

Supporting Information

Crystal-phase control of GaAs-GaAsSb core-shell/axial nanowire heterostructures by a two-step growth

Chen Zhou,^a Kun Zheng,^{b,c} Ping-Ping Chen,^d Syo Matsumura,^e Wei Lu,^d

Jin Zou^{*a,b}

^aMaterials Engineering, ^bCentre for Microscopy and Microanalysis, and ^cAustralian Institute for Bioengineering and Nanotechnology, The University of Queensland, Brisbane, Queensland 4072, Australia. *E-mail: j.zou@uq.edu.au

^dState Key Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 500 Yutian Road, Shanghai 200083, People's Republic of China.

^eDepartment of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Motooka 744, Nishi-ku, Fukuoka 819-0395, Japan

To verify the crystal structure of nanowire core of samples A and B, TEM investigations were employed. Figure S1a,b is HRTEM images taken from top regions of the nanowires cores in two samples, in which the lateral dimension of nanowire is similar with the catalyst diameter. It is noted that the catalyst contact angle is measured as $\sim 120^\circ$ in sample A and 130° - 140° in sample B, due to the catalyst annealing under Sb flux in sample B, and corresponding crystal structures are wurtzite and zinc-blende. Figure S1c shows EDS spectra taken from the grown nanowires, confirming the GaAs nanowires cores in two samples. It has been established that the contact angle of Au catalyst can be increased under the increased Sb flux, due to the surfactant nature of Sb, which is related to the surface energy of the catalyst. It was suggested that the change of catalyst surface energy can alter the crystal structure of the grown nanowire, in which an increased catalyst contact angle results in the increased barrier for wurtzite nucleation. Therefore, with a large catalyst contact angle, zinc-blende structured nanowires are facile to grow.

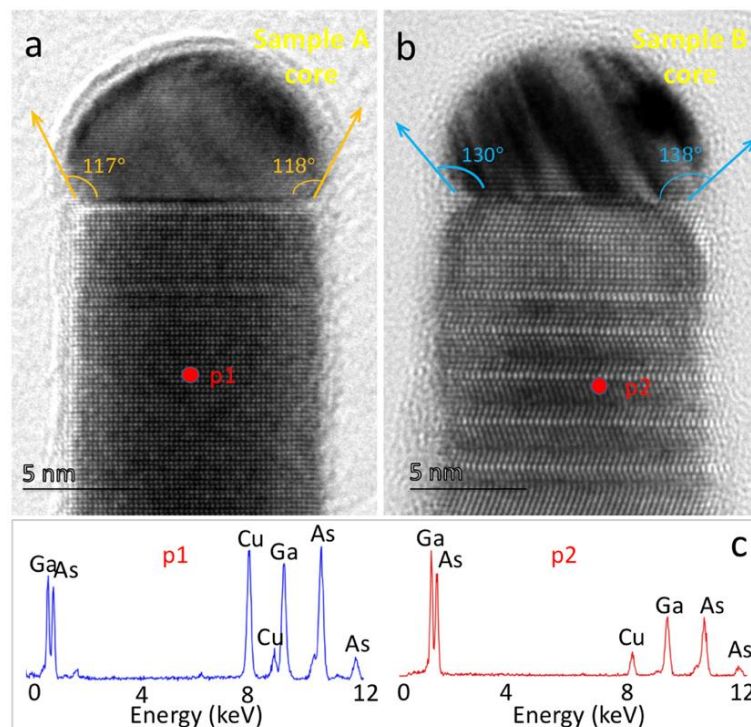


Figure S1. HRTEM images taken from top regions of GaAs nanowires cores in samples A (a) and B (b). (c) Corresponding EDS spectra taken from the nanowire core as typically marked in (a,b).

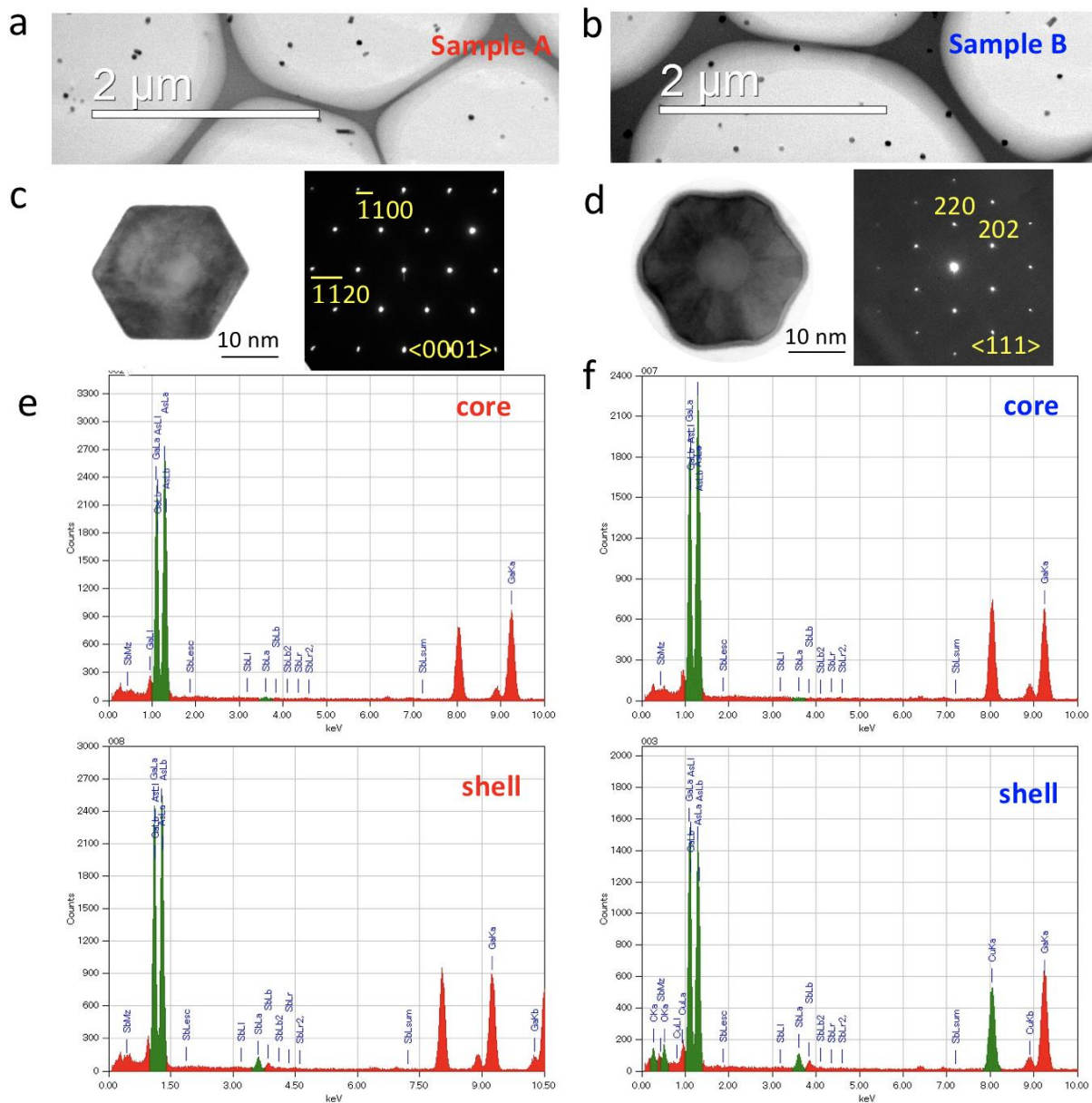


Figure S2. (a,b) BF TEM images of cross-sections taken from nanowire middle regions of sample A – wurtzite structured GaAs-GaAsSb core-shell nanowires and sample B – the zinc blende structure. (c,d) TEM images of a typical cross-section from this region and corresponding SAED patterns viewed from $\langle 0001 \rangle$ and $\langle 111 \rangle$ zone-axes, respectively. (e,f) Typical EDS spectra taken from the cores and shells from the cross-sections in each sample, in which the counts are significant to ensure a reliable composition quantification by the ZAF method.

Figure S3a,e is TEM images taken from typical cross-sections from nanowires bottoms in samples A and B, in which core-shell structures were kept to grow and they have similar lateral dimension. Figure S3b,c and Figure S3f,g are HAADF HR-STEM images taken from the core and the shell in sample A and sample B, which show the wurtzite and zinc-blende core-shell structures, respectively. Figure S3d,h shows the EDS spectra taken from the core and shell in two samples, in which the grown nanowire has a GaAs core and a GaAsSb shell with ~15 at.%.

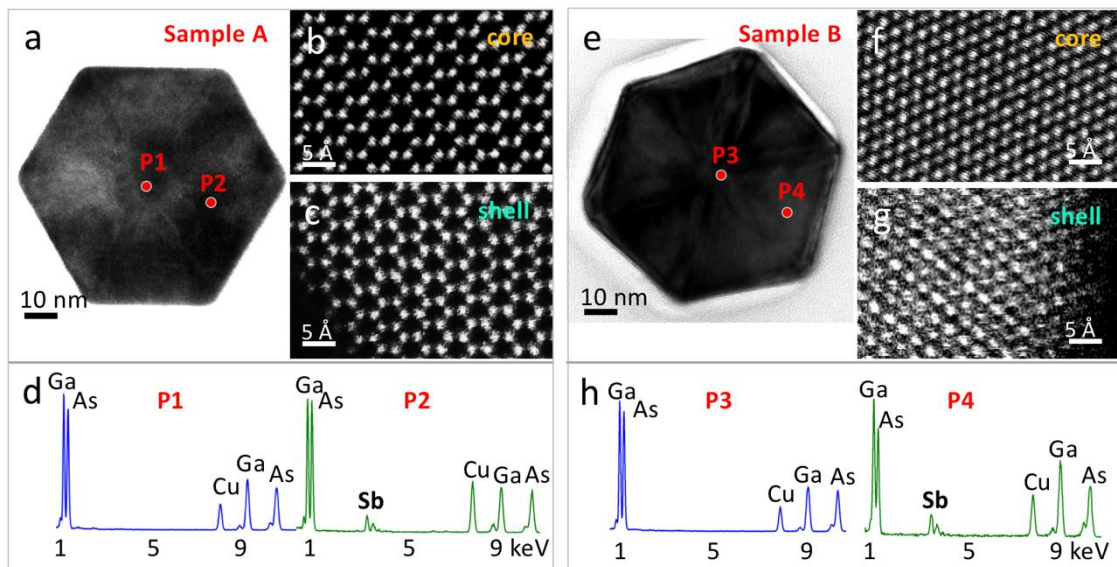


Figure S3. (a,e) TEM images taken from the nanowires bottoms from samples A and B. HAADF HR-STEM images taken from the core and the shell of (b,c) sample A and (f,g) sample B. (d,h) Corresponding EDS spectra taken from the core and the shell.

Figure S4a is a TEM image of grown nanowire in sample C and Figure S4b is HRTEM image taken from the nanowire bottom, indicating the wurtzite structured grown nanowire. Figure S4c is BF TEM image taken from a typical cross-section at the nanowire bottom and Figure S4d is HAADF HR-STEM image taken in the middle of the cross-section, in which grown nanowires maintained the core-shell structure. Figure S4e is HAADF HR-STEM image taken from the nanowire core and shell, indicating the wurtzite core-shell structure. Figure S4f shows Ga, As and Sb EDS maps taken from the cross-section, suggesting the GaAs nanowire core and GaAsSb shell. This is further confirmed by the EDS point analysis. Figure S4g shows the measurements of Sb concentration in the core and the shell, in which the core is indeed GaAs and the shell is GaAsSb with ~ 28 at.%. This is similar with that in sample A, in which the higher Sb concentration in the grown nanowires can be resulted from the higher Sb flux in the growth environment, leading to the increased Sb incorporation in grown nanowires.

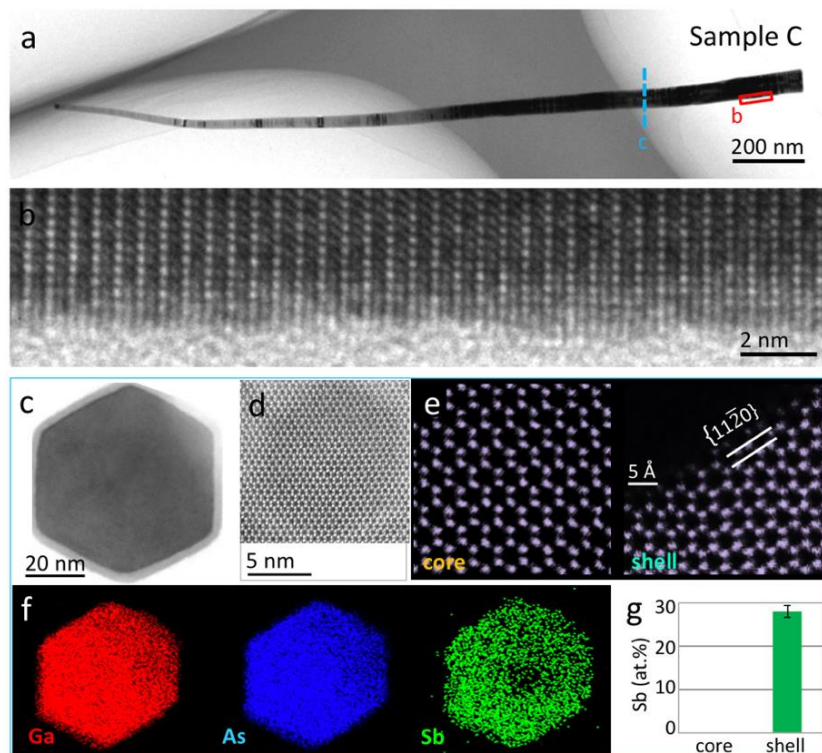


Figure S4. (a) BF TEM image of a typical grown nanowire in sample C. (b) HRTEM image and (d) TEM image of a typical cross-section taken from the nanowire bottom as marked in (a). (d) (d,e) HAADF HR-STEM images taken from the core-shell structure. (f) EDS elemental maps of the cross-section. (g) Plot of Sb concentration in the nanowire core and shell.

Figure S5a is a TEM image taken from a typical grown nanowire in sample D and Figure S5b is a $\langle 111 \rangle$ zone-axis TEM image of the cross-section taken from the nanowire middle region, in which nanowire has the core-shell structure with a lateral dimension measured ~ 100 nm. It is noted that the cross-section has a “distorted” shape. This is because nanowire significantly bent from the middle region and since the cross-section was cut parallel to the $\{111\}$ substrate surface, when it was viewed from the $\langle 111 \rangle$ zone-axis, the top and bottom surface of the cross-section cannot be fully overlapped. Figure S5c is a EDS line scan profile measured across the cross-section, showing the GaAsSb core-shell structure. Figure S5d,e is typical EDS spectra taken from the cores and shell, in which both core and shell were confirmed as GaAsSb and have Sb concentration of ~ 20 at.% and 70 at.%, respectively.

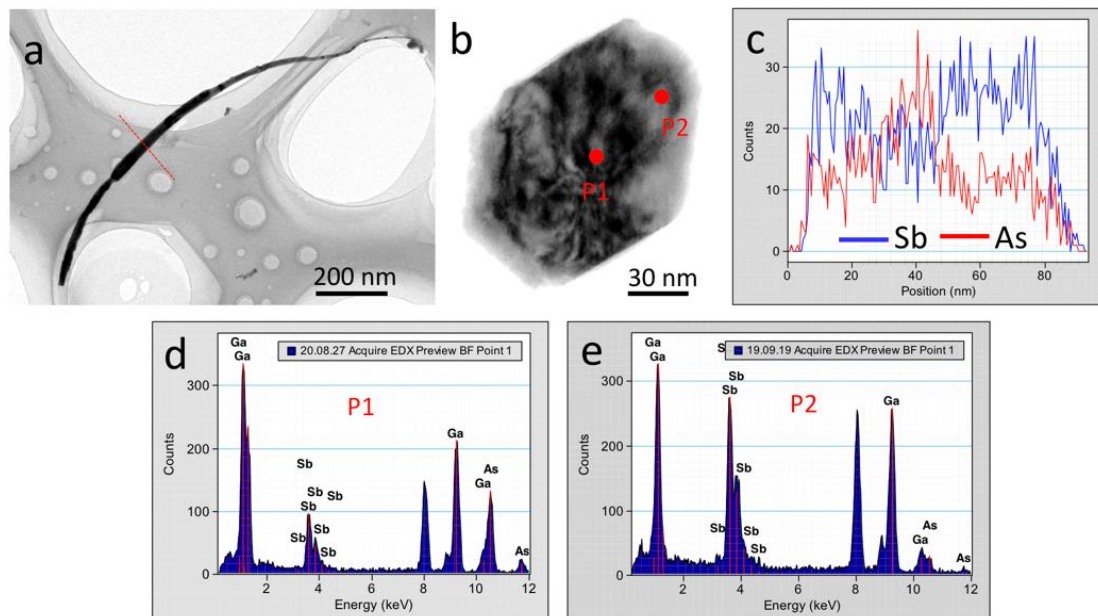


Figure S5. (a) BF TEM image of a typical grown nanowire in sample D. (b) BF TEM image of the cross-section taken from the nanowire middle region, as marked in (a). (c) EDS line scan profile of the cross-section. (d,e) EDS spectra taken from the core and shell.