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## **Supplementary information**

## For paper

Natural occurrence of the diamond hexagonal structure in silicon nanowires grown by plasma assisted vapour-liquid-solid method

by

J. Tang<sup>a</sup>, J.-L. Maurice<sup>a</sup><sup>+</sup>, F. Fossard<sup>b</sup>, I. Florea<sup>a</sup>, W. Chen<sup>a</sup>, E. V. Johnson<sup>a</sup>, M. Foldyna<sup>a</sup>, L. Yu<sup>c</sup> and P. Roca i Cabarrocas<sup>a</sup>

b. LEM, CNRS, ONERA, 92322 Châtillon, France.

This file is to present chemical analyses that have been performed by energy-dispersive X-ray spectroscopy (EDX) in the transmission electron microscope (TEM) and the scanning TEM (STEM) on the Si nanowires (NWs). The NWs presented in the paper had undergone a 700°C anneal that had significantly modified their catalysts (Sn melting point is at 232 °C). Thus the present analyses were performed on NWs grown in another run.

The TEM-STEM was a FEI Titan 80-300, working at 300 kV, equipped with an Oxford-INCA X-ray detector.

Figure 1 shows a NW grown on the Cu TEM grid, with a 2H volume fraction of about 60%. On the left is a high-resolution TEM image showing the 2H hexagonal and cubic regions, to the right are EDX spectra recorded on the catalyst and on the a-Si close to the NW. The comparison of the two spectra shows that Sn is present indeed in the catalyst. The Cu signal essentially comes from the fact that a large amount of elastically scattered electrons impinge on the grid, thus generating X-rays there. It cannot be conclusive on the presence of that element in either case. The larger Cu peak in spectrum 6 (catalyst) than in spectrum 3 (amorphous silicon) is just due to more matter under the beam and more scattered electrons.

Figure 2 shows a more complete analysis, however recorded on a NW grown during the same run but on the carbon membrane, and where the crystalline phase could not be determined. This analysis shows again the presence of Sn in the catalyst. The signal is low due to a significant degradation during the recording, which obliged to stop the analysis early.

<sup>&</sup>lt;sup>a.</sup> LPICM, CNRS, Ecole polytechnique, Université Paris-Saclay, 91128 Palaiseau, France.

<sup>&</sup>lt;sup>c.</sup> School of Electronics Science and Engineering, Nanjing University, Nanjing 210093, China.

<sup>†</sup> jean-luc.maurice@polytechnique.edu

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Fig. 1: EDX analysis on a partially 2H NW grown on Cu TEM grid

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Fig.2 High-angle annular dark field (HAADF) and EDX images recorded in STEM mode on nanowires grown on the carbon membrane. In HAADF, the intensity increases monotonously with the mass of matter present under the beam. The Cu signal appears to be proportional to the HAADF intensity. This is consistent with the fact that it would be due to the scattered electrons that have hit the Cu grid rather than from the sample itself.

100nm