_2\text{ZnSnS}_4$ and $\text{AgCu}_2\text{ZnSnS}_4$ films as a starting material since these films preserve their thickness during the synthesis. During the in-situ annealing of $\text{AgCu}_2\text{ZnSnS}_4$, we observed the nucleation of the kesterite $\text{Cu}_2\text{ZnSn(S)Se}_4$ phase, which is preceded by the formation of Ag- and Se-containing nanoprecipitates. Those partially disappear during higher annealing temperatures, when the $\text{AgCu}_2\text{ZnSnSe}_4$ grains grow. By in-situ EELS analysis and post-annealing EDS measurements of the thin layers we could follow the chemical modifications of the crystallites forming a core-shell structure.

When the $\text{Cu}_2\text{ZnSnS}_4$ is synthesised, the replacement of S by Se causes an expansion of the lattice parameter. We applied a Hough transform to extract the lattice plane spacing from the diffraction patterns and conclude that in $\text{Cu}_2\text{ZnSnS}_{(4-x)}\text{Se}_x$, Se is inserted at a concentration of 50 ± 10 %. One goal of this annealing process is to increase the grain size to reduce the impact of grain boundaries on carrier transport. Whereas the starting kesterite has a grain size in the 10 nm range, after the annealing process, a grain size of 50 nm is reached.

Conclusion

Using in situ HVTEM synthesis of $\text{Cu}_2\text{ZnSnS}_{(1-x)}\text{Se}_x$ kesterite structures, we could successfully demonstrate the grain growth and replacement of S by Se in the kesterite crystal. This replacement reaction happens at elevated temperatures of 400-500 °C.

Graphic:



Keywords:

high voltage TEM, insitu, kesterite