## Colossal injection of catalyst atoms into silicon nanowires

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The incorporation of impurities during the growth of nanowires from the vapour phase alters their basic properties substantially, and this process is critical in an extended range of emerging nanometrescale technologies<sup>1-4</sup>. In particular, achieving precise control of the behaviour of group III and group V dopants has been a crucial step in the development of silicon (Si) nanowire-based devices<sup>5-7</sup>. Recently<sup>8-11</sup> it has been demonstrated that the use of aluminium (Al) as a growth catalyst, instead of the usual gold, also yields an effective p-type doping, thereby enabling a novel and efficient route to functionalizing Si nanowires. Besides the technological implications, this self-doping implies the detachment of Al from the catalyst and its injection into the growing nanowire, involving atomic-scale processes that are crucial for the fundamental understanding of the catalytic assembly of nanowires. Here we present an atomic-level, quantitative study of this phenomenon of catalyst dissolution by three-dimensional atomby-atom mapping of individual Al-catalysed Si nanowires using highly focused ultraviolet-laser-assisted atom-probe tomography. Although the observed incorporation of the catalyst atoms into nanowires exceeds by orders of magnitude the equilibrium solid solubility<sup>12</sup> and solid-solution concentrations in known non-equilibrium processes<sup>13,14</sup>, the Al impurities are found to be homogeneously distributed in the nanowire and do not form precipitates or clusters. As well as the anticipated effect on the electrical properties, this kineticsdriven colossal injection also has direct implications for nanowire morphology. We discuss the observed strong deviation from equilibrium using a model of solute trapping at step edges, and identify the key growth parameters behind this phenomenon on the basis of a kinetic model of step-flow growth of nanowires. The control of this phenomenon provides opportunities to create a new class of nanoscale devices by precisely tailoring the shape and composition of metalcatalysed nanowires.

The nanowires investigated in this study were grown on Si(111) in an ultrahigh-vacuum chemical deposition system<sup>10,15</sup>. Their growth was accomplished with Al-Si nanoparticles, which act catalytically as the energetically favoured sites for vapour-phase reactant (SiH<sub>4</sub>) adsorption and (when saturated) as the nucleation sites for crystallization and one-dimensional growth<sup>16</sup>. The resulting nanowires are aligned along the [111] direction and display morphological characteristics that are sensitive to the growth temperature (Supplementary Figs 1 and 2). Growth at the highest temperature (470 °C) yields tapered nanowires with an average height and base diameter of  $475 \pm 30$  nm and  $94 \pm 8$  nm, respectively (Supplementary Fig. 1). Figure 1a displays a high-resolution transmission electron microscopy (TEM) micrograph of an Al-catalysed Si nanowire near the interface with the catalyst. This micrograph demonstrates that both nanowire and catalyst nanoparticle are single crystals with a coherent interface between them. However, the close atomic numbers of <sup>13</sup>Al and <sup>14</sup>Si make them indistinguishable in high-resolution TEM images of nanowires. Energy-dispersive X-ray analysis (EDX) in an aberrationcorrected TEM did not find a significant Al signal in Si nanowires

grown at the lowest temperature (410 °C). This indicates that the Al concentration is less than the EDX detection limit, which is typically ~0.5 atomic per cent (at.%). For a rigorous analysis, we used atomprobe tomography (APT), which has a superior detection sensitivity of less than ten atomic parts per million (p.p.m.), with atomic-scale spatial resolution<sup>17</sup>. Pulsed evaporation of individual atoms was achieved using a focused picosecond ultraviolet (wavelength  $\lambda = 355$  nm) laser. The use of a highly focused ultraviolet laser beam decreases local heating, thereby improving the detection limits and mass resolving power ( $m/\Delta m$ , where *m* is the mass of an isotope)<sup>18</sup>.

Figure 1b shows a three-dimensional atom-by-atom map of a single Al-catalysed Si nanowire covered by a protective nickel (Ni) layer. The inset in Fig. 1b displays a cross-sectional TEM image of an identical nanowire. Figure 1c shows two projections of an 80-nm-long segment of a Si nanowire delineated by an isoconcentration surface drawn at the 50 at.% Si level.

The 50 at.% Al isoconcentration surface of the catalyst nanoparticle is displayed in Fig. 2a. Axial and radial concentration profiles of Al and Si, taken from the top 10 nm of the nanoparticle, are presented in Fig. 2b and c, respectively. Both concentration profiles demonstrate Si segregation close to the nanoparticle's surface, possibly as a result of Si expulsion during post-growth cooling or simply due to oxidation on exposure to air. The average Si concentration measured at the core of the nanoparticle is in the range of 2.7  $\pm$  0.9 to 3.1  $\pm$  0.4 at.%, which is nearly twice the solubility of Si in Al at the eutectic temperature<sup>19</sup>. This indicates that Si solubility in Al increases in undercooled catalyst. Figure 2d displays the three-dimensional distribution of Al atoms detected in an as-grown Si nanowire. The average Al solid concentration ( $x_{Al}^{S}$ ) measured for Si nanowires grown at 410 °C is  $\sim$ (2.0 ± 0.5)  $\times 10^{20}$  atom cm<sup>-3</sup> (~0.4 at.%). Strikingly, this is about four orders of magnitude greater than the extrapolated equilibrium solubility of Al in Si (ref. 12), which corresponds to an increase of two to three orders of magnitude compared to Al-assisted recrystallization<sup>13</sup> or solid-phase epitaxy<sup>14</sup> at a similar temperature. Notwithstanding this colossal Al concentration, clusters or precipitates of Al do not form. To verify this quantitatively, we statistically analysed the spatial distribution of Al atoms (Fig. 2e) and performed partial Al-Al radial distribution function analyses. This analysis shows that the concentration frequency distribution is not different from a binomial distribution with the same mean at 99% confidence, and thus confirms that Al does not form precipitates or clusters in Si nanowires.

Figure 3a displays a set of radial concentration profiles measured in 8-nm-diameter cylinders in different regions across the nanowire grown at 410 °C, perpendicular to the growth direction (Fig. 3a insets). The estimated mean  $x_{AI}^S$  value varies between 0.39 and 0.45 at.%. The profiles display random fluctuations indicative of a random distribution of Al in Si nanowires. This is also consistent with the Al axial concentration profiles (Fig. 3b). Indeed,  $x_{AI}^S$  averaged over a cylindrical volume remains practically the same regardless of the diameter of the selected volume, thereby confirming the uniform distribution of

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## **Figure 1** Structure and three-dimensional map of Al-catalysed Si nanowires. a, High-resolution cross-sectional TEM image (left) displaying the interface between the catalyst particle and the nanowire. The right panel exhibits a close-up image of the interface (top), the fast Fourier transform of the image (middle), and the corresponding colour-filtered image (bottom, Al and Si regions correspond to red and blue regions, respectively) indicating that the interface is epitaxial. **b**, Three-dimensional APT atom-by-atom map of a

Al. Analysis of  $x_{Al}^{S}$  in Si nanowires grown at a higher temperature (470 °C) demonstrates a significantly stronger incorporation of Al, leading to concentrations sufficiently large to be detected by EDX (Fig. 3c). Interestingly, the Al radial concentration displays flat profiles, indicating a uniform distribution of Al in the nanowire. Surface segregation of Al would have led to 'U'-shaped profiles. Similarly, the Al axial concentration profile indicates a uniform concentration (~4.3 at.%) along the nanowire. We note the ~10-fold increase in  $x_{Al}^{S}$  when compared to the nanowires grown at 410 °C.

It is generally recognized that nanowire tapering is induced by vapour–solid growth on sidewall surfaces<sup>8</sup> and/or catalyst diffusion from one nanowire to another<sup>20</sup>. As demonstrated here, this is not the case for Al-catalysed nanowires, for which the observed incorporation of catalyst atoms during growth is the key element determining nanowire morphology. It is noteworthy that the uniform Al radial concentration profile (Fig. 3c) rules out vapour–solid deposition on the nanowire sidewalls as a possible mechanism for nanowire tapering. Specifically, if homoepitaxy did take place on the nanowire's sidewalls,

nanowire grown at 410 °C. For the sake of clarity, only a limited number of atoms is displayed ( $2.5 \times 10^4$  atoms of each element). Inset, a cross-sectional TEM image of an identical Si nanowire (scale bar, 40 nm). c, Si 50 at.% isoconcentration surface of an 80-nm-long segment of a nanowire determined by analysing a three-dimensional atom-probe tomographic reconstruction: left, side view; right, top view.

the overgrown layer would have been Al-free, because Al diffusion is negligible under these growth conditions<sup>21</sup>. The strong incorporation of Al catalyst atoms into the nanowire that we observe should involve a continuous dissolution of the catalyst throughout the growth process, with direct implications for nanowire morphology (Supplementary Information, section D). For instance, at 470 °C, the total volume of Al atoms incorporated in the completely grown Si nanowire is  $\sim$ 5.5  $\times$  10<sup>4</sup> nm<sup>3</sup>, which is significantly larger than the volume of the catalyst at the end of growth ( $\sim 1.3 \times 10^4$  nm<sup>3</sup>). This means that there is more Al in the Si nanowire than in the nanoparticle at the end of the growth process-that is, the catalyst has lost more than 80% of its initial volume. This leads to a continuous reduction of the diameter of the catalyst nanoparticle during growth, and thus to nanowire tapering. We note, however, that the catalyst's volume loss is very small ( $\sim$ 6%) at 410 °C, which explains the absence of tapering at this temperature (Supplementary Fig. 2).

The observed uniform Al concentration distributions suggest that the dissolution of Al atoms and their injection into the growing nanowire



Figure 2 | APT data obtained for a catalyst nanoparticle and a Si nanowire. a, Al 50 at.% isoconcentration surface of a catalyst nanoparticle. b, c, Axial (b) and radial (c) concentration profiles of Al and Si in the catalyst nanoparticle; error bars,  $\pm 1$  s.d. calculated for the analysed volume containing  $2.9 \times 10^5$  Al

atoms and  $8 \times 10^3$  Si atoms. **d**, Three-dimensional distribution of Al atoms in a Si nanowire grown at 410 °C. **e**, Results of statistical analysis of Al concentration frequency (histogram) and of binomial analysis (solid line). The binomial analysis was performed by sampling blocks containing 200 atoms.



**Figure 3 Al concentration profiles in individual nanowires. a**, Al radial concentration profiles (left) measured in different regions of a Si nanowire. Each concentration profile is taken from a cylindrical segment having a diameter of 8 nm, as indicated in the images (right). **b**, Al axial concentration profiles (left) measured for cylindrical segments (right) with a diameter of 10 nm (top) and 20 nm (bottom). The horizontal dashed line in all concentration profiles denotes the average concentration, which is given as

occurs at a constant rate during the growth process. Moreover, the fact that Al displays uniform radial and axial concentration profiles suggests the existence of a single atomic pathway behind this colossal incorporation. We anticipate that surface effects, capillarity and related nanoscale stresses will shift the boundaries in the phase diagram of the catalystnanowire system in comparison to those of a bulk system<sup>22</sup>. However, by taking into account these thermodynamic considerations and including the nanowire tapering (Supplementary Information, section E), we found that the calculated solid composition of the nanowire is always smaller than the equilibrium content, which is of the order of 1 atomic p.p.m. at the growth temperature of our Si nanowires (Supplementary Fig. 11). This stands in sharp contrast to the observed excess concentrations (that is, concentrations above the equilibrium value) of orders of magnitude in our Si nanowires, which demonstrates that kinetic factors must be responsible for the incorporation of Al atoms.

Supersaturations of several orders of magnitude occur as a result of deviations from local equilibrium in ultra-rapid solidification of a melt<sup>23-25</sup>. This phenomenon (so-called solute trapping) has been observed for a variety of solutes in Si for growth rates of the order of metres per second (refs 24, 25). In general, solute trapping is quantified in terms of a partition coefficient, k, which is the ratio of the solute concentration in the solvent to its concentration in the melt at the solidliquid interface, as a function of the equilibrium partition coefficient  $(k_e)$ , the average interface velocity  $(v_{min})$ , and a characteristic velocity known as diffusive velocity  $(v_D)^{25}$ . Because nanowires grow by successive addition of bilayers through step flow<sup>26</sup>, the average interface velocity is defined as  $v_{\min} = b/\tau$ , where b = 0.3 nm is the thickness of a Si(111) bilayer and  $\tau$  is the total time needed for one bilayer to grow ( $\tau$  includes the time needed to reach the supersaturation (the incubation time,  $\tau_{\rm I}$ ) and the time between the end of the incubation period (that is, the beginning of nucleation) and the complete growth of the bilayer,  $\tau_{\rm BL}$ ). Note that the incubation time is a nanoscale phenomenon, not

blue numerals; the shaded band is the uncertainty interval; and error bars in **a** and **b** represent  $\pm$ 1s.d. The number of Al atoms in the sampling volumes varies between  $\sim$ 2,000 and 4,500. **c**, EDX Al concentration profiles: left and middle plots, radial concentration profiles near the base and middle of the Si nanowire, respectively; right plot, axial concentration profile. Error bars, approximately  $\pm$ 0.5 at.%, which is the sensitivity of the instrument. Insets, the corresponding TEM images with EDX scan lines (dashed lines).

expected for macroscopic systems<sup>26</sup>. Under our growth conditions,  $v_{min}$  equals 0.4 and 0.2 nm s<sup>-1</sup> at 470 and 410 °C, respectively. Intriguingly, from studies of rapid solidification of melts<sup>25</sup>, one can infer that solute trapping should not occur for systems with an interface velocity of the order of nanometres per second, and thus the anticipated amount of Al in Si nanowires should not exceed the equilibrium concentration. We note that the influence of temperature on the rate of the thermally activated jumps is not sufficient to explain the observed incorporation of Al at exceedingly low interface velocities (Supplementary Information, section F).

Current solute trapping models<sup>25</sup> involve the assumption that atomic jumps occur over the entire infinite liquid-solid interface, and solute atoms are trapped only after the passage of the next layer across the nanowire surface. Although this mechanistic picture describes the behaviour in bulk systems very well<sup>25</sup>, it cannot be extended to nanowire growth, which is characterized by a relatively large delay between two successive bilayers. During this incubation time, there is no driving force for atoms to leave the catalyst and thus the exchange (that is, the process of atomic jumps) should stop until the system reaches supersaturation. It is also important to note that in step-flow growth, atoms at the step edges have few nearest neighbours, which provides them with more steric freedom for an exchange process. Thus, it is reasonable to assume that atomic jumps are more favourable at the step edges than at terraces. This suggests that the impurity atoms become frozen in the solid immediately after the formation of the next row of atoms at the step edge. Therefore, the time,  $\tau_{e}$ , during which the local exchange is possible corresponds to the average time needed to add one row, and can be expressed as  $\tau_e = a/v_{step}$ , where *a* is equivalent to the width of one row of atoms and  $v_{\text{step}}$  is the average step velocity. This latter can be expressed as a function of nanowire radius  $R_{\rm NW}$ :  $v_{\rm step} = 2R_{\rm NW}/\tau_{\rm BL}$ . Thus, at fixed radius,  $\tau_e = \tau_{\rm BL}(a/a)$  $2R_{\rm NW}$  =  $\tau_{\rm BL}/n$ , where  $n = 2R_{\rm NW}/a \gg 1$ . The parameter *n* depends

only on step speed (Supplementary Information, section F). Experimentally, we can only determine the average time between the completion of one bilayer and the completion of the next,  $\tau = \tau_{\rm I} + \tau_{\rm BL}$ . By taking  $f = \tau_{\rm BL}/\tau$ , the exchange time can be written as  $\tau_{\rm e} = (f/n)\tau$ .

The transport of impurity atoms between the two sides of the interface for  $0 < t < \tau_e$  can be described on the basis of chemical rate theory and mass conservation<sup>27,28</sup>. Assuming that the step growth is random rather than periodic<sup>29</sup> (Supplementary Information section F), the partition coefficient can be expressed as:

$$k = \frac{k_{\rm e} + \frac{b^2}{D_{\rm i}\tau} \times \frac{n}{f}}{1 + \frac{b^2}{D_{\rm i}\tau} \times \frac{n}{f}} = \frac{k_{\rm e} + \frac{v_{\rm min}}{v_{\rm D}} \times \frac{n}{f}}{1 + \frac{v_{\rm min}}{v_{\rm D}} \times \frac{n}{f}}$$

where  $D_i$  is the coefficient of interdiffusion at the interface ( $v_D = D_i/b$ ). Figure 4a displays the evolution of the calculated k in (f:n) space for nanowires grown at 470 °C ( $\tau = 0.75$  s and  $k_e = 2.6 \times 10^{-6}$ ) using  $v_D = 6.7$  nm s<sup>-1</sup> obtained from earlier solute trapping models (Supplementary Information section F). We note that any pair (f:n) (except around (1;1)) predicts Al trapping at levels always significantly higher than the measured value ( $k = 5.6 \times 10^{-2}$ ). At these trapping levels, nanowire growth cannot occur. Obviously, diffusive velocities of the order of nanometres per second cannot describe the observed Al injection in nanowires. The complete map of  $v_D$  values fitting the measured kvalues is displayed in Fig. 4b. Note that the expression for  $\tau_{BL}$  can be



Figure 4 | Calculations of partition coefficient and diffusive velocity. a, The calculated partition coefficient, *k* (on colour scale and labelled on contours), for nanowires grown at 470 °C using a diffusive velocity ( $\nu_D$ ) of 6.7 mm s<sup>-1</sup> obtained from an early solute trapping model<sup>25</sup>. Axes show *f* (given by  $\tau_{BL}/\tau_e$ ); see text for details. Inset, the calculated *k* near (f;n) = (1;1). **b**, The map in (f;n) space of diffusive velocities,  $\nu_D$  (on colour scale and labelled on contours), fitting the measured partition coefficient at 470 °C ( $k = 5.6 \times 10^{-2}$ ). It is important to indicate that only low values of *f* have a physical meaning in nanowire growth as the incubation time is much larger than the growth time of a single bilayer (that is,  $\tau_{BL} \ll \tau_I$ , corresponding to  $f \ll 1$ ). Note the logarithmic scales. In both **a** and **b**,  $\nu_{min}$  is taken as 0.4 mm s<sup>-1</sup>, which is the average interface velocity corresponding to nanowires grown at 470 °C.

deduced from the model above:  $\tau_{\rm BL} \approx (2R_{\rm NW}/v_{\rm D})[(1-k)/(k-k_{\rm e})]$ . The extrapolation of the correlation between the equilibrium partition coefficient,  $k_e$ , and  $v_{\rm D}$  obtained in laser resolidification<sup>25</sup> to our experimental conditions yields a diffusive velocity of  $\sim 2 \times 10^{11}$  nm s<sup>-1</sup> at 470 °C ( $k_e = 2.6 \times 10^{-6}$ ), corresponding to  $\tau_{\rm BL} \approx 7$  ns. Interestingly, the time between two layers is  $\sim 0.75$  s, thus suggesting that the incubation time is very much larger than the time needed for the step to grow across the whole nanowire diameter, in qualitative agreement with *in situ* TEM observations<sup>8,26,29,30</sup>. Similarly, at the lowest growth temperature ( $k_e = 6.4 \times 10^{-7}$ ), the estimated  $\tau_{\rm BL}$  is  $\sim 18$  ns. A reduction in growth temperature is anticipated to affect not only the rate of the thermally activated atomic jumps, but also other growth parameters that are critical for the incorporation of the catalyst atoms, as discussed below.

Using a step-flow growth model that takes catalyst dissolution into consideration, we derived an expression for the Al content in the nanowire as a function of growth parameters (Supplementary Information section G). Note, however, that the elucidation of the kinetically controlled atomic processes involved in the incorporation of Al would require a deep understanding of Al-induced Si surface reconstructions (Supplementary Information section H). From our analysis, it emerges that the second derivative of the Gibbs free energy of the liquid evaluated at the equilibrium composition,  $g_1''$ , and the characteristic supersaturation at which the nucleation occurs deterministically,  $\mu_{c}$  are the two important parameters that influence catalyst injection. The quantity  $g_1''$  can be modified by adjusting Si solubility, whereas high  $\mu_c$ implies a high nucleation barrier. In principle, both parameters can be engineered through control of the catalyst chemistry (by adding impurities, for instance), thus providing the possibility of tailoring the properties of nanowires.

This flexibility in fabrication and functionalization of nanowires could be greatly enhanced owing to the availability of other catalysts that can act as dopants—for example, Bi (which yields n-type doping<sup>31,32</sup>) or Ga (which gives *p*-type doping<sup>33</sup>)—if their injection during the growth of Si or other group IV nanowires can be controlled. Our observations and predictions provide motivation to pursue the synthesis and characterization of atomically controlled nanowires with potentially adjustable morphology and physical characteristics that might offer new routes for catalytic assembly of nanowire-based devices.

## METHODS SUMMARY

The growth of Al-catalysed Si nanowires was accomplished by using monosilane, SiH<sub>4</sub>, (diluted to 5% in argon) as a precursor in the temperature range  ${\sim}400{-}470~^\circ\mathrm{C}$ (refs 10, 15). The partial pressure of the monosilane was held below 0.15 mbar during growth. Although the temperature used is below the Al-Si macroscopic eutectic temperature, the growth here is believed to be via the vapour-liquid-solid mechanism involving undercooled Al-Si nanodroplets. The morphology of Al-Si nanowires was characterized using an FEI dual-beam Nanolab 600 scanning electron microscope, a Philips CM 20T TEM operating at 200 kV, a JEOL JEM-4010 TEM operating at 400 kV, and an aberration-corrected FEI TITAN 80-300 analytical scanning TEM operating at 300 kV, which yields a spatial resolution of about 100 pm in both modes (TEM and scanning TEM). Additionally, this TEM is also equipped with an EDX detector having a detection limit of about 0.5 at.%. We use an ultraviolet laser-assisted LEAP (local electrode atom probe) tomograph (LEAP 4000XSi, Cameca). The three-dimensional reconstructions and statistical analysis of concentration frequency were performed using Cameca's IVAS program. For the preparation of nanowire LEAP specimens, we have developed a focused ion beam (FIB)-based damage-free methodology to attach individual nanowires to commercially available Si microtips (Supplementary Information section B). The Si microtips were subsequently inserted into the LEAP tomograph's ultrahigh-vacuum chamber and cooled to 60 K before pulsed ultraviolet-laser-assisted evaporation analyses. To confirm that the preparation and laser-assisted evaporation do not affect the accuracy of the analysis, a reference sample consisting of an Al-capped Si needle was also analysed under exactly the same conditions, and the results demonstrate that the needle is Al-free. The binomial analysis was performed by sampling blocks of 200 atoms. The entire volume was first divided into columns along the zaxis, with a cross-section in x- and y- directions, so that the volume dxdydz contains 200 atoms on average. To obtain blocks with exactly 200 atoms, each column with cross-section dxdy was then cut into sections with 200 atoms as dz is varied.



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Supplementary Information is available in the online version of the paper.

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