

Nanoscale insights into the synthesis of GaAs core-shell nanowires for water splitting applications via in situ heating in the transmission electron microscope

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Solar fuel cells represent one of the most promising approaches of alternative energy production in the global effort to diminish fossil fuels. In this context, III-V nanowires (NWs) based photoelectrodes are particularly attractive, as they present a high surface / volume ratio, and efficient charge separation and collection. NWs can be integrated in the form of arrays, on low cost substrate, for significantly improved light absorption [1]. However, III-V NWs suffer from corrosion in aqueous electrolyte that prevents their utilization for a long period. To avoid surface degradation during the photoelectrochemical cycle, the surface of the III-V NWs is coated with an oxide shell, which is transparent to visible light, and compatible with the carrier transfer from the III-V core to the electrolyte, hence increasing the viability of these photoelectrodes.

In this work, GaAs NWs were grown by Molecular Beam Epitaxy (MBE) using the Vapor Liquid Solid method on silicon substrate. The Nanowires present alternating zinc-blend domains, as shown in Figure 1. A capping / decapping process with an As shell was performed to protect III-V NWs facets, before the growth of the oxide-shell in another reactor [2, 3]. While this process can appear simple, controlling the surface state of the GaAs core after decapping is crucial prior to the growth of the oxide-shell, as it directly influences the efficiency of the carrier transfer between core and shell. In order to understand the nanoscale structural and chemical evolution during the decapping process, *in situ* heating experiments were performed in a FEI Titan ETEM G2 80-300, operated at 300 kV, using a high stability DENS Solutions Wildfire™ heating holder.

The decapping process of the As shell is shown to take place in two steps. First, the crystallization of the amorphous As phase is observed at $\sim 300^\circ\text{C}$, and then the As shell desorbs from $\sim 325^\circ\text{C}$, leading to unaffected GaAs core with clean facets at higher temperature as shown in Figure 2a. Chemical analysis using electron energy-loss spectroscopy (EELS) highlights that this decapping method leads to a high quality non-oxidized surface, with low defect density as shown in Figure 2b. At higher temperature, the GaAs core thins down through congruent decomposition, as shown in Figure 2c, confirming earlier reports [4]. The subsequently deposited TiO_2 shell, deposited by Atomic Layer Deposition or MBE, is shown to be amorphous and homogeneous over the whole NW length. This work highlights the complex decapping process occurring of the GaAs@As NWs, and the high quality of the core surfaces allowing adequate deposition of an oxide shell for homogeneous coverage and high efficiency photoelectrochemical measurements that will be shown.

[1] Colombo C. *et al.*, *Physical Review B*, **77**, 155326 (2008).

[2] Guan X. *et al.*, *Nanoscale*, **8**, 15637-15644 (2016).

[3] Guan X. *et al.*, *Nano letters*, **16**, 2393-2399 (2016).

[4] Loitsch B. *et al.*, *Advanced Materials*, **27**, pp.2195-2202 (2015).

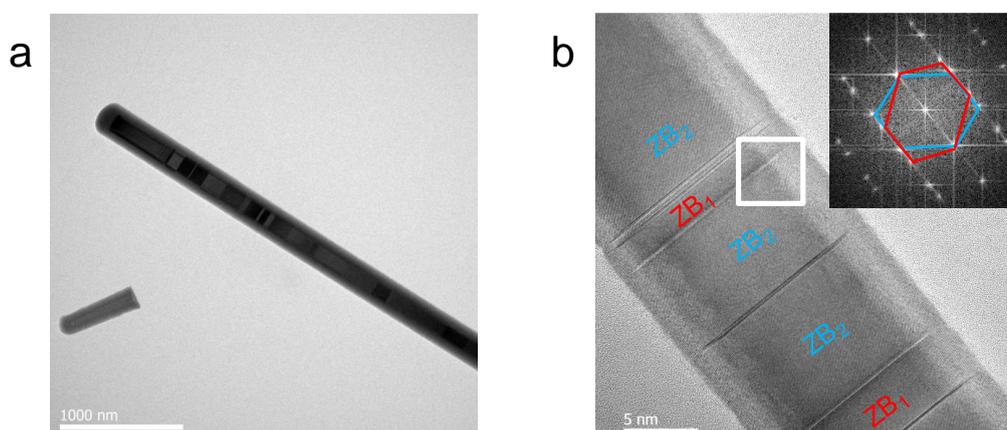


Figure 1. a. Example of a As@GaAs Nanowires prior to decapping, presenting alternating zinc-blende domains along the GaAs NW core as evidenced by the FFT in **b.**

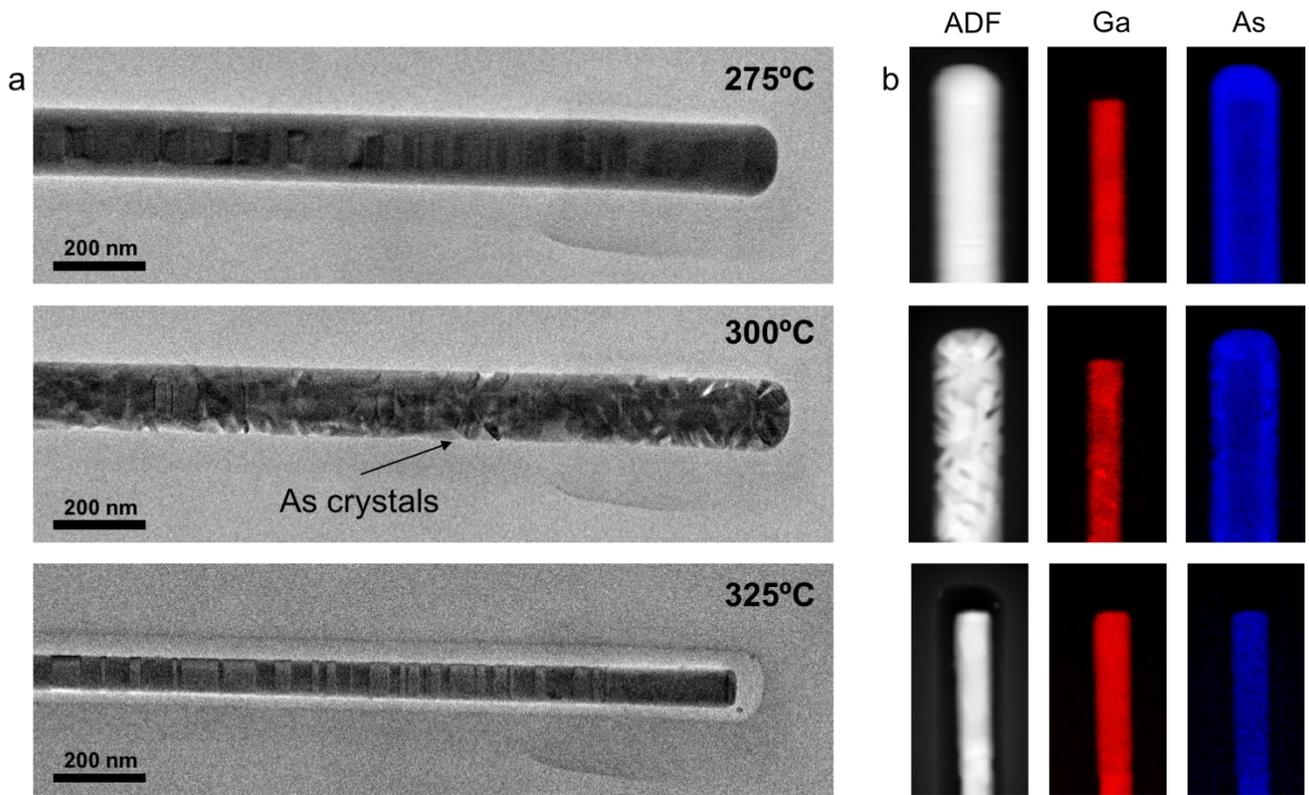


Figure 2. a. Structural Evolution of an As@GaAs nanowire during *in situ* decapping in the TEM. The As shell crystallizes before sublimation. **b.** Corresponding STEM-EELS chemical mapping at different steps of the decapping process.