Electronic Supplementary Material (ESI) for ChemComm.

SUPPLEMENTARY INFORMATION

Microwave-assisted Solution-Liquid-Solid Growth of $Ge_{1-x}Sn_x$ Nanowires with High Tin Content

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Experimental procedure

Precursor synthesis

Butyl lithium, hexamethyldisilazane, $SnCl_2$, 1,1,3,3-tetramethyldisiloxane and $GeCl_4$ were purchased from Sigma-Aldrich. All solvents were dried using standard procedures and stored under molecular sieve. $LiN(Si(CH_3)_3)_2$ was prepared in hexane and purified by sublimation under reduced pressure.[1] The $GeCl_2$•dioxane complex was prepared according to a published procedure.[2]

The synthesis of $Sn(N(Si(CH_3)_3)_2)_2$ was prepared by a modified procedure published by Lappert *et al.* [3]: 2 equiv. of $LiN(Si(CH_3)_3)_2$ dissolved in dry THF were added to a solution of 1 equiv. anhydrous tin(II) chloride in dry THF. During the addition of $LiN(Si(CH_3)_3)_2$ the reaction mixture became warm and turned red-orange in color. The reaction mixture was refluxed for 2h followed by the replacement of the solvent by toluene and the removal of the LiCl. The solvent was removed under reduced pressure and the $Sn(N(Si(CH_3)_3)_2)_2$ was purified by vacuum distillation. The product was collected as bright red oil in 85 % yield.

A similar procedure was used to synthesize $Ge(N(Si(CH_3)_3)_2)_2$ from $GeCl_2$•dioxane complex. The orange amide was isolated by distillation under reduced pressure in 66 % yield.

Materials synthesis

Ge nanowires were grown in 10 ml glass cells (Anton Paar GmbH) at temperatures between 200-240 ºC. The temperature is measured by an IR sensor as a standard setup from the microwave manufacturer (Monowave 300; Anton Paar GmbH, 2.46 GHz). At the last stages of the heating up cycle, the temperature is slowly rising accompanied with a smaller power input to avoid overheating of the solvent. The heating of the vessel is not crosschecked by a ruby thermometer in the solution, but the instrument is calibrated on a regular basis. The handling of the chemicals as well as the filling of the reaction vessels was carried out in a glove box under stringent precautions against water.

A stock solution containing 8 mM $Sn(N(Si(CH_3)_3)_2)_2$ and 32 mM $Ge(N(Si(CH_3)_3)_2)_2$ in dodecylamine was prepared. This solution was stirred for 12 h at room temperature to ensure the formation of the metal imides, which is accompanied with a color change to a bright orange. In a typical experiment, 3 ml of the dodecylamine stock solution were transferred in the glass cells for microwave synthesis and sealed with a Teflon coated rubber cap. This vial was then transferred to the microwave reactor (Monowave 300; Anton Paar GmbH, 2.46 GHz) with an IR temperature control unit. The solution was heated as quickly as possible to 230 °C (approx.. 3.5 min), the temperature held for 1-10 min and cooled down by a gas stream. The nanowires were collected by adding toluene (3 ml) and centrifugation, redispersed in toluene and centrifuged again (5 times) to remove the dodecylamine. The product was stored under ambient conditions in toluene.

Pre-nucleation was achieved by heating the precursor mixture to 115 °C on a hotplate with vigorous stirring and immediate removal from the heat source when the temperature was achieved. The stock solution was cooled down to room temperature and aged overnight before the actual microwave synthesis was performed as described above.

Characterisation

The $Ge_{1-x}Sn_x$ nanowires were analysed using a FEI Inspect F50 scanning electron microscope (SEM). The $Ge_{1-x}Sn_x$ nanowires were deposited on lacey carbon and carbon film copper grids for transmission electron microscope (TEM) characterisation (Plano). In this study, a FEI TECNAI F20 operated at 200 kV and equipped with high angle annular dark field (HAADF) STEM and EDX detector was used. The elemental maps were recorded using the AMETEK TEAM package. The images were recorded and treated using Digital Micrograph software. The X-ray diffraction (XRD) pattern were recorded on a PANalytical X-Pert PRO PW 3050/60 in Bragg–Brentano geometry and Cu-$K\alpha$ radiation. The Rietveld refinement was carried out using X-pert Highscore software.

The Raman spectra were acquired using a Horiba LabRam 800 HR with a laser power of 200 µW and a wavelength of 532 nm.

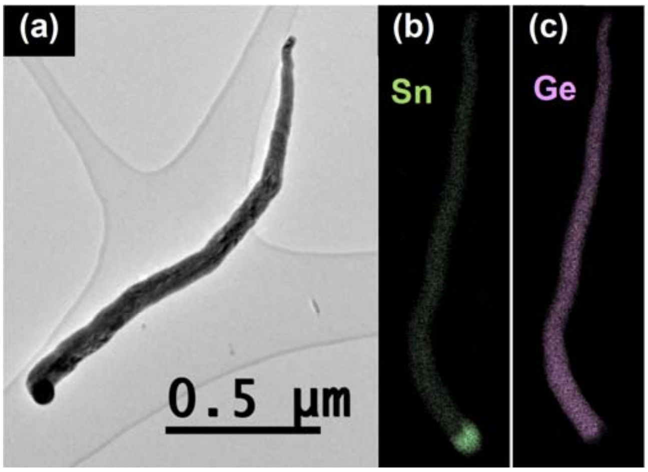


Figure S1. (a) TEM image of $Ge_{1-x}Sn_x$ nanowires grown via microwave synthesis without pre-nucleation at 230 °C from a Sn(II) and Ge(II) imide solution showing an increasing nanowire diameter and a particle terminating the nanowire. The darker Z-contrast of the particle is due to the accumulation of tin as illustrated in a STEM-EDX mapping images in (b) Sn L line and (c) Ge K line. The mapping images show a well dispersed tin content in a Ge-rich matrix.

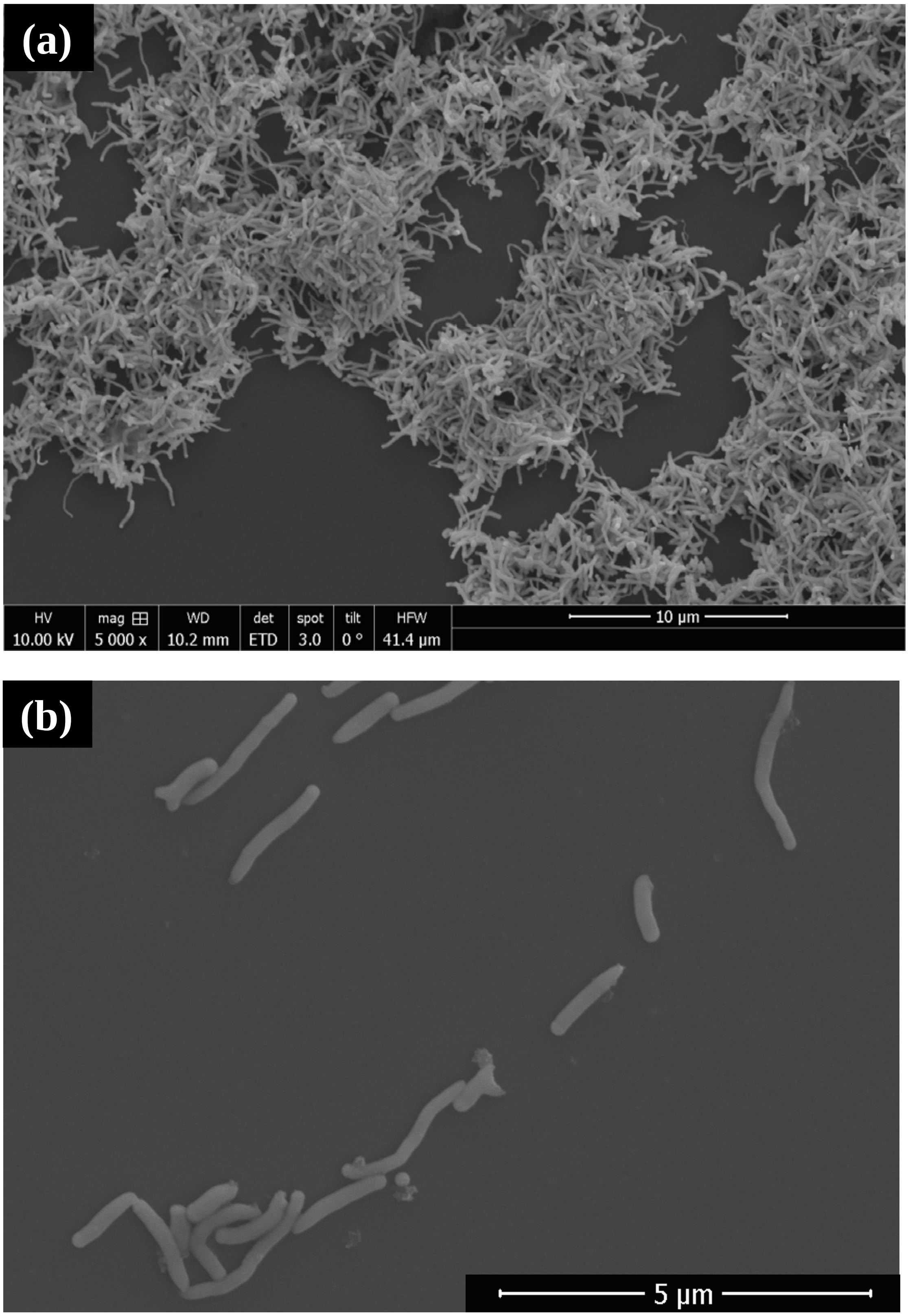


Figure S2. SEM images providing (a) an overview of $Ge_{1-x}Sn_x$ nanowires grown at 230 °C and (b) well dispersed nanowires illustrating the constant diameter along the nanowire axis using the pre-nucleation approach.

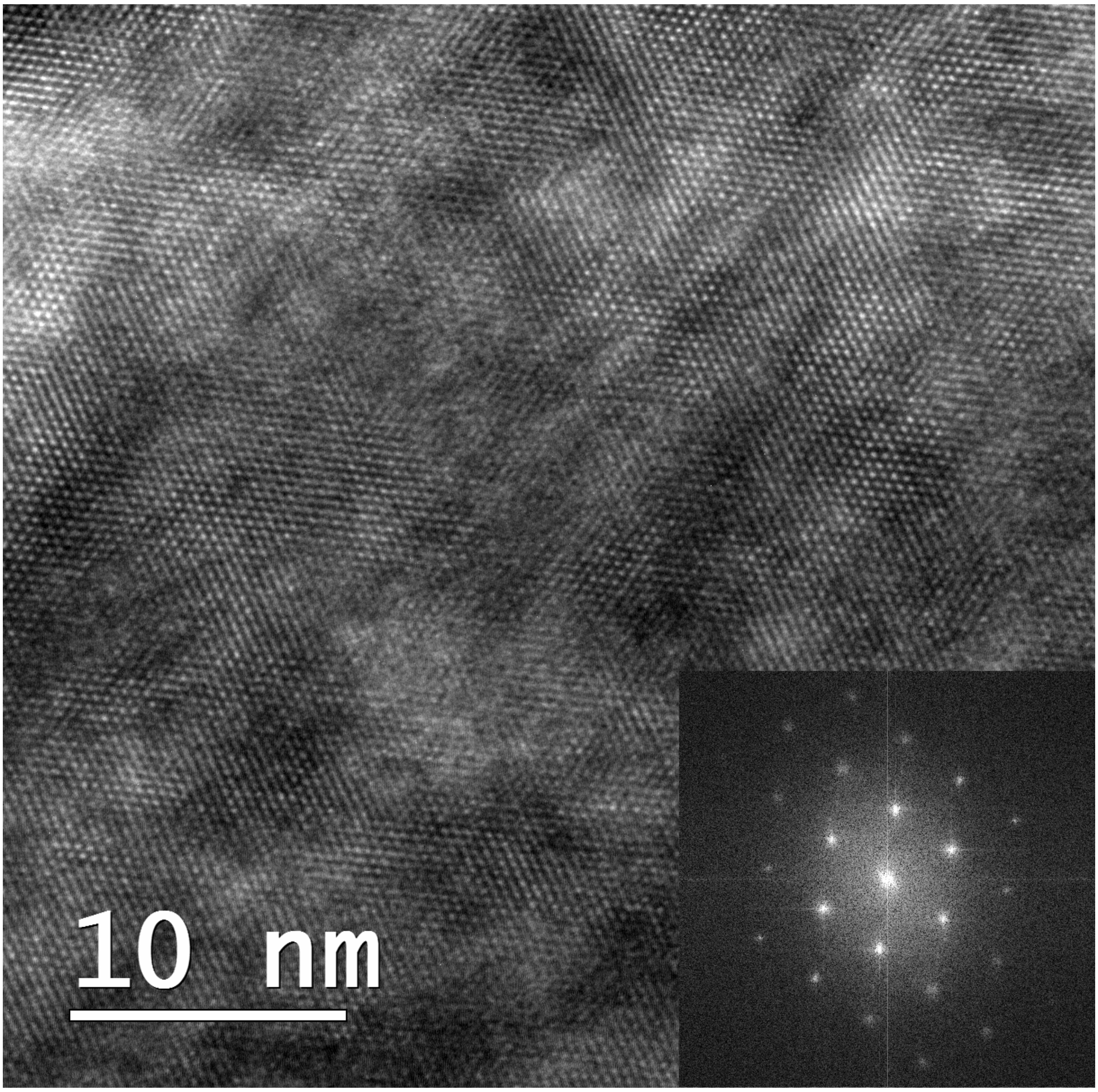


Figure S3. HRTEM image of a thicker $Ge_{1-x}Sn_x$ nanowire showing the high crystallinity and the corresponding FFT pattern in [111] zone axis.

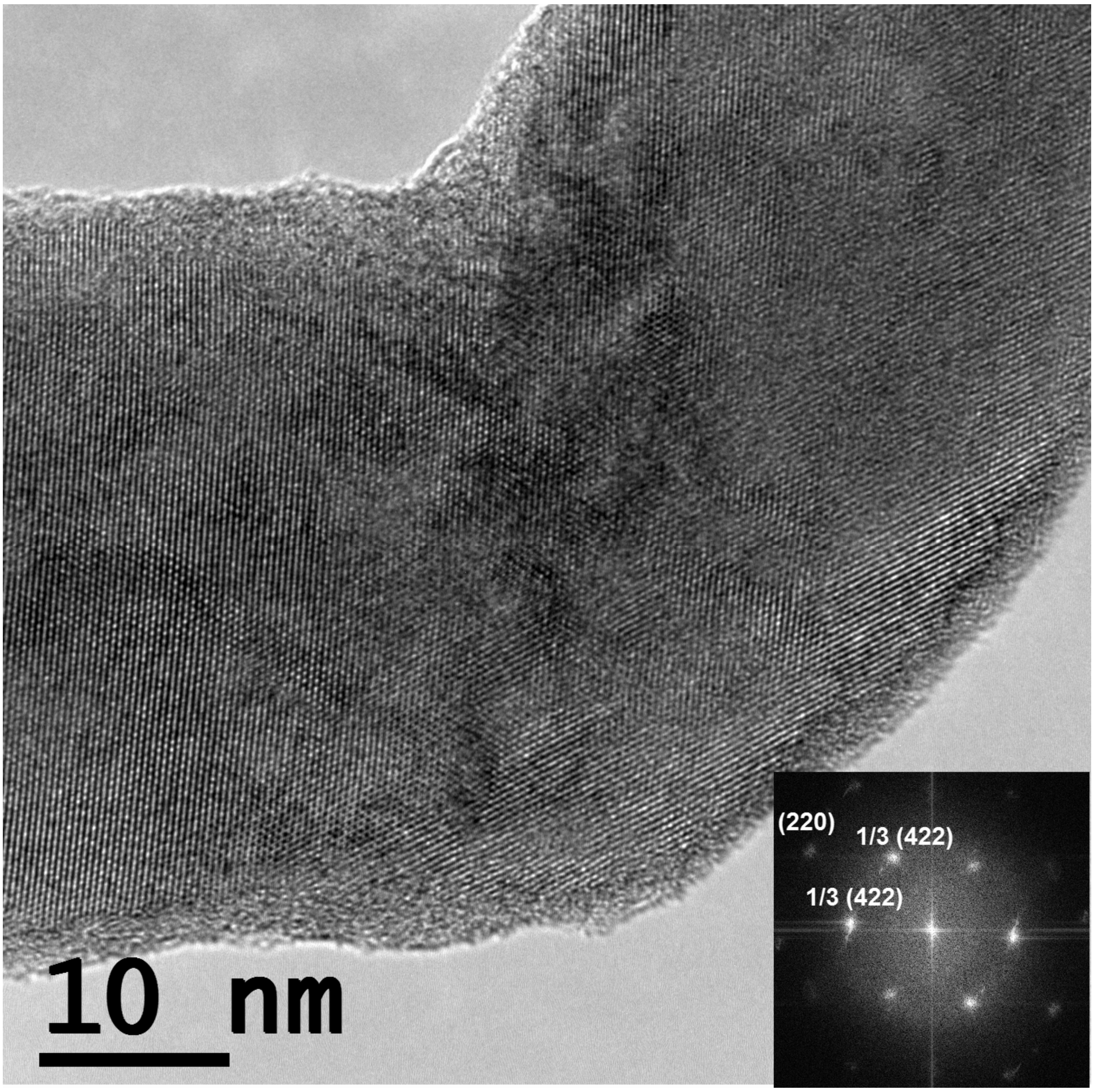
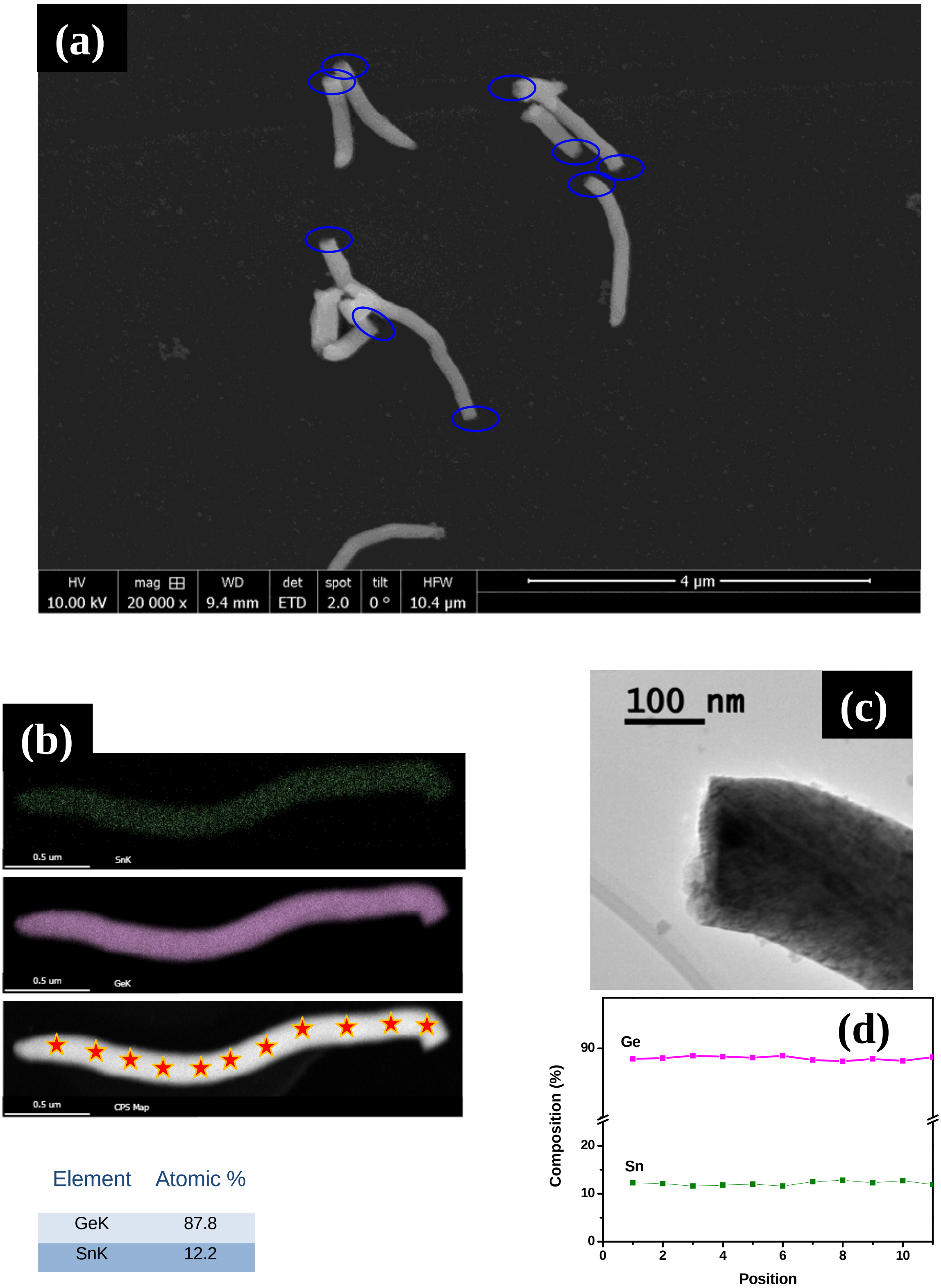
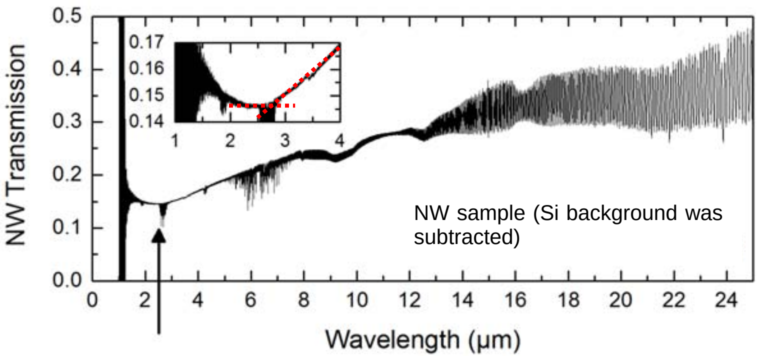


Figure S4. HRTEM image of an area where the nanowire is changing growth direction and the corresponding FFT pattern in [111] zone axis. There is no accumulation of defects observed at such a location.



Element	Atomic %
GeK	87.8
SnK	12.2

Figure S5. (a) SEM image and (b) STEM-EDX images of $Ge_{1-x}Sn_x$ nanowires after removal of the hemispherical Sn growth promoter. The average Ge:Sn ratio determined by EDX is also tabulated. (c) the initial interface between the Sn particle and the $Ge_{1-x}Sn_x$ nanowire is not smooth as shown for the section after Sn removal. (d) Shows the constant Sn distribution along the nanowire shown and marked in (b).



Inset region

“Roughness” due to H_2O absorption

Figure S6. Initial determination of the Ge$_{1-x}$Sn$_x$ nanowire optical absorption measured on a thin nanowire layer coated on a single-side polished Si wafer.

[1] Golloch, A.; Kuß, H. M.; Sartori, P. (1985). Anorganisch-Chemische Präparate: Darstellung und Charakterisierung ausgewählter Verbindungen, De Gruyter.

[2] Roskamp, C. A.; Roskamp, E. J. (2001). Germanium Dichloride–Dioxane Complex. Encyclopedia of Reagents for Organic Synthesis, John Wiley & Sons, Ltd.

[3] Lappert, M. F.; Power, P. P. (1976). Di- and Trivalent Trimethylsilyl-Substituted Tin Amides and Related Compounds Such as Sn[N(SiMe3)2]2 or 3. Organotin Compounds: New Chemistry and Applications, AMERICAN CHEMICAL SOCIETY. **157:** 70.