Supplementary information

GaAs nanowires with oxidation-proof arsenic capping for the growth of epitaxial shell

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1. GaAs NWs morphology, chemistry and structure

The SEM top view image (Figure S1) of the GaAs NWs shows the presence of vertical NWs and some nanocrystals. The Si substrate is still visible. Vertical NWs exhibit asix sided surface which can be indexed to {1-10} crystal plane. Moreover the lateral surfaces are systematically aligned with the in-plane Si{1-10} crystal plane. This morphology of the GaAs is in accordance with the following epitaxial relationship: GaAs[111] // Si[111] and GaAs[1-10] // Si[1-10].

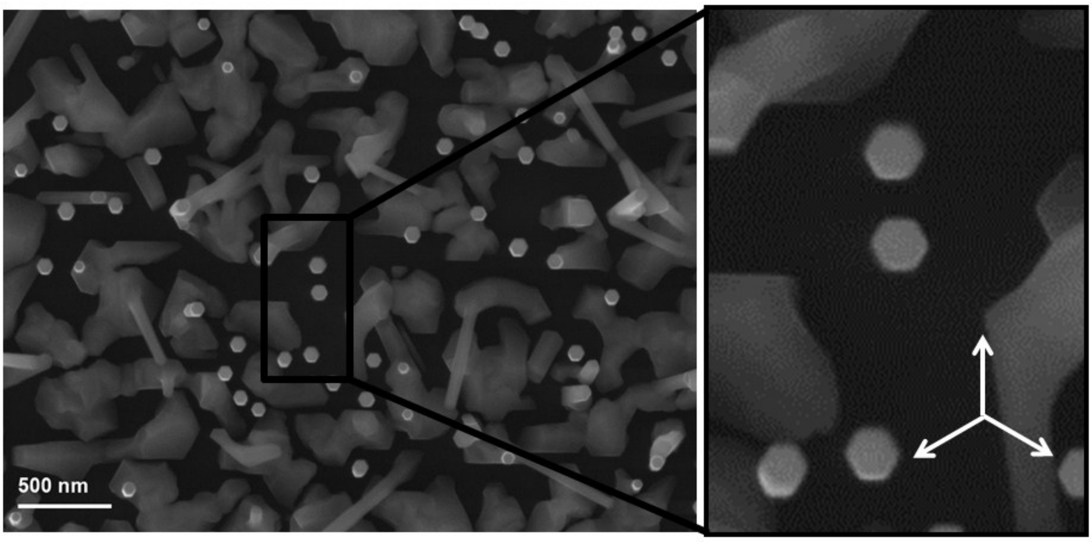

Figure S1 SEM top view of the as-prepared GaAs NWs. The arrows show the in-plane Si<110> directions

Figure S2 a shows the reciprocal space mapping of the GaAs NWs grown on Si(111), measured around the Si(111) reflection and the GaAs(111) reflection. The Si(111) peak is intense and narrow, typical for a substrate. Whilst the GaAs(111) peak is narrow along the radial direction (theta / 2theta) and larger along the rocking angle (omega) which is in accordance with epitaxial nanowires. The GaAs (111) peak located at 27.32 degrees (Figure S2 b) is in good agreement with bulk GaAs, showing the full relaxation of the GaAs NWs.

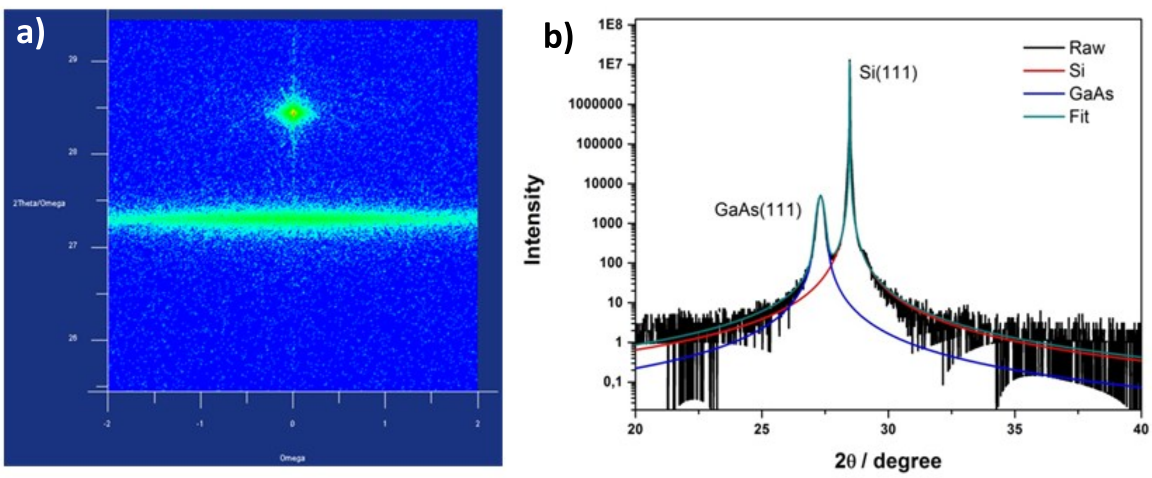

Figure S2 (a) the reciprocal space mapping and (b) theta-two-theta scan of GaAs NW array on Si (111) substrate.

Figure S3 a shows that the GaAs NWs are made of four different parts: the first segment is made of a perfectly pure zinc-blende (ZB) region (starting from the substrate); the second segment is a transition region with high density of twin boundaries and stacking fault; the third segment is defect-free wurtzite (WZ) phase and the last segment is a thin ZB part about 15 nm. The growth of NW is along the [111] direction and there is a thin layer of amorphous oxide on the surface of the NW because of the air oxidation (Figure S3 b).

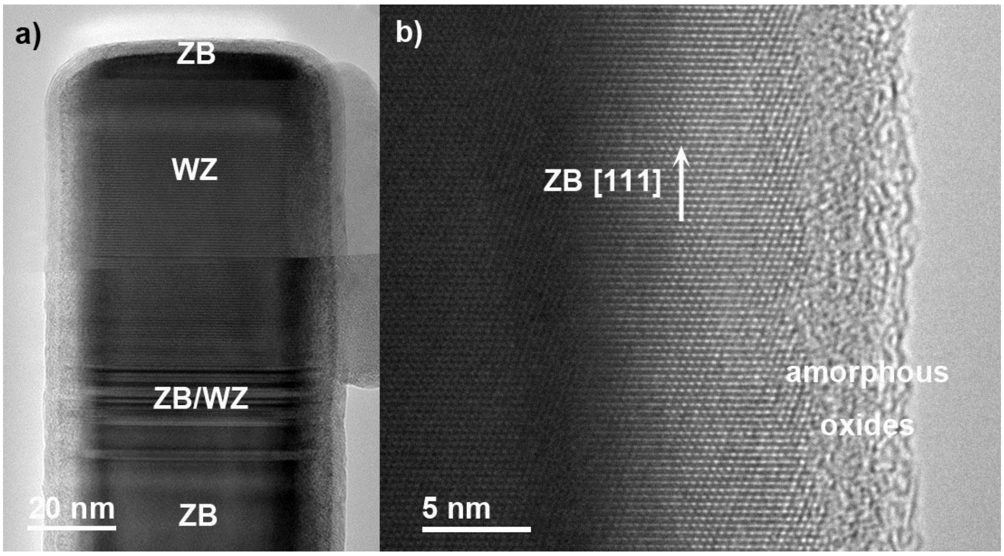

Figure S3 (a) the crystal structure of a typical GaAs NW; (b) the surface oxidation of the GaAs NW.

Figure S4 shows the As and Ga 3d core level spectra of bulk GaAs substrate measured by XPS. The two peaks are intense and with small FWHM (Figure S4 a). After deconvolution, the As 3d core level is comprised of As $3d_{3/2}$ at 41.69 eV and $3d_{5/2}$ at 41.00 eV (Figure S4b), while Ga 3d core level is constituted of Ga $3d_{3/2}$ at 19.55 eV and $3d_{5/2}$ at 19.10 eV.

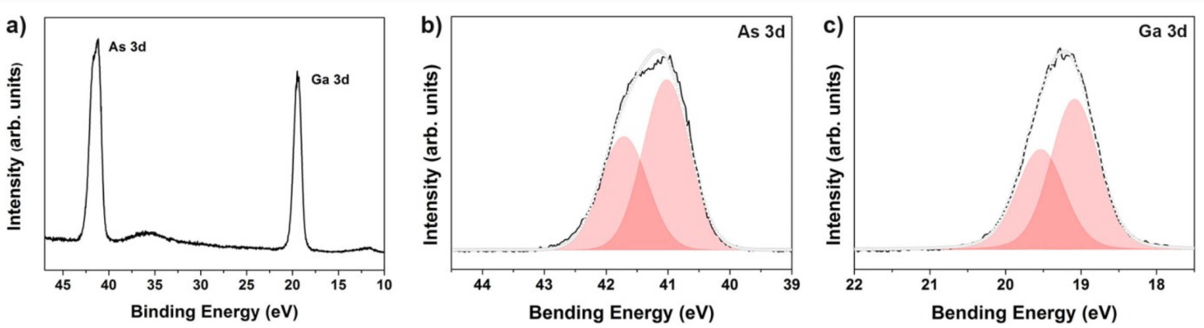

Figure S4 As and Ga 3d core levels of bulk GaAs substrate.

2. As capping and shell growth

Figure S5 is the STEM image of a typical As-capped GaAs NW and the corresponding EDX elemental mapping of Ga and As. Ga exists in the core part of the NW, while the As disperses in both the core and the shell. This proves that the NW is well packaged by the amorphous As layer.

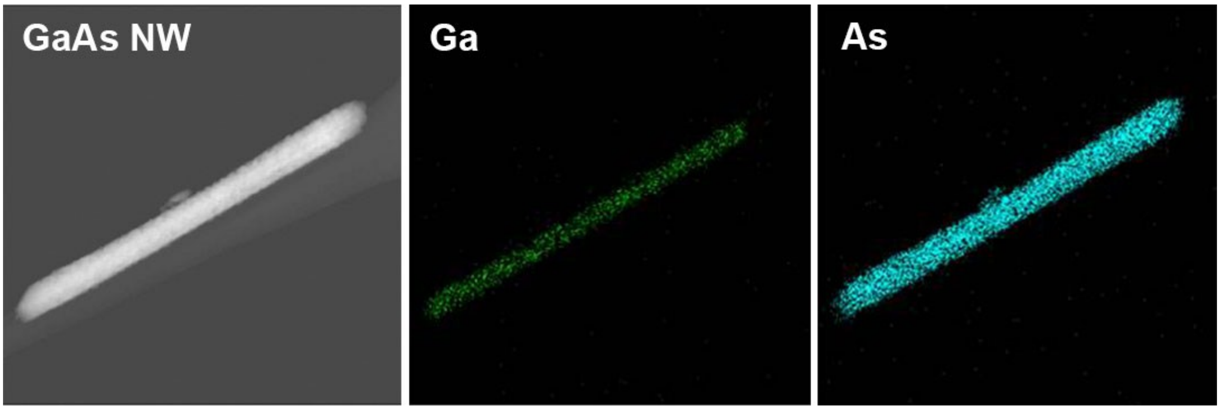

Figure S5 STEM image and EDX elemental mapping of the As-capped GaAs NW.

Figure S6 is the STEM image of a typical *in-situ* grown GaAs / AlGaAs core / shell NW and the corresponding EDX elemental mapping of Ga, As and Al. Ga and As disperses in both the core and the shell, while Al exists only in the shell (the intensity in the inner part is feeble).

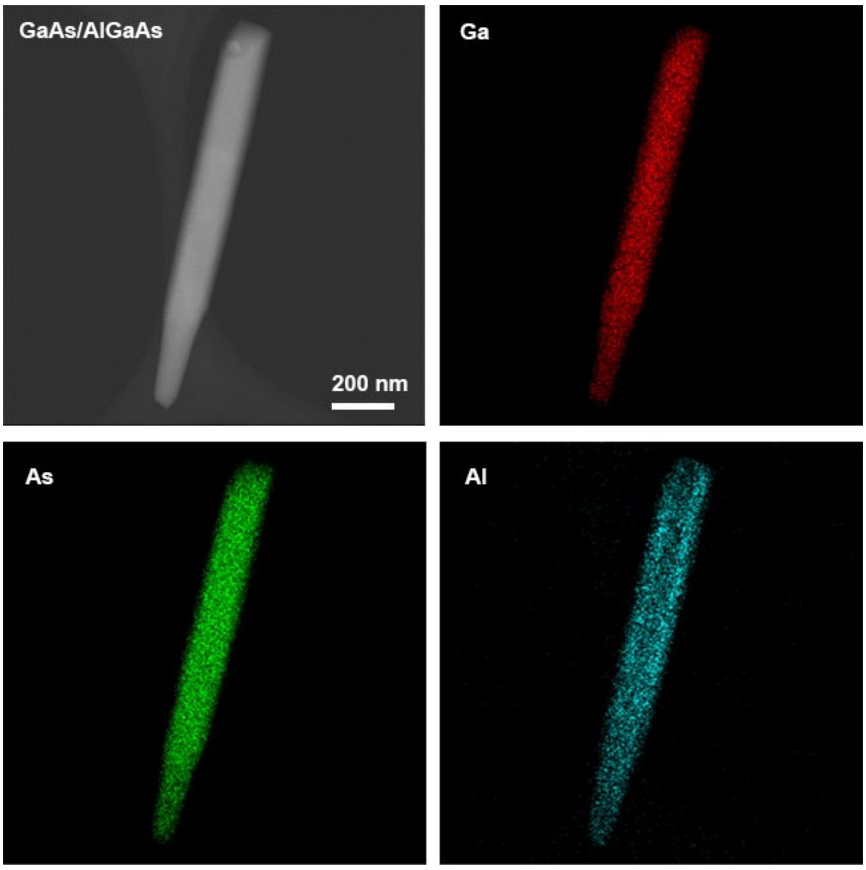

Figure S6 STEM image and EDX elemental mapping of one *in-situ* grown GaAs / AlGaAs NW.

Figure S7 is the XRD data of the in-situ growth core / shell NW. Except for the intense peak indexed to Si(111), another sharp peak is ascribed to the (111) crystal plan of GaAs and AlGaAs. The other two small peaks can be attributed to (220) and (222) crystal planes of GaAs and AlGaAs. This is proof of epitaxial growth of the AlGaAs shell.

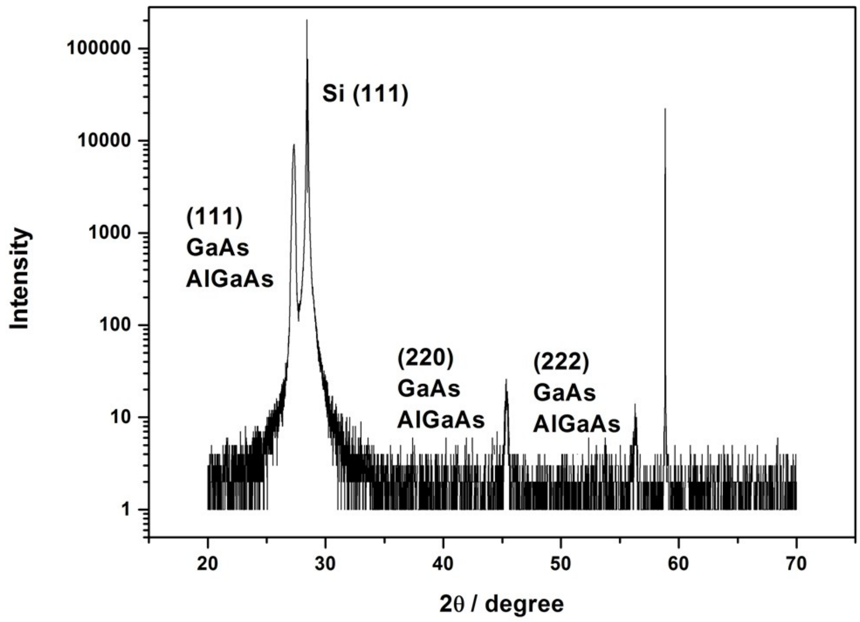

Figure S7 XRD pattern of the *in-situ* grown GaAs / AlGaAs core / shell NW array.

Figure S8 is the TEM image of oxidized-GaAs / AlGaAs NW. Unlike the *in-situ* growth GaAs / AlGaAs NW and the As-capped-decapped one, the surface of oxidized-GaAs / AlGaAs NW is prominently roughened, due to the abundant crystal defects in the entire shell, as shown in Figure S8 b. The non-epitaxial relationship between GaAs and AlGaAs could have detrimental effect on the physical properties of the NW array. This proved the necessary of the oxidation proof method.

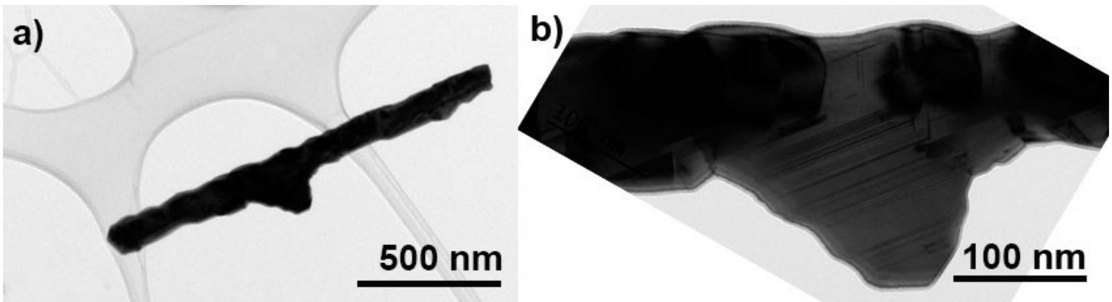

Figure S8 TEM and HRTEM images of an oxidized-GaAs / AlGaAs NW.

3. Optical properties

Time-resolved spectroscopy has been performed at 14 K on both the *in-situ* grown sample and the decapped sample (Figure S9 a and c). Figure S9 a, shows the PL decay of the *in-situ* grown sample for a lower excitation density (pulse excitation density of 24 nJ/cm². The PL decay for the *in-situ* growth sample (Figure S9 b) is obtained by integrating the emission over a 4 nm window around the low energy peak. It is difficult to extract an accurate decay time due to the small temporal window of the streak camera: a monoexponential decay provides a lifetime in the order of 4.6 ns. This long lifetime confirms the hypothesis of an emission related to a type II recombination. As far as the decapped sample, PL decay obtained for a pulse excitation density of 140 nJ/cm². The low energy transition presents a shorter lifetime ≈ 380 ps.

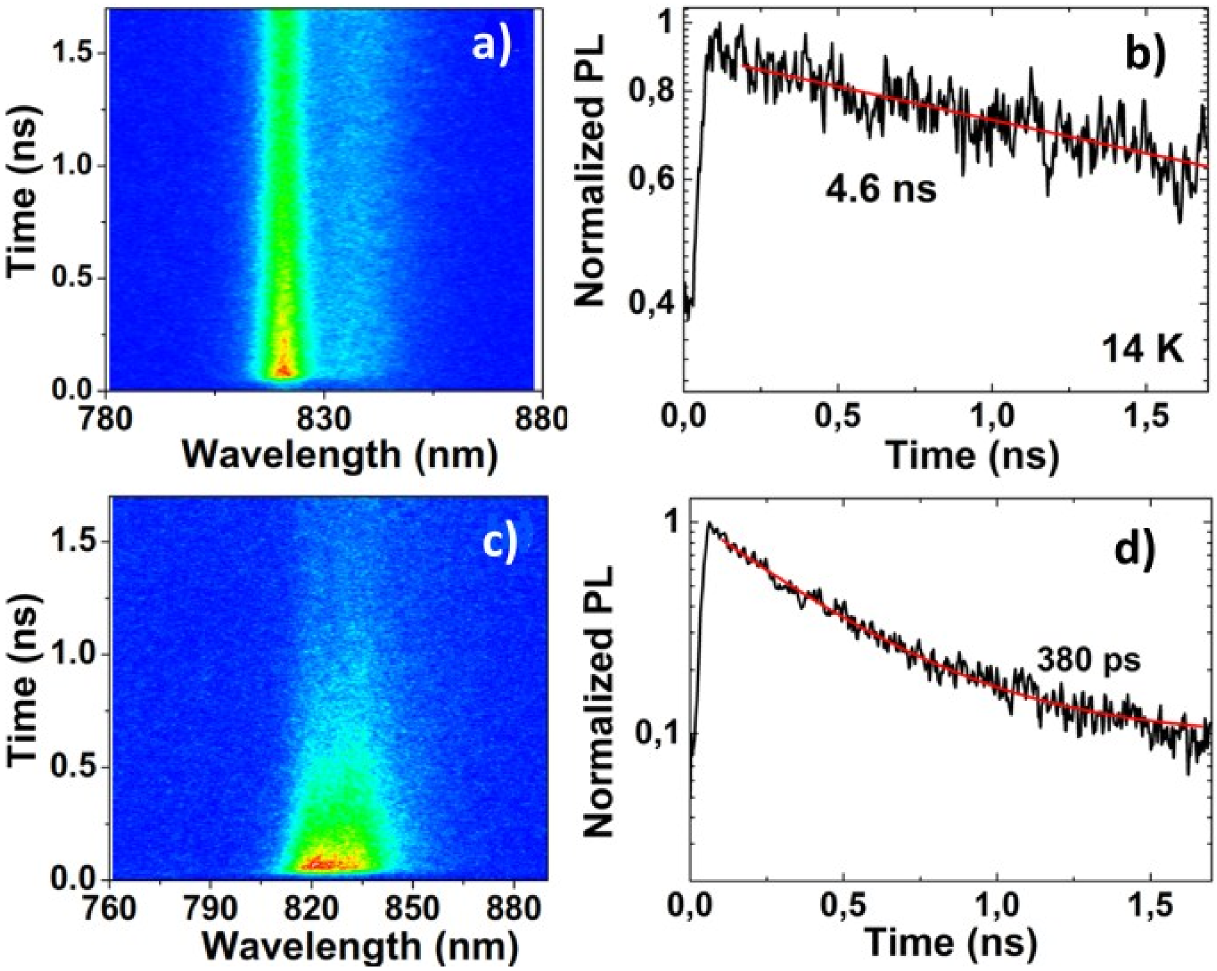

Figure S9 Time-resolved spectra and decays of the *in-situ* grown GaAs / AlGaAs NW (a)(b) and the decapped-GaAs / AlGaAs NW (c)(d) at 14 K.

Figure S10 shows the evolution of the integrated PL intensity as a function of the temperature (excitation provided by a 50 mW - 532 nm cw laser). Integration is performed over all the PL spectra including the low energy contribution. From 14 K to 300 K, the integrated PL emission has been multiplied by 15,000 and 50 for the *in-situ* growth and the decapped samples, respectively.

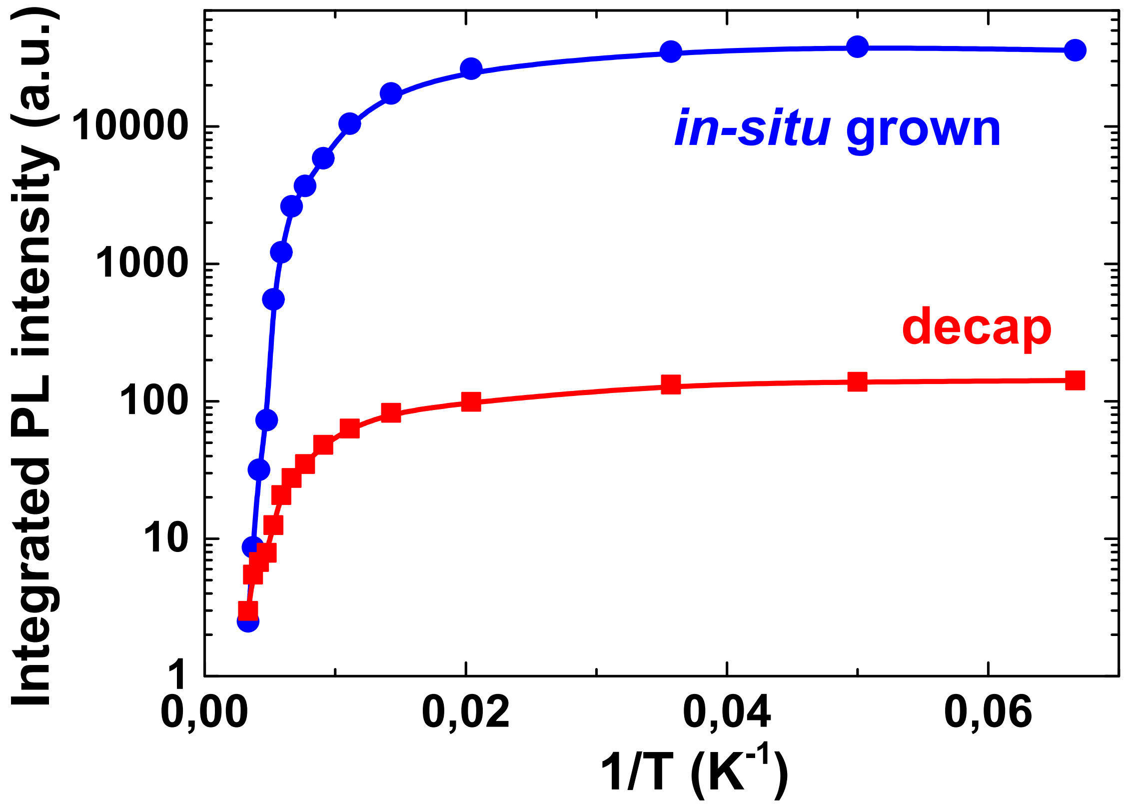

Figure S10 The integrated PL intensity as a function of the temperature for the *in-situ* grown GaAs / AlGaAs NW and the decapped-GaAs / AlGaAs NW.

4. Perspective

To testify whether the As capping-decapping method can be applied to grow heterogeneous shells, such as functional oxides, on III-V semiconductor NWs, GaAs (core) / $SrTiO_3$ (shell) NWs were fabricated using a two-step $SrTiO_3$ growth. We have observed that partial epitaxial-shell was achieved on As-capped/decapped GaAs NWs, on the contrary to the air-oxidized-GaAs NWs (Figure S11 b). We are still working on optimizing the experimental conditions for realizing the completely epitaxial functional oxide shell on semiconductor NW core.

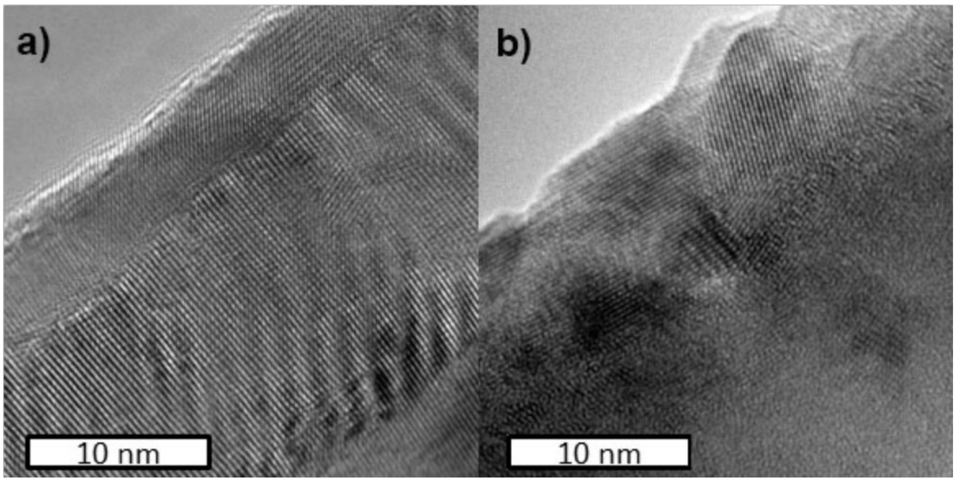

Figure S11 HRTEM images of (a) an As-capped / decapped-GaAs core / STO shell NW,

(b) an air-oxidized-GaAs core / STO shell NW.