Thermodynamic analysis of crystal growth of zinc oxide by CVT under addition of group XV elements

R. Heinemann[1]*, P. Schmidt[1]

[1] *BTU Cottbus – Senftenberg, Universitätsplatz 1, 01968 Senftenberg, Germany*
*E-Mail: robert.heinemann@b-tu.de

Beside its possible use as TCO or substrate for crystal growth of GaN, application of ZnO in optoelectronics is highly discussed. Therefore, one of the key aspects is the growth of p-doped single crystal phases. Group XV elements such as phosphorus, arsenic and antimony are currently discussed as promising dopants.
Chemical vapor transport (CVT[1]) using CO(g) as transport agent proved its worth as a well suited method for growth of ZnO single crystals. Thermodynamic modelling with TRAGMIN software package[2] (see figure 1) revealed that addition of P, As and Sb do not impair the transport equilibrium between ZnO and CO(g) in the temperature range in which CVT is performed. Furthermore, it is shown that the gaseous species Sb_4, Sb_2 and As_4, respectively, are involved as transport agent as well. First attempts of chemical vapor transport with zinc oxalate, graphite and the regarded group XV element as transport additive provided ZnO crystals up to 700 µm in length. The choice of the used group XV element affects the morphology of the grown crystals significantly. Transport attempts with P and As more likely produced crooked crystals with inclusions. Whereas addition of Sb to the initial mixture results rather in growth of well-formed hexagonal columns. Further optimization of transport conditions, especially the use of temperature profiles containing two deposition zones, results into an improvement of the crystals' morphology and size (more than 1 mm in length) as well as the yield of single crystals.

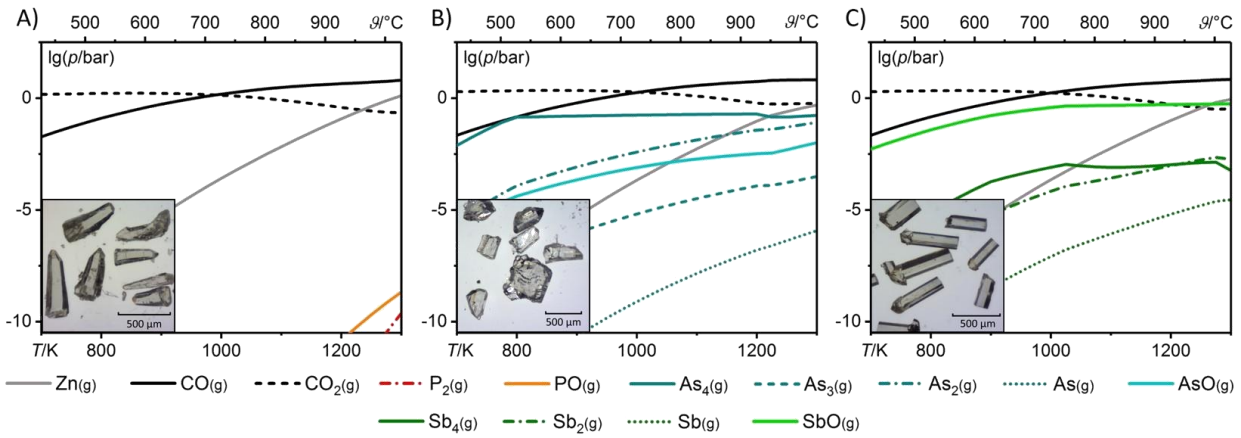

Figure 1: Composition of the gas phase, calculated by TRAGMIN and ZnO crystals grown by CVT for initial mixtures of zinc oxide, zinc oxalate, graphite, and addition of: A) phosphorus, B) arsenic, C) antimony

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[2] G. Krabbes, W. Bieger, K.-H. Sommer, T. Söhnel, U. Steiner *GMIN Version 5.0b, package TRAGMIN for calculations of thermodynamic equilibrium*, Dresden (2008)