

## Electronic Supplementary Information

### Nanowire growth kinetics in aberration corrected environmental transmission electron microscopy

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#### 1. Details of experimental procedure

The experiments were carried out in a Cs-corrected FEI Titan 80-300 ETEM that has capabilities for introducing multiple gases through mass flow controllers into a mixing manifold that is connected to the sample region of the microscope.<sup>1</sup> The base pressure of this instrument is  $10^{-7}$  Torr in standard mode, but  $2\text{--}4 \times 10^{-6}$  Torr (without cold finger) in ETEM mode, where some pumps are valved off to allow higher pressures at the sample region. The base pressure is determined by air arriving through the sample rod o-ring, so includes N<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O and other minor components. We examined Si nanowire growth, using Au for experiments on the VLS growth mode and AuAg alloys for experiments on both VSS and VLS modes. Pure disilane was used as the precursor and was flowed over Si samples heated to temperatures in the range 350–450°C. The maximum disilane pressure was  $5 \times 10^{-3}$  Torr with a measured flow rate of 0.2 sccm. On heating and exposure to disilane, image series were recorded at Gatan Ultrascan CCD with 2 frames per second and Gatan K2-IS CCD with 400 frames per second for in situ movie recording.

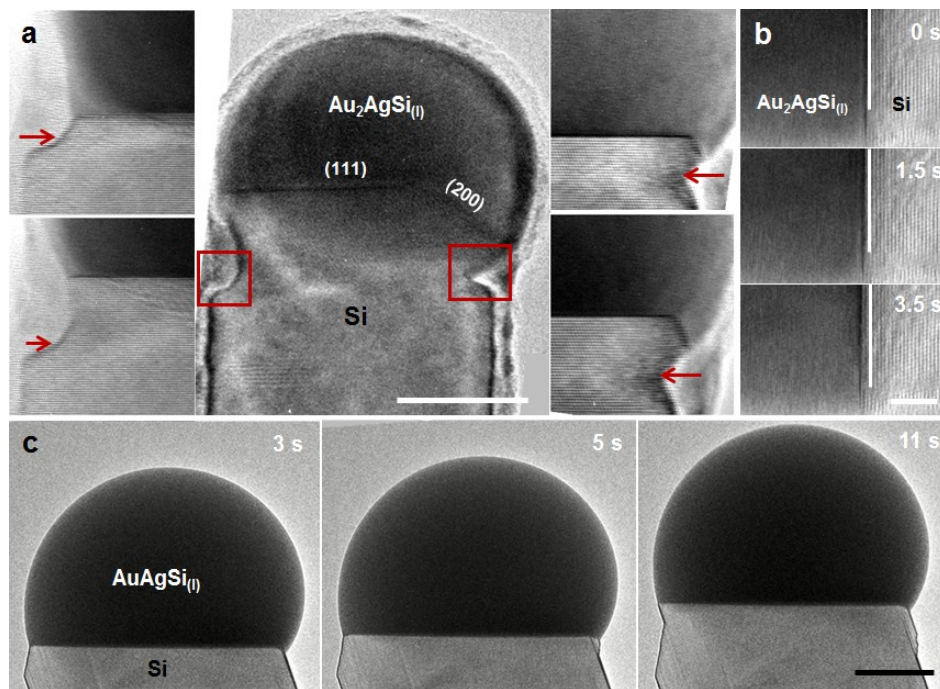
Rather than reacting the disilane with catalyst particles placed directly on the substrate, we imaged the dynamics at the tips of pre-grown nanowire “stubs”. These nanowire samples were prepared from substrates cut into the TEM sample size of  $3\text{mm} \times 500\mu\text{m} \times 500\mu\text{m}$ . Either Au or Au+Ag sequentially was deposited on the sample surface as a continuous film. The samples were heated to agglomerate the metal into droplets of diameter 20–50nm. The quoted AuAg compositions are approximate and based on the deposited Au and Ag thickness. There is a solid solution at all compositions, but each particle could have a somewhat different composition depending on diffusion of Au and Ag during agglomeration<sup>2</sup>. The exact composition is not critical for interpretation, since Ref. 2 shows little dependence of growth

kinetics on composition; the major effect of composition is to set the eutectic temperature. After catalyst agglomeration, disilane was flowed to grow Si nanowires to a length of 200-500nm. The catalyst deposition and nanowire growth were carried out in a UHV-TEM.<sup>2</sup> Since growth took place under observation, we could ensure that the resulting nanowires had suitable length, diameter and density. Experimental details of the UHV-TEM growth are provided elsewhere.<sup>2</sup> The samples were transferred through air and cleaned by HF-vapor etching immediately before loading into the ETEM. Growth in ETEM is at different temperature and pressure, leading to a transient change in the nanowire diameter (see Section 3 below for an image).

## **2. Effect of surface layer on growth morphology and step flow kinetics: VLS**

Fig. S1(a) shows a nanowire at lower magnification after the end of a typical disilane exposure without the surface cleaning protocol described in the text, and Fig. S1(b) shows growth via step flow. The segment that has grown in the ETEM is visible above a narrower region. This narrowing of the nanowire is commonly observed in the ETEM samples. It is not present when the samples are first grown, and is a consequence of the processing that is necessary between making the samples and carrying out ETEM. Cooling the sample after growth, solidifying the catalyst, exposing to air, etching with HF, and reheating in the ETEM result in a liquid droplet and nanowire of slightly altered geometry. because the growth temperature in the ETEM is slightly different from that in the UHV-TEM, changing the amount of dissolved Si in the catalyst; or because the nanowire sidewalls have oxidized, changing their surface energy and hence the contact angle at the trijunction.

During growth, the surface layer appears to pin the trijunction and the growth front does not advance uniformly. The growth interface can show facets of (111) and (200), and the addition of ledges is slow and not regularly timed, presumably related to the overall morphology and surface condition of the nanowire during growth in the ETEM.



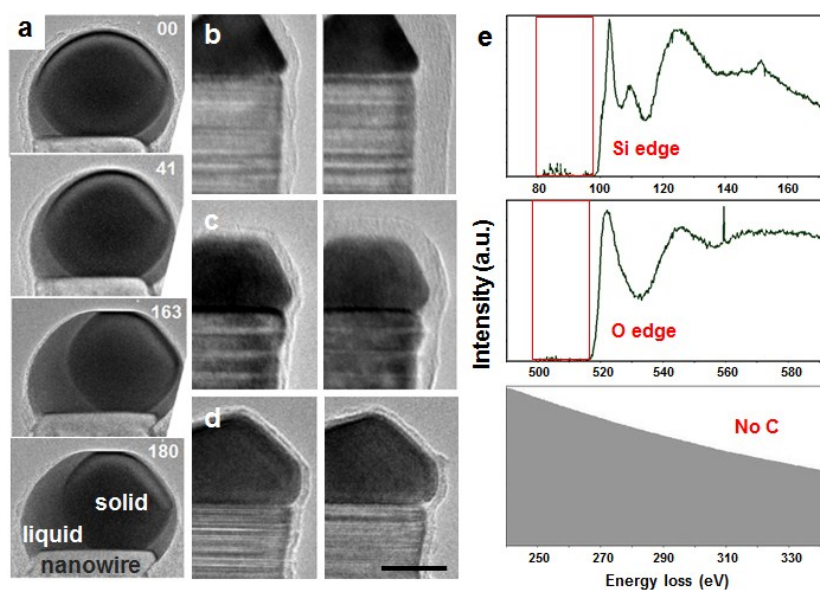
**Fig. S1** Si nanowire growth by VLS in ETEM from AuAgSi at 425°C with  $5 \times 10^{-3}$  Torr  $\text{Si}_2\text{H}_6$ . (a) A lower magnification image of another Si nanowire. The interface before growth is indicated by red arrows at the trijunctions. The inset images show stages of growth at both trijunctions. Scale bar = 30nm. (b) Images recorded during growth at 425°C with  $5 \times 10^{-3}$  Torr disilane. During the sequence, Si bilayers (0.31nm) flow across the interface within one frame. Scale bar = 4nm. (c) Images recorded during growth of a Si nanowire in ETEM at 500°C and  $5 \times 10^{-5}$  Torr disilane with clean appearance of the surfaces as comparison. Scale bar = 20nm.

### 3. Surface layer formation in ETEM

We observed two types of surface layer; each prevents or slows incorporation of Si from disilane into the catalyst and nanowire.

(1) An oxide forms during air exposure of the sample before loading, and persists even with HF vapor treatment. Removal of this layer can be accomplished by focusing the electron beam onto the sample surface. Fig S2(a) shows progressive removal, allowing facets to form in the solid parts of the catalyst and Si to incorporate into the catalyst and transform solid AuAg to solid plus liquid (AuAgSi).

(2) A surface layer of silicon oxide forms under the electron beam, Fig S2(b-e). The example shown here illustrates a surface layer forming on a sample even without deliberate disilane, but with residual disilane present from a previous growth experiment. The formation rate is slowed by introducing  $\text{O}_2$  to react with and remove disilane; venting the microscope effectively removed residual disilane.

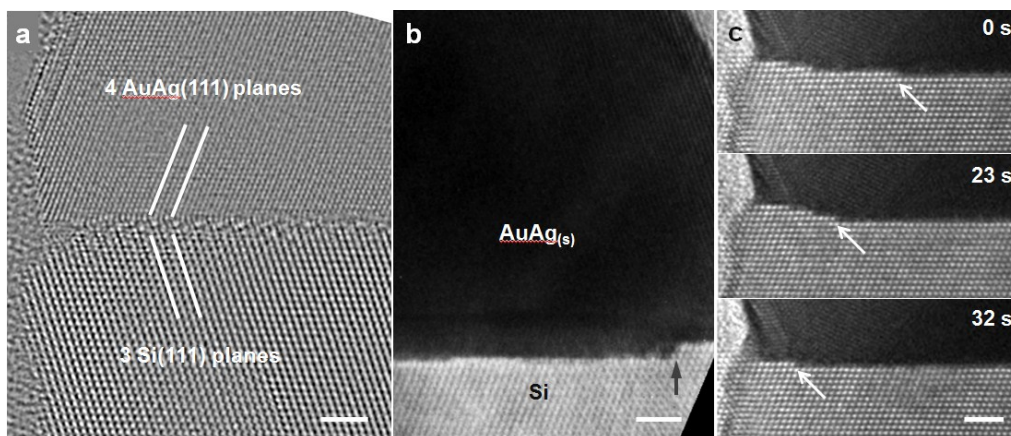


**Fig. S2** (a) Surface layer removal using a focused electron beam shower at 550°C and  $9.5 \times 10^{-3}$  Torr disilane. From the AuAg-Si phase diagram we expect the catalyst to be fully liquid at temperatures over 525°C. The reaction is slowed because Si can not add easily to the droplet until the surface is cleaned. The time is shown in seconds. (b) The rate of surface oxide layer formation on a GaP nanowire is 1 nm/min in ETEM at RT with residual disilane. (c) The rate slows to 0.5 nm/min after flowing  $O_2$  to remove residual disilane. (d) No surface layer growth after the microscope was vented to remove residual disilane. Different regions of the sample were imaged in each case. Scale bar = 25 nm. (e) EELS results showing that the surface layer is  $SiO_x$  and does not contain carbon. A GaP nanowire was used for this analysis so that no Si was present in the sample.

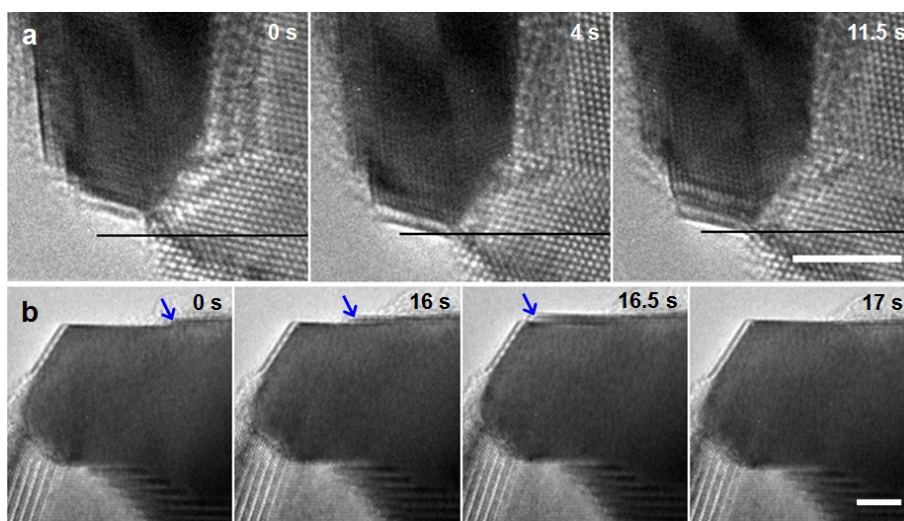
#### 4. Effect of surface layer on growth kinetics: VSS; catalyst surface rearrangement

Fig. S3(a) shows the structure of the AuAg/Si catalyst/nanowire interface after VSS growth from AuAg then imaged post-growth at room temperature. Note the periodic structure visible along the interface due to the lattice mismatch (all AuAg compositions have FCC structure and almost identical lattice parameters.) Steps at this interface are shown in the manuscript. Fig S3(b) shows interface rearrangements observed on heating samples such as in (a) in disilane in the ETEM. The rate of net addition of Si is small, and may even be negative: Fig. S3(c) and Movie 5 show a backwards movement of a VSS catalyst/nanowire interface as Si from the nanowire dissolves into the catalyst on heating. Since we expect growth rates of a few nm per minute<sup>2</sup>, it appears that (as was the case for VLS growth), the incorporation rate of Si is slower than expected for the temperatures and pressures used.

Fig. S4(a, b) shows the catalyst shape changing as the catalyst/nanowire interface rearranges during growth with ledges moving at the surface.



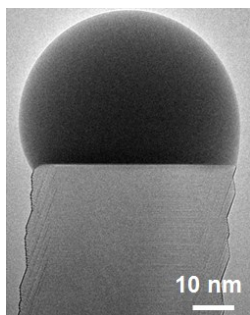
**Fig. S3** Structure and ledge flow at solid AuAg/Si interfaces. (a) Post-growth aberration corrected image showing the solid AuAg/VSS-grown Si nanowire interface; exit wave reconstruction recorded before growth in ETEM. The match between 3 Si(111) planes and 4 AuAg(111) planes is shown. (b) ETEM image showing flow of triple bunched Si bilayers during rearrangement of solid AuAg catalyst and Si at 380 °C and  $1.5 \times 10^{-3}$  Torr disilane. (c) Sequence of ETEM images showing a backwards movement of Si from a VSS catalyst/nanowire interface during heating at 400 °C. Scale bars = 2 nm.



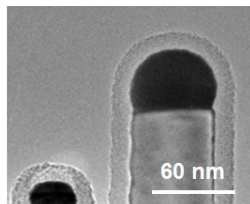
**Fig. S4** Ledge flow on solid catalyst sidewalls. (a) Rearrangement of the side wall of a solid AuAg catalyst in ETEM at 380°C and  $1.5 \times 10^{-3}$  Torr disilane. Black line is for reference. (b) Ledge flow on solid AuAg catalyst in ETEM at 380°C and  $1.5 \times 10^{-3}$  Torr disilane. Scale bars = 5 nm.

## 5. Movie captions

### Movie 1 (Fig. 1a, Fig. 1e):

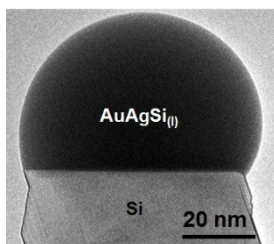


a, (Fig. 1a) ETEM movie showing VLS growth of a Si nanowire with clean surface from AuSi in ETEM at 500 °C with  $5 \times 10^{-5}$  Torr disilane,  $2 \times$  speed.

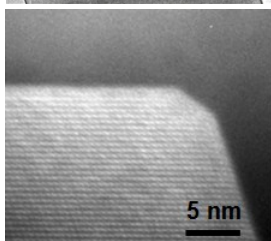


b, (Fig. 1e) ETEM movie showing amorphous shell formation on a pre-grown Si nanowire at 550°C and  $6 \times 10^{-3}$  Torr disilane. The amorphous shell becomes thicker with time. The movie is at  $10 \times$  speed.

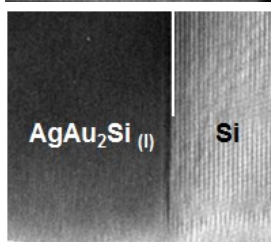
### Movie 2 (Fig. S1c, Fig. 2b, Fig. S1c):



a, (Fig. S1c): ETEM movie showing VLS growth of a Si nanowire with clean surface from AuAgSi in ETEM at 500 °C with  $5 \times 10^{-5}$  Torr disilane, actual speed.

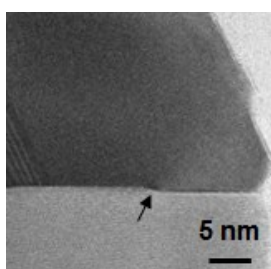


b, (Fig. 2b): Changes in the configuration at the truncated corner between two  $\{111\}$  planes, during VLS Si nanowire growth from AuAgSi at 370°C and  $1.5 \times 10^{-3}$  Torr disilane in ETEM,  $2.5 \times$  speed. The size of the truncation fluctuates as layers are added and removed at the Si/AuSi interface.

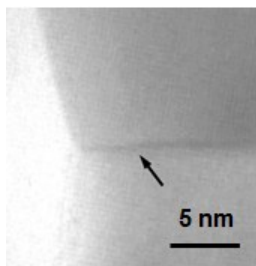


c, (Fig. S1b): ETEM movie showing VLS growth of a Si nanowire from AuAgSi at 425°C and  $5 \times 10^{-3}$  Torr  $\text{Si}_2\text{H}_6$ ,  $2.5 \times$  speed. VLS growth occurs by rapid single Si bilayer addition.

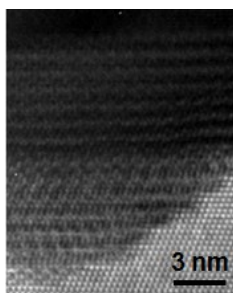
### Movie 3 (Fig. 3a, b, c, and d):



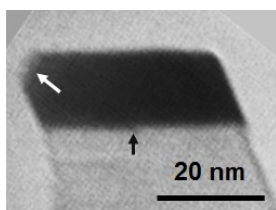
a, (Fig. 3a): ETEM movie showing flow of a single Si bilayer during VSS growth of Si nanowire with clean surface from solid AuAg catalyst,  $5 \times 10^{-4}$  Torr disilane at 450°C, actual speed.



b, (Fig. 3b): UHV-TEM movie showing VSS growth of a Si nanowire from AuAgSi at 480°C and  $9.3 \times 10^{-6}$  Torr disilane, 2× speed. Si ledges move along the interface between catalyst and Si nanowire. The movie was recorded at a magnification of 300kx, close to the maximum available in the UHVTEM.

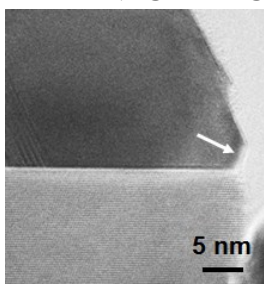


c, (Fig. 3c): ETTEM movie showing flow of triple bunched Si bilayers during rearrangement of solid AuAg catalyst and Si on exposure to  $1.5 \times 10^{-3}$  Torr disilane at 380°C, 2.5× speed.

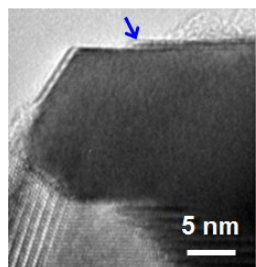


d, (Fig. 3d): UHV-TEM movie showing VSS growth of a Si nanowire from AuAgSi at 470°C and  $3 \times 10^{-5}$  Torr disilane, 3× speed. Si ledges move along the interface between catalyst and Si nanowire in the [211] direction of the (111) plane. The upper left corner of the catalyst, a {100} plane, varies in size during growth.

#### Movie 4 (Fig. 4b, Fig. S4b):

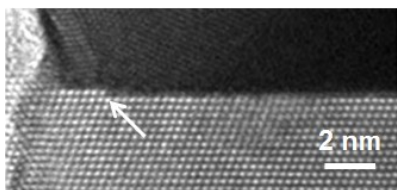


a, (Fig. 4b) Rearrangement of AuAg solid catalyst during growth at 450°C and  $5 \times 10^{-4}$  Torr disilane, shown at actual speed.



b. (Fig. S4b) ETTEM movie showing ledge flow on solid catalyst during VSS growth on exposure to  $1.5 \times 10^{-3}$  Torr disilane at 380°C, 8× speed.

#### Movie 5 (Fig. S3c)



ETEM movie showing retraction of the Si/VSS catalyst interface at steady conditions (400 °C) and without surface treatment. This sequence is extracted from a longer movie of etching lasting 2.5 minutes. The movie is at 4× speed.

## References

- 1 Y.-C. Chou, M. C. Reuter, E. A. Stach, and F. M. Ross, *Microsc. Microanal.* 2012, **18(S2)**, 1084-1085; F. Panciera, Y.-C. Chou, M. C. Reuter, D. Zakharov, E. A. Stach, S. Hofmann, F. M. Ross, *Nat. Mater.*, 2015, **14**, 820.
- 2 Y.-C. Chou, C.-Y. Wen, M. C. Reuter, D. Su, E. A. Stach and F. M. Ross, *ACS Nano*, 2012, **6**, 6407.