Supplemental information

Surface tension

Neman quadrilateral relation,[9] interacting surface tensions, where the contact angle, θ_c can be related to the surface tensions, the line tension τ, and the inclination angle θ_i as:

$$\gamma_{In-ND}\cos(\theta_c) = \gamma_{Si}\cos(\theta_i) - \gamma_{Si-In-ND} - \frac{\tau}{r} \qquad (1)$$

In Eq. (1), the γ_{In-ND}, $\gamma_{Si-In-ND}$ and γ_{Si} are the surface tension of the In ND surface, the In ND–solid(Si) interface tension, and the Si surface tension, respectively. The droplet has a contact area of radius r_0 and a contact angle, θ_c so that the radius R of the In ND can be expressed as $R = r_0/\sin(\theta_c)$. After the flow of Si-atoms is switched on, the growth of Si NWs starts and the initial stage of growth is schematically depicted in Fig. S1. In the limit $\theta_i \rightarrow 0$, Eq. (1) can be reduced to the modified Young's equation. In our case, where the Si NWs are grown on a flat Si substrate, θ_i equals zero at the beginning. As growth starts, the angle θ_i has to increase and accompanied by an increase of θ_c, which means that the In ND approaches a larger solid angle of a spherical section. But this causes a decrease of the contact area and a decrease of the radius r. Consequently, the final radius of the Si NW should be smaller than the initial radius r_0 of the contact area of the In ND or, in other words, the NW diameter is largest at the NW base.

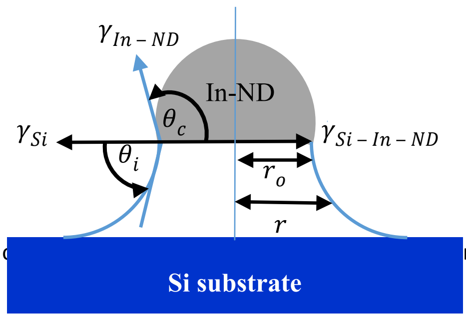

Fig. S1: Schematic … rilateral relation.

In migration

Figures S2 show the results of BF-STEM measurement and EDX mapping of In-L. The In NP migration, and contact points were confirmed by BF-STEM as shown in Fig. S2(a), and the EDX In-L image with dotted lines which give the shape of Si NWs as shown in Fig. S2(b). The dotted circles labelled P1 and P2 in Fig. S2(a) represent NPs on the Si NWs. The NPs in Fig. S2(a) were confirmed as In from Fig. S2(b), suggesting there are In NPs on the tip of Si NWs and In NPs on the sidewall of Si NWs which are migrated from the tip of Si NWs (as shown in Fig. 4(a)). The EDX intensity of In-L signal originated from the tip of Si NWs at P1 were found to be smaller than the EDX intensity of In-L signal originated from sidewall of In NP on Si NW at P2 as shown in Fig. S2(c) and Fig. S2(d) respectively. We do not know clearly the root cause of these In NPs migration from the tip of Si NWs. Although In-L signal is weak, we confirmed the In-L peak from the Si NW area as shown in Fig. S2(b). It is expected that In ND on the tip of Si NW became small during the growth owing to the trapping of In atoms by Si NWs, which yielded tapering of the Si NWs, and resulted in cone shaped vertically aligned Si NWs. It is also expected that In ND size on the tip of Si NW can became smaller during the growth owing to the migration of In NPs but the influence of the In NPs migration on the tapering as well as on the height restriction of Si NWs are not yet known.

Recently Chen *et al.*, (Nature Communications 5, 4134 (2014)), observed that the metal impurities like In-Sn were incorporated uniformly into Si NWs during the growth, and then segregate to the nearby structural defects if they are present. But the Si NWs grown in their case was randomly oriented. Moutanabbir *et al.*, (Nature 496, 78 (2013)), discussed about the colossal injection of Al-catalyst atoms into the randomly oriented Si NWs. It is also mentioned about the step-flow growth, that atoms at the step edges have few nearest neighbours, which provides them with more steric freedom for an exchange process. They pointed out that “Atomic jumps are more favourable at the step edges than at the 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.”

It shows that the trapping of metal solute can occur as mentioned by Moutanabbir *et al.*, and then can segregated to the nearby defects if present as quoted by Chen *et al.* The segregation of these metal particle toward the defects might be governed by the thermal kinetic phenomenon during the high temperature growth in VLS mode. In our case not only trapping of In metal occurred but some In NPs migration also occurred at the same time, as shown in Fig. S2(a) and confirmed by Fig. S2(b)–(d), and Fig. 4(a). We can speculate that the tapering of the Si NWs and height of the Si NWs were restricted by In NDs disappearance from the top of Si NWs. The average diameter of In NDs about 70 nm were estimated prior to the growth of Si NWs. However, in this experiment, the diameter of Si NWs around 18 nm were achieved, indicating the last diameter size of In NDs just before the disappearance of In atoms could be around 18 nm. The In NDs size was about 70 nm and this could possibly limit the height of Si NWs due to the gradual trapping of In atoms as well as In NPs migration.

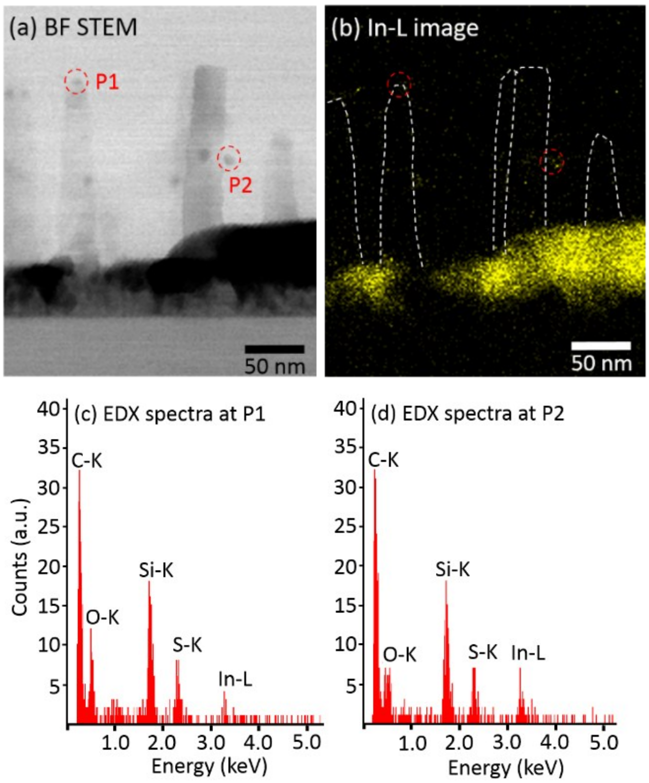

Fig. S2: (a) Bright-Field STEM of Si NWs, and (b) EDX mapping of In-L. The dotted lines are the shapes of Si NWs. (c) EDX spectra obtained from the tip of Si NWs at P1 shown in (a), and (b) EDX spectra obtained from the sidewall at P2 of Si NWs shown in (a).