X-ray Energy Dispersive Spectroscopy During Growth and Decomposition of GaAs Nanowires using Transmission Electron Microscopy

Tornberg, M.[1,2], Maliakkal, C.B.[1,2], Jacobsson, D.[2,3], Persson, A.R.[2,3], Wallenberg, R.[2,3], Dick, K.A.[1,2,3] and Kodambaka, S.[4]

[1] Division of Solid State Physics, Lund University, Sweden, [2] NanoLund, Lund University, Sweden, [3] Centre for Analysis and Synthesis, Lund University, Sweden, [4] Department of Materials Science and Engineering, University of California Los Angeles, United States

The advances of environmental transmission electron microscopy(TEM) has made it an essential tool for the fundamental understanding of droplet assisted formation of semiconductor nanowires, such as Si or GaAs[1,2]. The assisting droplet, commonly gold, is not pure but instead an alloy including at least one of the reactants of the growth. The specific alloy composition has been predicted to play a large role in the growth process[3] but has now only been investigated ex-situ, after the nanostructures have been cooled down. High temperature chemical analysis during growth or decomposition has until now not been investigated, making this a step forward for work on nanowire dynamics using environmental TEM.

We report on in-situ TEM real-time investigation of growth and decomposition dynamics along with quantitative determination of elemental composition, using X-ray energy dispersive spectroscopy (EDS), of the droplet governing both reactions at the nanowire-droplet interface. We have investigated thermal stability of GaAs nanowires grown along an [$\bar{1}\bar{1}\bar{1}$]-axis, with an Au-Ga alloy on the top facet at temperatures above 300˚C in a high-vacuum (1e-5 Pa) environment of the TEM column. We observe layer-by-layer decomposition of GaAs at the droplet-nanowire interface, as shown in figure 1a. The rate of bilayer removal increases with increasing temperature. During this process, we find that the gallium content in the droplet also depends on the temperature, increasing from ~ 22 atomic percent (at.%) Ga at 300˚C to ~ 29 at.% at 400˚C. We carried out complementary experiments, where tri-methyl-gallium and arsine were introduced to grow GaAs nanowires. For nanowire growth at different temperatures, we observe a similar increase in gallium content of the droplet. The gallium content in the Au-Ga droplets increase from 25 at.% at 420˚C to 36 at.% at 500˚C. It is to be compared to the ex-situ measurements, where the gallium concentration in the particle has been reported between ~5 and 50 at.% depending on reactor and cooling conditions[4]. Our work highlights the importance of chemical analysis, such as EDS, at the temperature at which the process is taken place, as ex-situ measurements of a cooled particle will not reflect its state during growth or decomposition.[5]

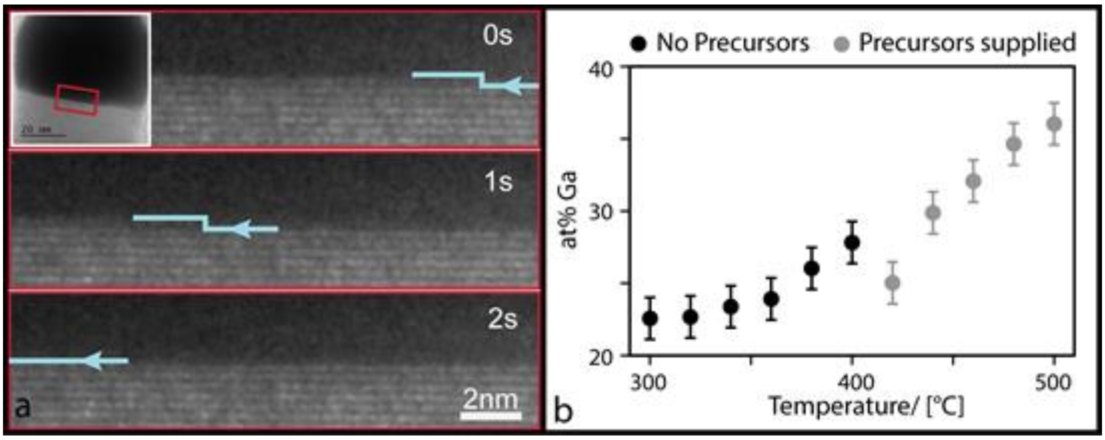

Figure 1. (a) In situ TEM images acquired from Au-Ga/GaAs nanowire interface while annealing the nanowires in vacuum at 360˚C. These images reveal removal of a bilayer of GaAs, highlighted by the blue arrows. (b) Gallium composition in the Au-Ga droplet plotted as a function of temperature. Black and gray symbols correspond to data obtained while annealing the nanowire in vacuum and during

the growth of the nanowire as the Ga and As precursors (tri-methyl-gallium and arsine) are introduced into the TEM resulting in a total pressure of 0.28 Pa.

[1] D. Jacobsson, F. Panciera, J. Tersoff, M.C. Reuter, S. Lehmann, S. Hofmann, K.A. Dick, and F.M. Ross, Nature **531**, 317 (2016).

[2] K.W. Schwarz, J. Tersoff, S. Kodambaka, and F.M. Ross, Phys. Rev. Lett. **113**, 1 (2014).

[3] V.G. Dubrovskii, Appl. Phys. Lett. **104**, (2014).

[4] S. Lehmann, J. Wallentin, D. Jacobsson, K. Deppert, and K.A. Dick, Nano Lett. **13**, 4099 (2013).

[5] We gratefully acknowledge *Knut and Alice Wallenberg Foundation* and *NanoLund* for financial support.