Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Low Temperature Solution Synthesis of Silicon, Germanium and Si-Ge Axial Heterostructures in Nanorod and Nanowire Form

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Experimental

Evaporated Substrate Preparation. Sn substrates were prepared by evaporating 99.999 % Sn (Kurt J. Lesker) in a glovebox based evaporation unit, onto stainless steel substrates. The nominal film thickness investigated was 20 nm. The substrates were stored in an Ar glovebox prior to reactions and contact with O_2 was kept to a minimum. After synthesis, the substrates were rinsed with toluene to remove excess HBS and dried using a nitrogen line. No additional cleaning steps were required.

Sn Nanoparticle Preparation. The Sn NPs were synthesized using a previously reported procedure as follows:[1] Tin (II) acetate $Sn(C_2H_3O_2)_2$, poly(vinyl pyrrolidone) (PVP) (mw~55,000), 1,5-Pentanediol and sodium borohydride ($NaBH_4$) were purchased from Aldrich and used without purification. In a typical synthesis of Sn nanoparticles, 144 mg of $Sn(C_2H_3O_2)_2$, 1.69 g of PVP and 20 mL of 1,5 pentanediol were mixed together and loaded into a three neck flask. This mixture was evacuated under vacuum for 30 min and refilled with Argon. This mixture was heated to 120 °C. 231 mg of $NaBH_4$ was added with 6 mL of 1.5-Pentanediol and sonicated for 5 min. $NaBH_4$ was introduced into the reaction mixture at 120 °C and upon addition, the color changed immediately to dark brown indicating the formation of Sn nanoparticles. It was further reacted for 10 min and the heating mantle was removed. At room temperature, this entire reaction mixture was transferred into a vial and stored in a glove box to avoid oxidation.

Ligand exchange with oleic acid: 0.2 ml of dark brown reaction mixture was added with 2 mL of hexane, 4 mL Octadecene and 0.4 ml of Oleic acid. This was shaken well and centrifuged at 5000 rpm for 5 min. The bottom, colorless layer was discarded and the brown top layer containing Sn nanoparticles was recovered. This step was repeated with and the brown solution was again recovered. 4 ml of acetone was added to the brown solution and this was centrifuged at 5000 rpm for 5 min. The acetone was then discarded and the Sn nanoparticles were dispersed in 10 ml of squalane.

Reaction Setup. Reactions were carried out in a three-neck flask containing 10 ml of squalane (99 % Aldrich). For reactions carried out using the thin stainless steel substrate, the substrate was simply curved and placed into the solution within the flask. For reactions carried out using Sn NPs, the NPs were immersed in the 10 ml of squalane, with this mixture then being placed into the flask. The flask was connected to a Schlenk line via a water condenser. A water condenser was used to control the reflux of the Si and Ge precursors and ensure that the reaction was kept under control. This set-up was evacuated at 125 °C for 40 min. The solution was then heated to the chosen reaction temperatures under a constant Ar flow. The chosen temperatures for the different reactions ranged from 200 °C to 300 °C. To terminate the reaction, the heating mantle was removed from the three-neck flask and the setup was allowed to cool to room temperature before removing the NW material.

Si NW growth: At the selected reaction temperature, 0.75 ml of the liquid precursor phenylsilane (PS) (98 % Fluorochem) was injected through a septum cap into the system. After 5 min, 0.05 ml of a $LiBH_4$ solution (2.0 M in THF Aldrich):squalane (1:1) mixture was injected. The reaction was allowed to proceed for 1 hour in total. An increase in the reflux was observed following the injection of the reducing agent, with the reflux ceasing completely after approximately 5 min. It was noted that shortly after the introduction of the reducing agent mixture, the solution in the flask turned a strong yellow colour, which remained for the entire reaction. Following the removal of the substrate, some yellow color remained which was washed off with toluene and IPA. (For the synthesis at 200 °C, the reaction was initially ramped to 250 °C for 10 min to form the Sn seeds, before being ramped down to 200 °C and the PS and reducing agent were injected as above).

Ge NW growth: At the selected reaction temperature, 0.25 ml of the liquid precursor diphenylgermane (DPG) (> 95 % Gelest) was injected through a septum cap into the system. After 5 min, 0.05 ml of a $LiBH_4$/squalane (1:1) mixture was injected. The reaction was allowed to proceed for 40 min in total. The solution turned a dark purple/brown colour after approximately 5 – 10 min, which remained for the entire reaction. (For the synthesis at 200 °C, the reaction was initially ramped to 250 °C for 10 min to form the Sn seeds, before being ramped down to 200 °C and the DPG and reducing agent were injected as above).

Si-Si_xGe_{1-x} NW growth. A typical Si reaction (consisting of a PS injection and reducing agent injection) was carried out at 300 °C for 1 hour. The temperature was either maintained at 300 °C or dropped to 260 °C before 0.25 ml of a TPG/squalane mixture (1:4 w/v) was injected and allowed to react for 40 min.

Si-Ge NW growth. A typical Si reaction (consisting of a PS injection and reducing agent injection) was carried out at 300 °C for 1 hour. The reaction temperature was dropped to 240 °C and 0.25 ml of DPG was injected and allowed to react for 10 min.

Ge-Si_xGe_{1-x} NW growth. A typical Ge reaction (consisting of a DPG injection and reducing agent injection) was carried out at 250 °C for 40 min. 0.75 ml of PS was then injected and allowed to react for 1 hour.

Post Synthetic Treatment. After synthesis, the substrates were rinsed with toluene to remove excess HBS. No additional cleaning steps were required. For the syntheses with the Sn NPs, the resulting solution containing the NWs was centrifuged at 4000 rpm for 10 min. The solution was discarded and the product was washed in a toluene/IPA mixture (1:2) and sonicated for 10 min. This was centrifuged at 4000 rpm for 10 min and this washing was performed 2 more times before the final product was dispersed in toluene.

Analysis. SEM analysis was performed on a Hitachi SU-70 system operating between 3 and 20 kV. The substrates were untreated prior to SEM analysis. For TEM analysis, the NWs were removed from the growth substrates through the use of a sonic bath. TEM analysis was conducted using a 200 kV JEOL JEM-2100F field emission microscope equipped with a Gatan Ultrascan CCD camera and EDAX Genesis EDX detector. TEM/STEM/EDX analysis of the NWs was conducted on Cu TEM grids. XRD analysis was conducted using a PANalytical X'Pert PRO MRD instrument with a Cu Kα radiation source (λ = 1.5418 Å) and an X'celerator detector.

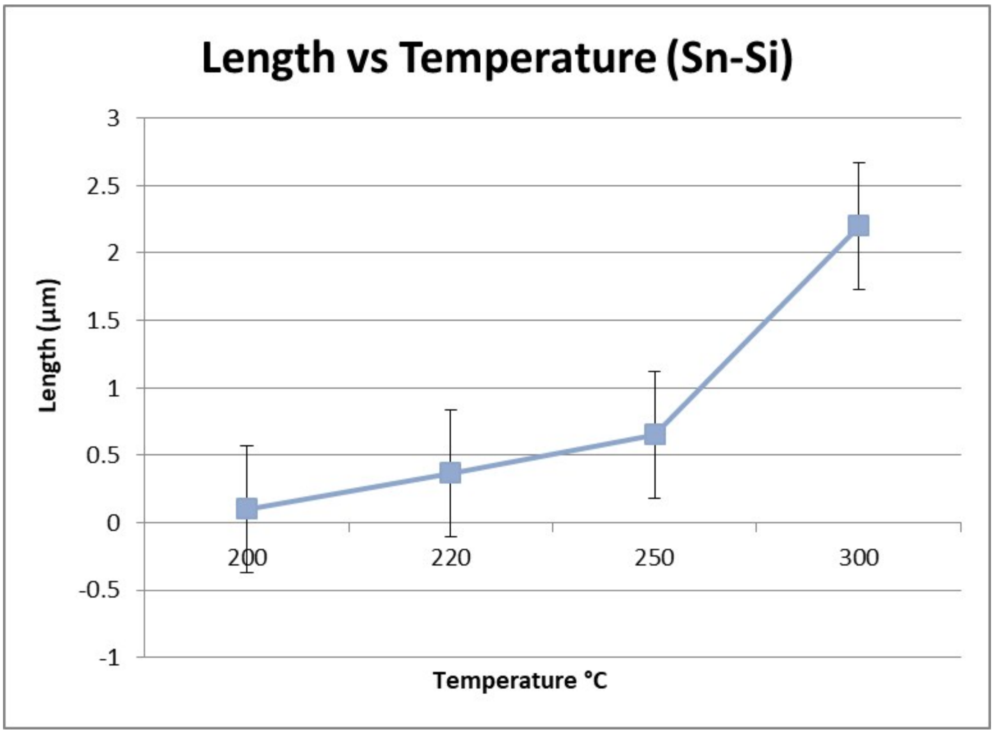

Figure S1: Graph of Length vs Temperature for the Sn seeded Si structures grown between 200 °C and 300 °C, with standard error bars included, showing a correlation between the average lengths of the structures produced and the growth temperature used.

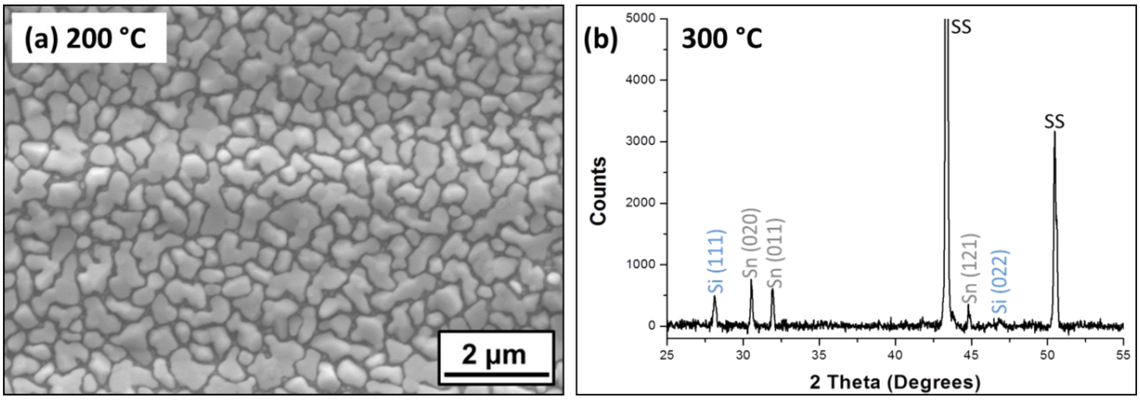

Figure S2: (a) SEM image of the substrate following a Sn-Si synthesis at 200 °C where no Sn seeds have formed. (b) XRD pattern for the as synthesized Sn-Si NW substrate at 300 °C showing peaks for cubic Si and tetragonal Sn.

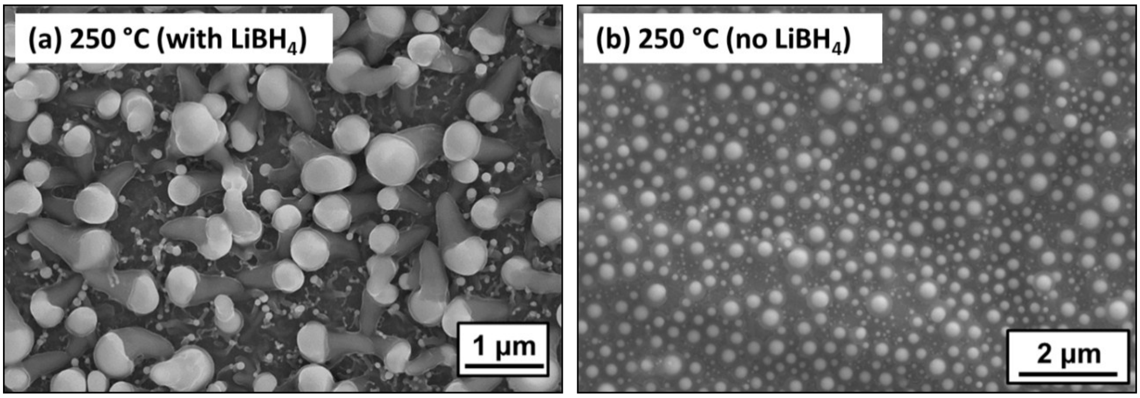

Figure S3: (a) SEM image of Sn-Si NWs synthesized using the reducing agent at 250 °C, showing average lengths of 1 µm. (b) SEM image of the substrate following a Sn-Si NW synthesis at 250 °C in the absence of the reducing agent where *in situ* Sn seeds are formed but no NW growth occurs.

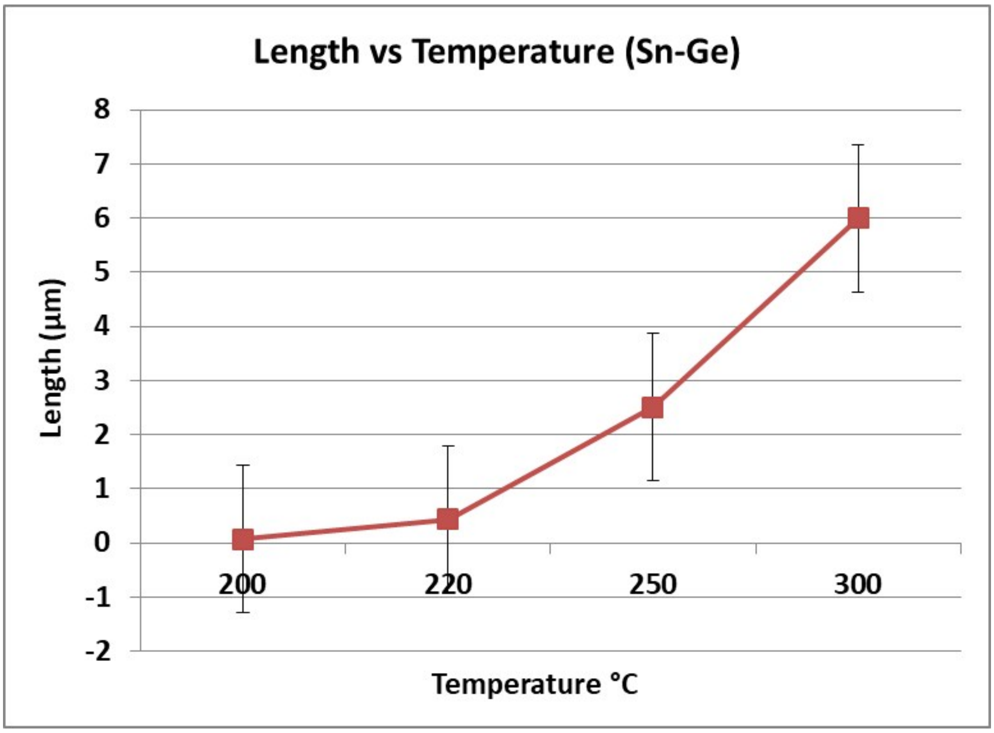

Figure S4: Graph of Length vs Temperature for the Sn seeded Ge structures grown between 200 °C and 300 °C, with standard error bars included, showing a correlation between the average lengths of the structures produced and the growth temperature used.

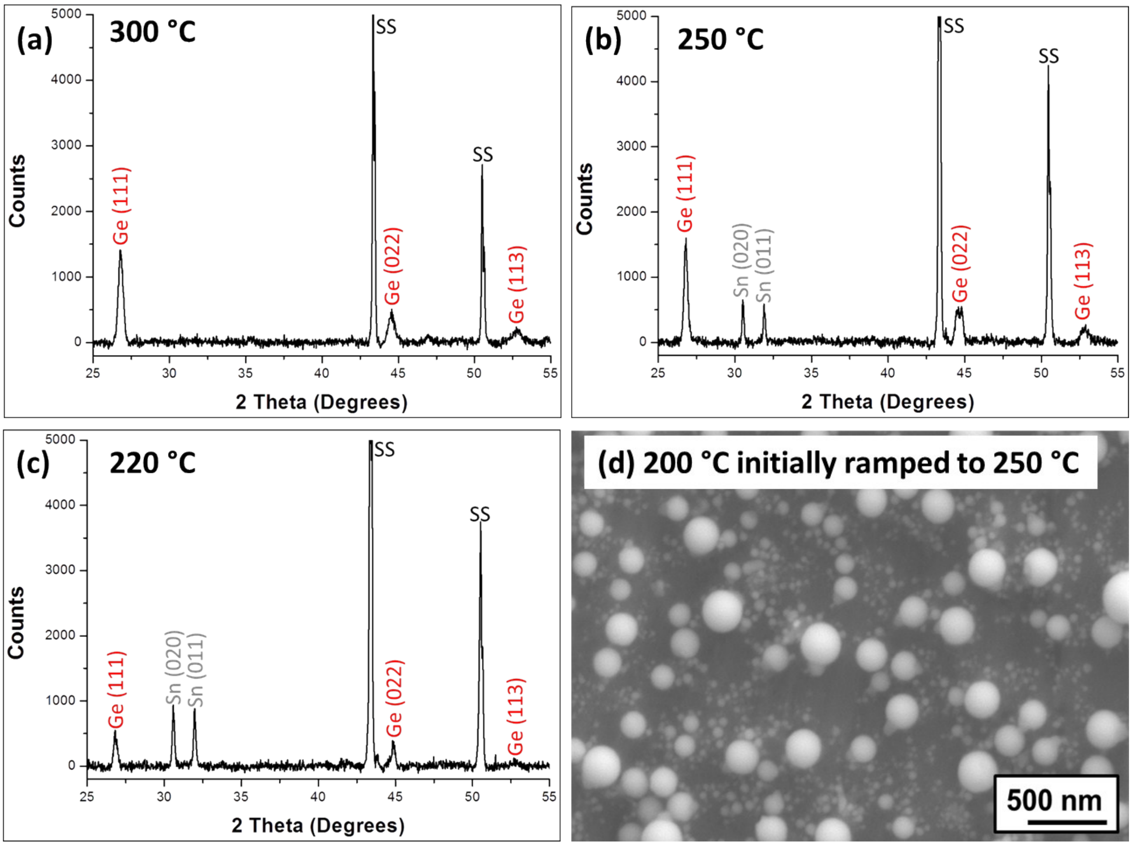

Figure S5: (a) – (c) XRD patterns of the as synthesized Sn-Ge NW/NR substrates at 300 °C, 250 °C and 220 °C respectively showing peaks for cubic Ge and tetragonal Sn. (d) SEM image of a Sn-Ge NR synthesis at 200 °C, where the reaction was initially ramped to 250 °C before the DPG and reducing agent were injected, showing NW lengths of approximately 60 nm.

Sn NP catalyzed Si and Ge NWs

The Si and Ge NW reactions can also be performed using preformed Sn NPs as the seeds, synthesized using a modification of a previously reported procedure,[1] resulting in the growth of non-bound NWs, directly in solution. The Sn NPs, capped with oleic acid, are suspended in the squalane and this mixture is then added to the reaction flask prior to precursor and reducing agent injection. TEM and DF-STEM analysis, (Figure S6 a-b), for a silicon reaction performed at 200 °C, shows the typical wire dimensions and confirms the presence of Sn in the seed and Si in the NW section, with very little overlap. The seeding protocol works equally well for Ge at 200 °C, with narrow diameter wires forming, with a sharp interface between the wire and the metal seed (Figure S6 c-d). Additionally, the possibility for further reductions to the reaction temperatures may be possible through the use of catalysts which exhibit lower eutectics with both Si and Ge.

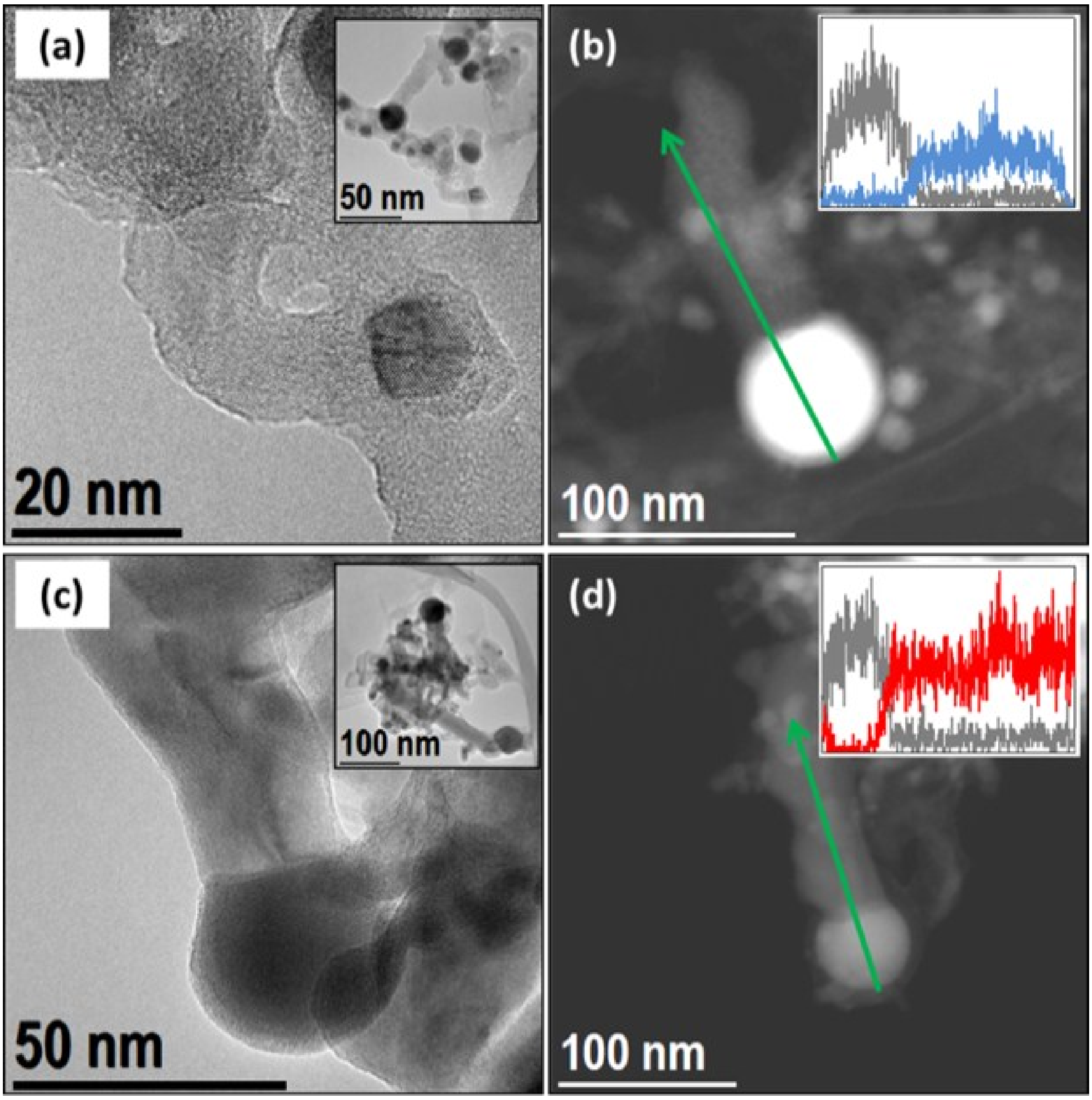

Figure S6: TEM and EDX analysis (Sn in gray, Si in blue, Ge in red) of Sn NP seeded Si, Ge and Si-SixGe1-x NWs. (a) and (b) TEM and DF-STEM images of Sn NP seeded Si NWs synthesized at 200 °C with corresponding EDX line profile inset in (b). (c) and (d) TEM and DF-STEM images of Sn NP seeded Ge NWs synthesized at 200 °C with corresponding EDX line profile inset in (d).

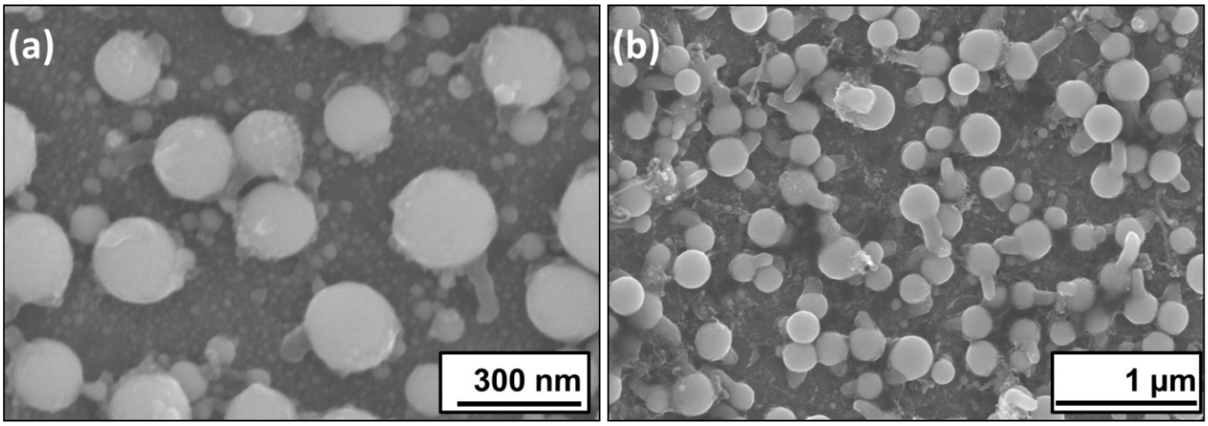

Figure S7. Preliminary results for the low temperature solution synthesis of In seeded (a) Si and (b) Ge NRs synthesized at 190 °C, where initial NR growth can be seen for the Si reaction while longer NRs can be observed for the Ge reaction.

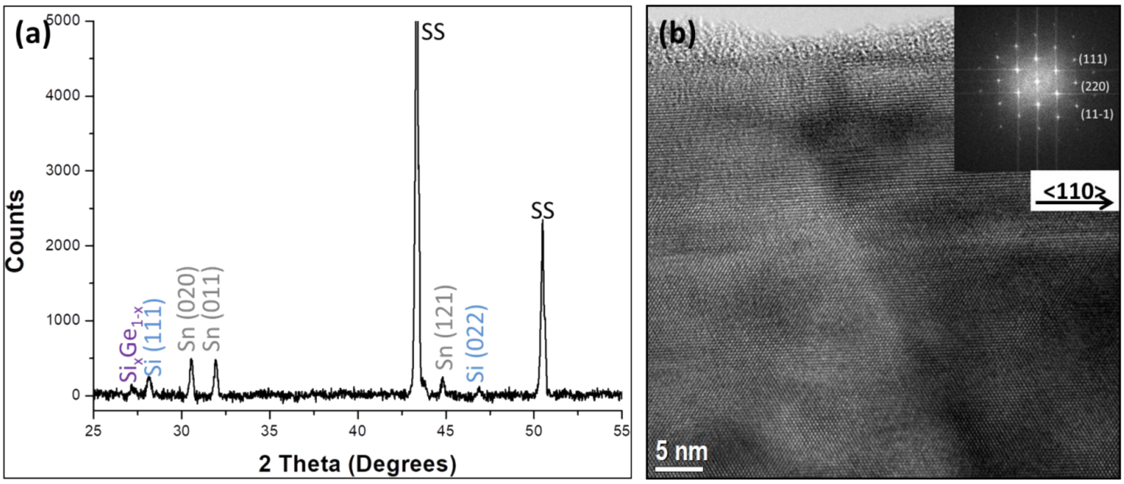

Figure S8: (a) XRD pattern of the as synthesized Sn-Si-$Si_{1-x}Ge_x$ hNWs produced at 300 °C (PS and TPG producing a second segment with approximate 1:4 ratio Si:Ge) showing peaks for cubic Si, tetragonal Sn with a small, slightly broadened peak at 27° which may be attributed to Si_xGe_{1-x}. (b) A HRTEM image of the interface of the hNW shown in the main text in Figure 3(d) with inset indexed FFT.

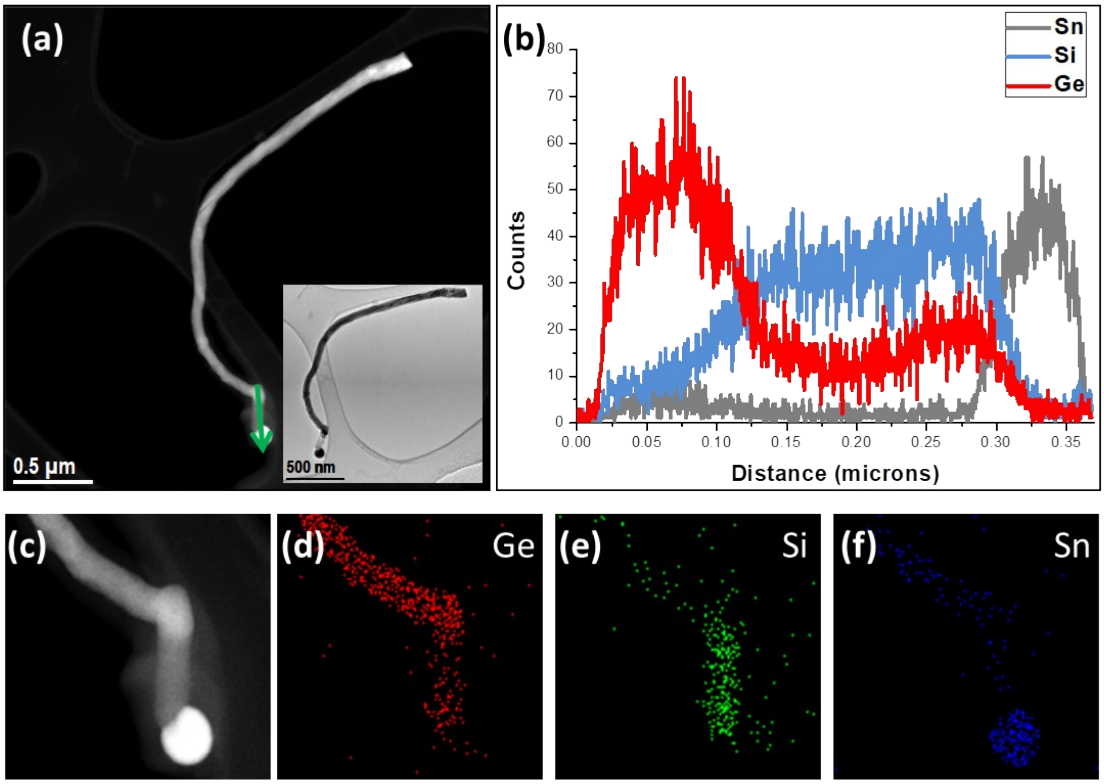

Figure S9: (a) DF-STEM image of a Sn-Ge-Si_xGe_{1-x} hNW synthesized at 250 °C with the corresponding line scan in (b) showing the presence of both Si and Ge signals in the second segment. A more gradual shift in elemental composition can be seen in this line scan compared to the transitions for the heterostructures beginning with Si growth which can be attributed to the higher reactivity of the Ge precursor, diphenylgermane, compared to the less reactive Si precursor, phenylsilane. This gradual composition change has been previously reported at higher temperatures.[2] A higher magnification DF-STEM image of (a) can be observed in (c) with corresponding elemental maps (d-f) showing Ge, Si and Sn respectively.

References

1. Y. H. Jo, I. Jung, C. S. Choi, I. Kim and H. M. Lee, *Nanotechnology*, 2011, **22**, 225701.
2. G. Flynn, Q. M. Ramasse and K. M. Ryan, *Nano Letters*, 2016, **16**, 374-380.