Supporting Information

Size-Controlled Growth of Germanium Nanowires from Ternary Eutectic Alloy Catalysts

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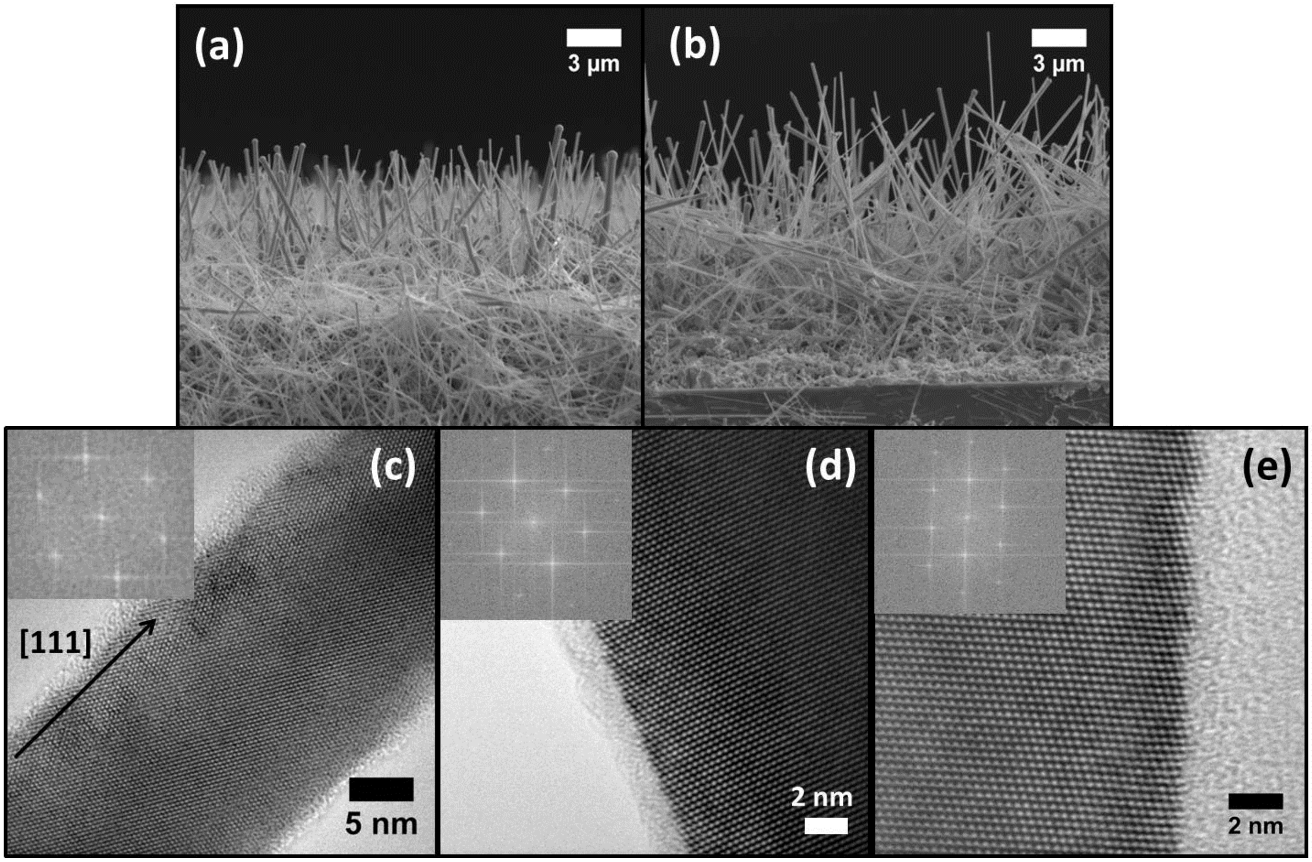


Figure S1. SEM and TEM images showing Ge nanowire growth. (a) SEM image showing Ge nanowires grown from Au-Ge binary alloy catalysts, at a 90 degree angle to the beam (b) SEM image s howing Ge nanowires grown from Au-Ag-Ge ternary alloy catalysts at a 90 degree angle to the beam. (c) TEM image of a Ge nanowire grown from a Au film. (d) TEM image of Ge nanowire grown from a Au-Ag bi-layer. (e) Ge nanowire grown from a Au-Ag-Ge tri-layer. The TEM images all show monocrystalline Ge nanowires with a [111] growth orientation. Insets are the fast Fourier transforms (FFTs) taken of the respective nanowires confirming the growth direction.

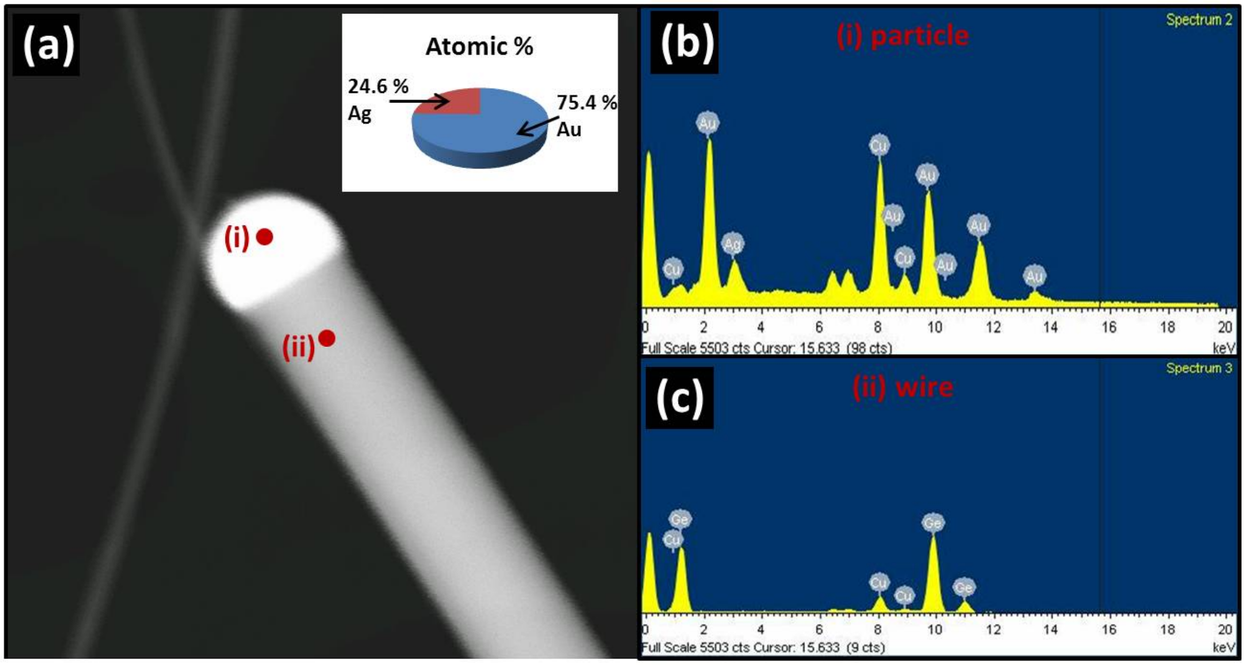


Figure S2. STEM analysis of a Ge nanowire grown from a Au-Ag seed. (a) High angle annular dark field (HAADF) STEM image of a Ge nanowire grown from a Au-Ag seed. Inset shows the atomic % of Ag and Au in the seed particle on top of the nanowire. (b) EDX spectrum of the seed taken at point (i) in (a). (c) EDX spectrum of the wire taken at point (ii) in (a).

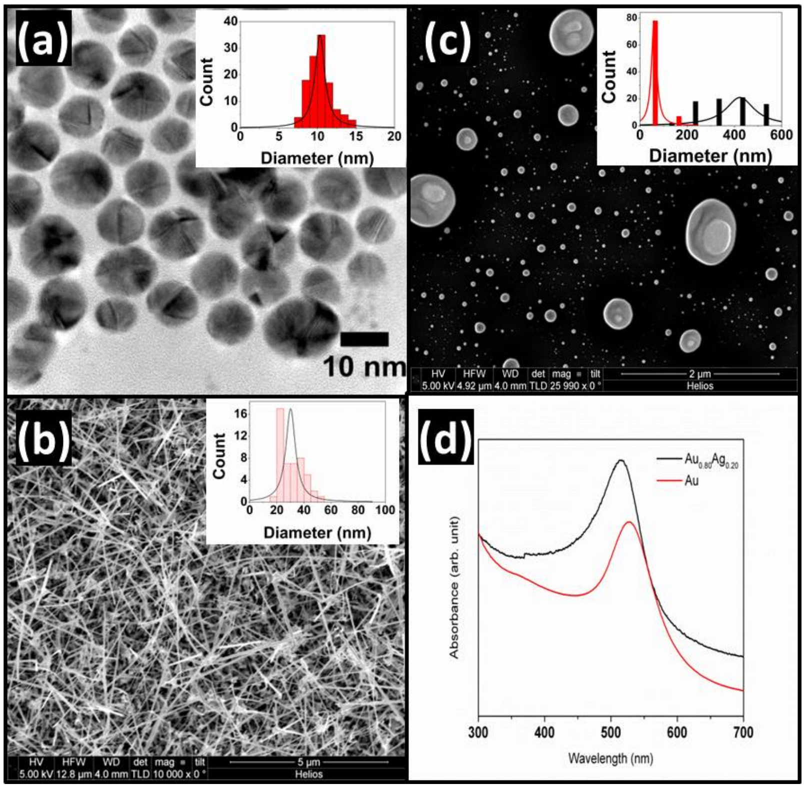


Figure S3. (a) TEM image of Au nanoparticles used to seed Ge nanowire growth. (b) SEM image of nanowires grown from the Au seeds shown in (a). (c) SEM image of Au-Ag-Ge tri-layer after annealing for 30 min at 465 ºC. The insets in (a), (b) and (c) reveal the diameter distribution of the particles and nanowires. (d) UV-visible spectra of $Au_{0.75}Ag_{0.25}$ and Au nanoparticles.

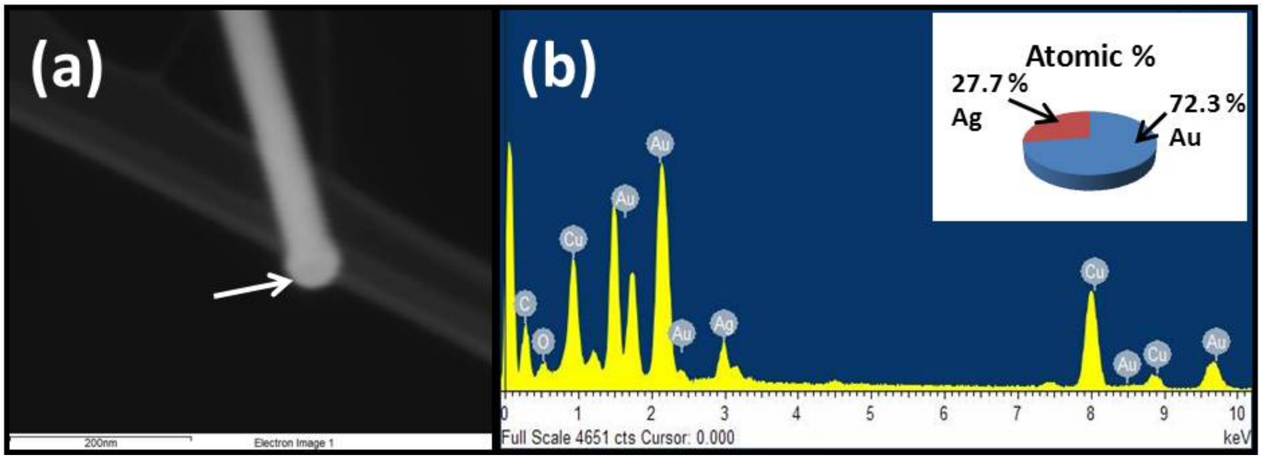


Figure S4. STEM analysis of a Ge nanowire grown from a $Au_{0.75}Ag_{0.25}$ nanoparticle. (a) Dark field STEM image of a Ge nanowire grown from a $Au_{0.75}Ag_{0.25}$ nanoparticle. (b) EDX spectrum of the seed marked by the white arrow in (a). Inset shows the atomic % of Ag and Au in the seed particle on top of the nanowire.

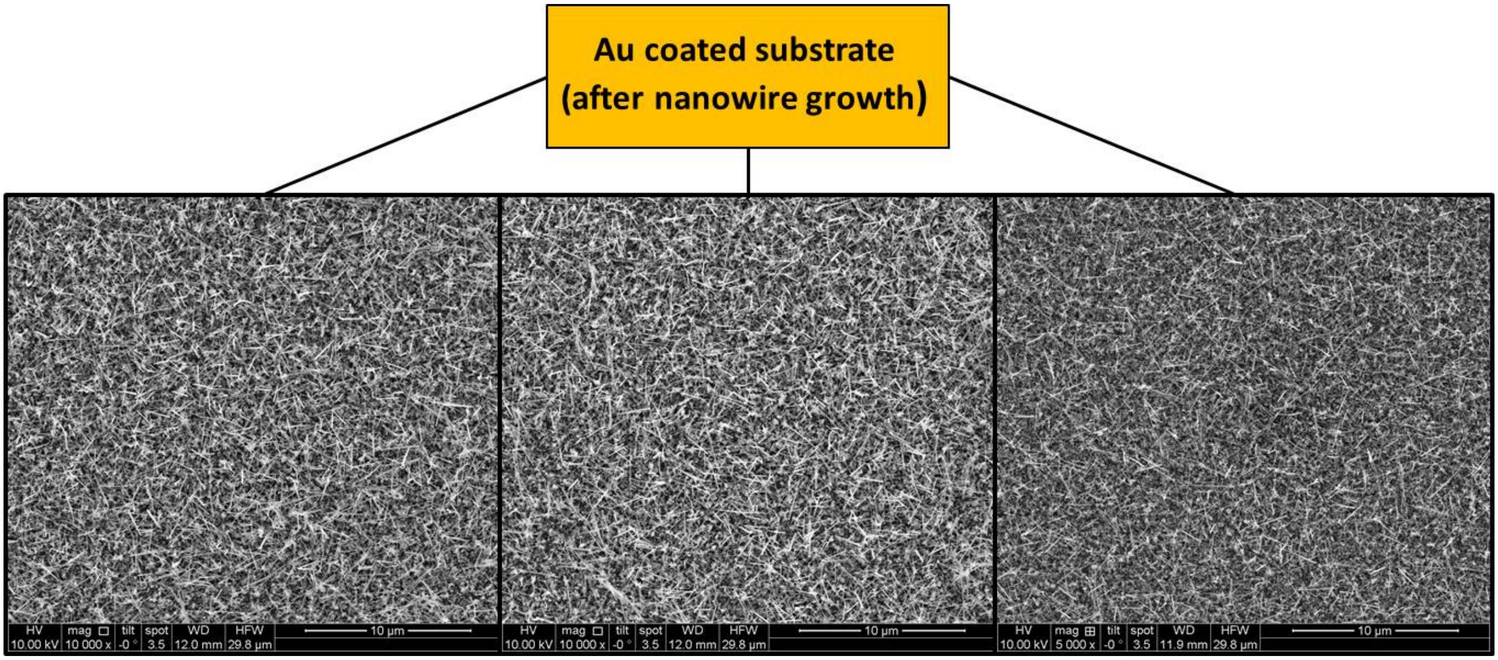
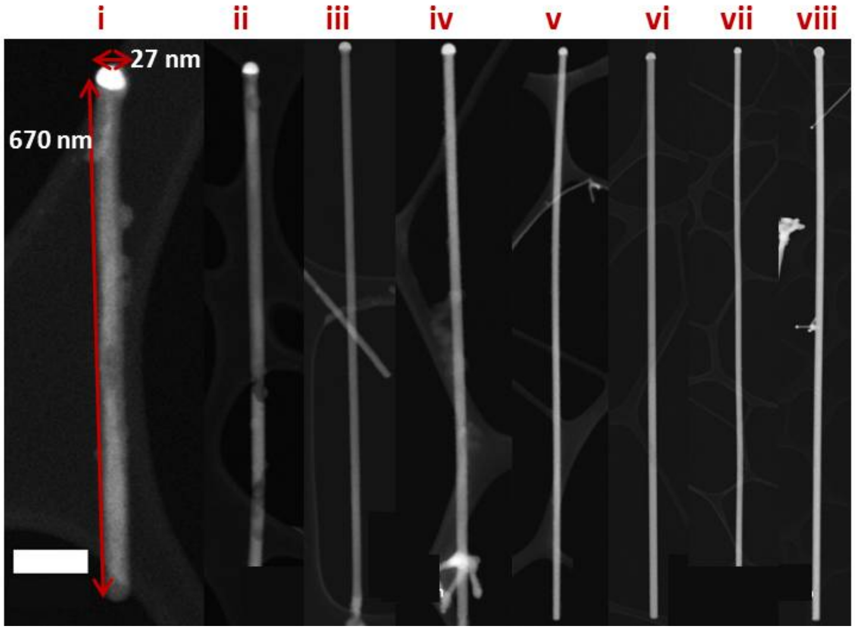


Figure S5. SEM images of Ge nanowires grown from a Au coated substrate. The images show consistent nanowire growth on the left, middle and right portions of the substrate.



Wire	Length (μm)	Diameter (nm)	Scale bar (μm)
i	0.67	27	0.1
ii	1.6	35	0.15
iii	2.6	40	0.3
iv	3.2	60	0.4
v	5.4	70	0.5
vi	7.3	90	0.50
vii	9.9	100	1
viii	10.5	150	1.2

Figure S6. Eight separate STEM images of nanowires synthesised from $Au_{0.75}Ag_{0.25}$ nanoparticles. STEM was used to measure the lengths and diameters of nanowires for the Gibbs-Thomson study presented in figure 5(b). The nanowires increase in length and diameter from left to right. Image i shows how the length and diameter were measured and this method was repeated for about 30 nanowires (Au and $Au_{0.75}Ag_{0.25}$ seeds), after which the dimensions were plotted in figure 5(b). The table identifies the length and diameter for each nanowire imaged on the left and shows an increasing scale bar from image i to image viii.

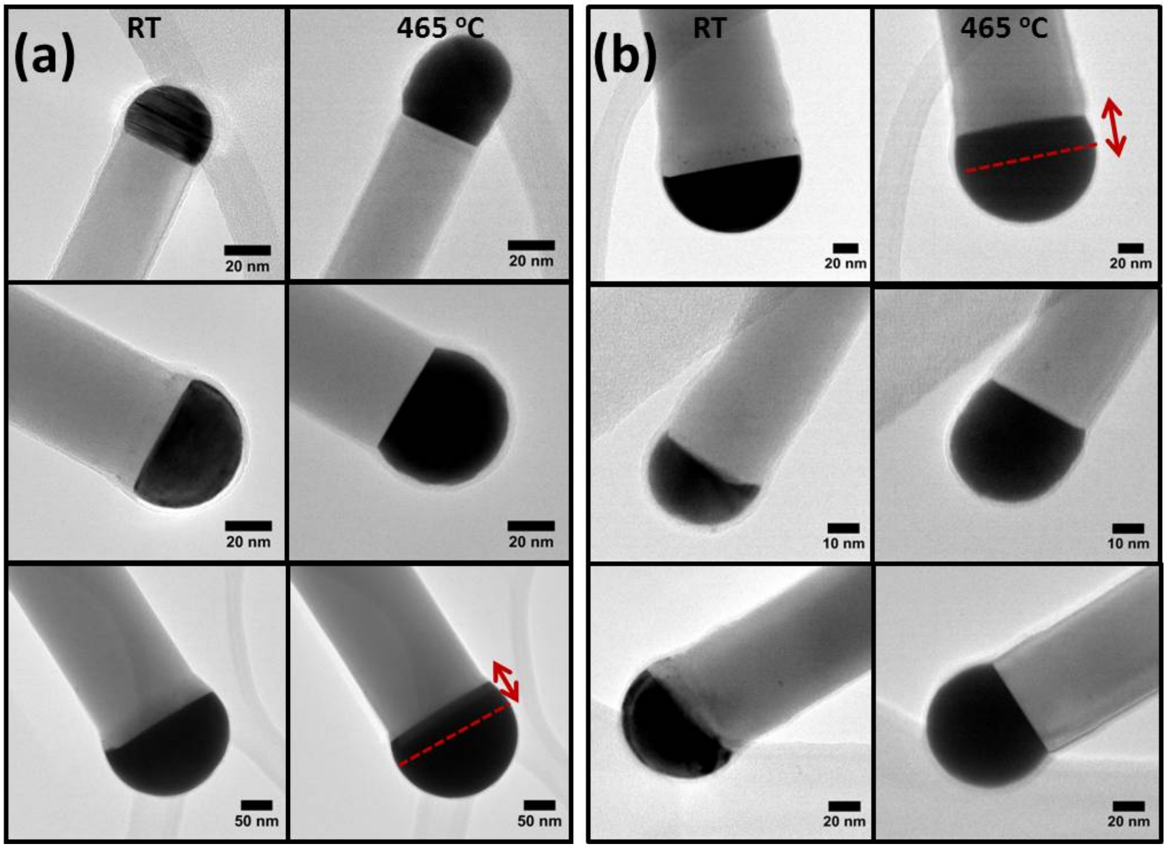
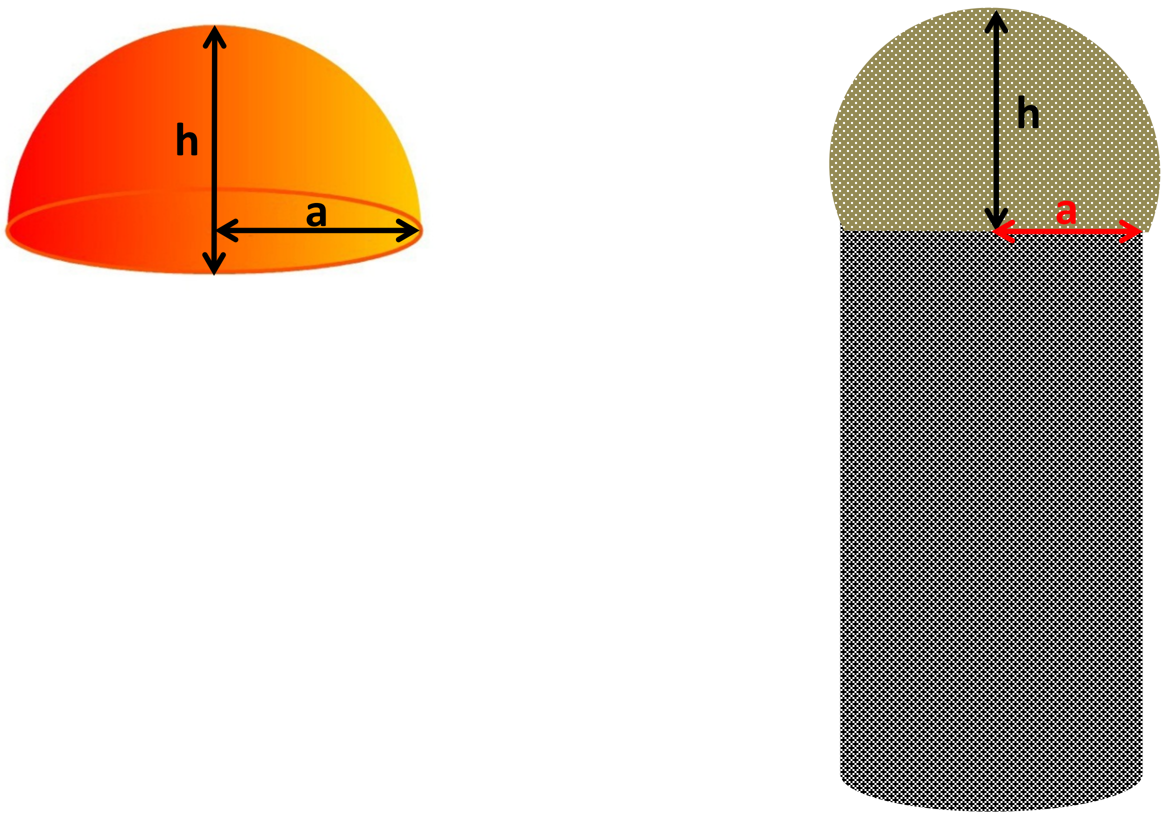


Figure S7. In-situ TEM heating of Ge nanowires grown from nanoparticles. (a) Ge nanowires grown from $Au_{0.75}Ag_{0.25}$ seeds. (b) Ge nanowires grown from Au seeds. In both (a) and (b), the panels on the left represent nanowires at room temperature and the panels on the right are the same nanowires after heating to the growth temperature of 465 ºC. The expansion of the liquid-solid interface into the nanowire is clearly evident.

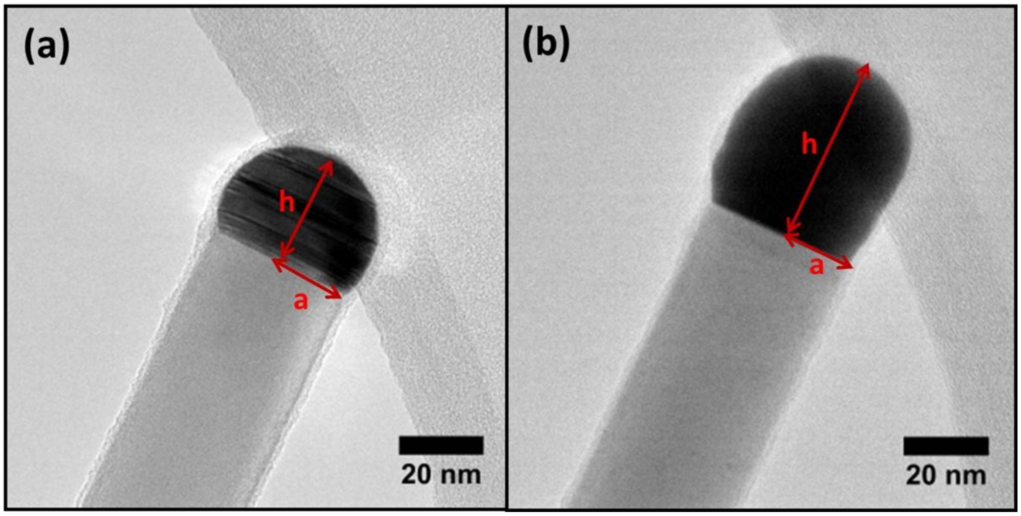
Calculation of Ge atomic percent for figure 6(c)

These calculations follow the general method outlined by Sutter *et al.*[1, 2]



Taking ***h*** as the height of the particle and ***a*** as the radius before expansion (Figure 1 (a)), we first use the formula for the volume of a hemispherical cap to calculate the volume of Au in the seed particle:

$$V = \frac{\pi}{6} \times h(3a^2 + h^2)$$



As an example, taking ***a*** as 54.525 and *h* as 54.97, we can input these values into the equation:

$$V\,(RT) = \frac{\pi}{6} \times (54.97) \times [3(54.525)^2 + (54.97)^2] = 343677$$

Multiplying this by 53.21 (takes into account density and atomic number of Au) to calculate the number of Au atoms:

$$N_{Au} = 343677\ \times 53.21 = 18287097$$

Next, we calculate the volume of the particle <u>after</u> expansion due to heating to the growth temperature of 480 ^{o}C (figure 1 (b)), using the same formula:

$$V\,(480\,^{o}C) = \frac{\pi}{6} \times (80.81) \times [3(50.68)^2 + (80.81)^2] = 598062$$

Hence, the expansion volume due to Ge uptake is:

$$598062 - 343677 = 254385$$

Hence, the amount of Ge atoms:

$$N_{Ge} = 254385 \times 45.54 = 11584692.9$$

Finally:

$$At\%\ Ge = \frac{N_{Ge}}{(N_{Au} + N_{Ge})} \times 100$$

$$= 38.78\ \%$$

The above calculation was performed for a nanowire from the Au-Ge system with a diameter of 97 nm.

It was repeated for several nanowires of varying diameters for both the Au-Ge and Au-Ag-Ge system.

1. E. A. Sutter and P. W. Sutter, *ACS Nano* 2010, **4**, 4943.
2. E. Sutter and P. Sutter, *Nano Lett.* 2008, **8**, 411.