

Size-Induced Switching of Nanowire Growth Direction: a New Approach Toward Kinked Nanostructures

Youde Shen, Oleg I. Lebedev, Stuart Turner, Gustaaf Van Tendeloo, Xiaohui Song, Xuechao Yu, Qijie Wang, Hongyu Chen, Shadi A. Dayeh, and Tom Wu*

Exploring self-assembled nanostructures with controllable architectures has been a central theme in nanoscience and nanotechnology because of the tantalizing perspective of directly integrating such bottom-up nanostructures into functional devices. Here, the growth of kinked single-crystal In_2O_3 nanostructures consisting of a nanocone base and a nanowire tip with an epitaxial and defect-free transition is demonstrated for the first time. By tailoring the growth conditions, a reliable switching of the growth direction from [111] to [110] or [112] is observed when the Au catalyst nanoparticles at the apexes of the nanocones shrink below \approx 100 nm. The natural formation of kinked nanoarchitectures at constant growth pressures is related to the size-dependent free energy that changes for different orientations of the nanowires. The results suggest that the mechanism of forming such kinked nanocone–nanowire nanostructures in well-controlled growth environment may be universal for a wide range of functional materials.

Y. Shen

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Division of Physics and Applied Physics School of Physical and Mathematical Sciences Nanyang Technological University Singapore 637371, Singapore Dr. O. I. Lebedev Laboratoire CRISMAT ENSICAEN CNRS UMR 6508 6 Boulevard du Maréchal Juin 14050 Caen, France Dr. S. Turner, Prof. G. Van Tendeloo FMAT University of Antwerp Groenenborgerlaan 171 B-2020 Antwerpen, Belgium X. Song, Prof. H. Chen Division of Chemistry and Biological Chemistry Nanyang Technological University Singapore 637371, Singapore X. Yu, Prof. Q. Wang School of Electrical and Electronic Engineering Nanyang Technological University 50 Nanyang Ave., Singapore 639798, Singapore Prof. S. A. Dayeh Department of Electrical and Computer Engineering University of California San Diego La Jolla, CA 92093, USA Prof. T. Wu Materials Science and Engineering King Abdullah University of Science and Technology (KAUST)

1. Introduction

Over the past two decades, semiconductor nanowires (NWs) have been intensively studied because of their wide application in electronics, photonics, chemical/ biological sensing, and energy harvesting/ technologies.^[1,2] conversion Rational design and control of growth dynamics and NW architecture is of tremendous interest.^[3] So far, some novel structures, such as superlattice NWs,^[4] axial heterostructures,^[5,6] in-plane NWs,^[7] branched nanostructures,^[8–11] kinked NWs,^[12] nanosprings,^[13] and nanowebs,^[14] have been reported. Among them, kinked nanostructures not only bring new understandings into the dominant growth mechanisms but also promise potential applications. For example, V-shaped kinked Si NWs

were exploited as probes to monitor 3D intracellular signals in biological systems.^[15–17] Near-infrared photodetectors were also constructed based on kinked GaSb/GaInSb heterojunctions.^[18] Furthermore, the kinking point itself was used as a natural marker for placing the gate electrodes for Ge-Si field-effect transistors whose composition and doping modulation were referenced.^[19]

Switching the growth direction during the NW synthesis is a vital step toward constructing nanoarchitectures with tailored structural complexities. It has been reported that the NW growth direction can be switched by modulating the growth conditions, i.e., growth pressure,^[20] reactant concentration,^[21] growth temperature,^[22] reactant species,^[23,24] interface engineering,^[25] and NW surface passivation.^[26,27] Although the underlying mechanism is not fully understood yet, modulated supersaturation in the catalyst particles might lead to abrupt change of their contact angles with the solid NWs, and the resultant change of the growth direction results in the formation of kinked nanostructures. However, such modulations of the growth conditions may induce structural defects such as twin boundaries or stacking faults into the nanostructures.[23,24,28-32] Though the approach of NW surface passivation may avoid the generation of structural defects,^[26,27] it may cause chemical contamination. Therefore, there is an urgent need to develop a new approach for the fabrication of kinked nanostructures. Furthermore, most kinked nanostructures so far are based on group IV (Si and Ge) and III-V (InP, GaP, and GaAs) semiconductors. It remains an open question whether kinked NWs can be synthesized from other materials in a highly controlled manner.

DOI: 10.1002/adfm.201600142

Thuwal 23955, Saudi Arabia

E-mail: tao.wu@kaust.edu.sa





Metal oxide NWs are promising building blocks for electronic devices owing to their wide bandgap, excellent optical and electrical properties, high stability in oxidizing environment, and low-cost fabrication.^[33] Among them, In₂O₃ is an important metal oxide semiconductor with extensive applications in UV detectors, gas sensors, and transparent transistors.^[34-45] In this work, we demonstrate for the first time the formation of kinked nanocone-nanowire (NC-NW) structures of In2O3. Such kinked metal oxide nanostructures may have potential applications in photonics such as plasmonic and waveguide devices due to their low loss in the near-infrared regime compared to the noble metal counterparts. Different from previous reports,^[20-24,26,27,29-31] our synthesis of kinked In₂O₃ nanostructures does not entail any abrupt modulation of growth conditions, and these kinked nanostructures are free of structural defects and chemical contamination. In addition, our systematic experiments revealed a strong correlation between the morphology of the In₂O₂ nanostructures and the growth conditions during the vapor transport growth. Our observations suggest that the switching of growth orientations appears to be induced by the dynamic variation of free energies of NWs which depend on their diameter and direction. Besides advancing the vaporliquid-solid (VLS) growth mechanism toward creating novel 3D nanoarchitectures, our findings may be generalized to other functional nanomaterials as well.

2. Results and Discussion

 In_2O_3 nanostructures were grown on [111]-oriented yttriastabilized zirconia (YSZ) substrates in a horizontal furnace with controlled gas delivery and pumping (see Experimental Section for details). YSZ is a perfect substrate for the epitaxial growth of In_2O_3 nanowires due to the small lattice mismatch

(≈1.6%).^[46] The vertical nanocone (NC) base and the kinked NW tip can be clearly identified in Figure 1a. The angle selective backscattered (ASB) scanning electron microscopy (SEM) image in Figure 1b reveals the presence of catalyst nanoparticles at the apex of the NWs, which confirms the dominant role of the VLS mechanism in NW growth. However, the tapered morphology of the NCs indicates that the contribution of the vapor-solid (VS) growth mechanism cannot be excluded. In contrast to the NCs, the NW tips are not obviously tapered, which might be due to the different diffusion rates of surface atoms on the facets of bottom nanocones and top nanowires. Furthermore, as shown in Figure 1c, NW tips form an angle of either 118° or 145° with respect to the NC bases. Extensive top-view SEM images were collected, and typical examples are shown in Figure 1d,e. At first sight, the NW tips seem to exhibit random orientations. However, careful examinations revealed that these NWs could be divided into two types. For the type-I NWs, the tips point to one of the three equivalent directions, following the threefold symmetry of [111]-oriented YSZ substrate. For type-II NWs, there are small connection segments between the NC bases and the NW tips, and the NW tips exhibit six growth directions, forming an angle of $\approx 19^{\circ}$ with the type-I NW tips (Figure 1f).

In order to better observe their morphologies, the kinked NC–NW nanostructures were scratched from the YSZ substrate, transferred to a Si wafer, and examined using SEM. As shown in Figure S1 (Supporting Information), the cross section of the NC base is hexagonal. In addition, we observed that the NC sidewalls are not flat but consist of tilted (111)-terminated facets (Figure S2, Supporting Information), which are energetically favored due to their lower surface energy.^[47] The surface atoms on such (111) facets may have a lower diffusion rate, which favors the VS growth and the formation of tappered bottom NCs.



Figure 1. a) SEM image (tilting angle: 60°) of the kinked In_2O_3 nanostructures grown for 10 h with a growth temperature of 800 °C and a pressure of 1 mbar. Scale bar: 2 µm. b,c) Angle-selective backscattered (ASB) SEM images of the kinked nanostructures at different magnifications (tilting angle: 60°). The Au catalyst nanoparticles at the apex can be clearly observed. The angles formed by the NCs and NWs are either 118° or 145° by taking into account of the tilting of the SEM observation and the tapering of the NCs. Scale bars: b) 1 µm and c) 500 nm. d,e) SEM top-view images of the kinked nanostructures at different magnifications. Scale bars: d) 1 µm and e) 500 nm. In f), different orientations of the NW tips are denoted. The [110]-oriented NW tips have three equivalent directions, while the [112]-oriented ones have six equivalent directions.



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The crystalline structure of these two types of kinked NC–NW nanostructures was investigated by X-ray diffractometry (XRD) and high-resolution transmission electron microscopy (HRTEM). The XRD pattern (Figure S3, Supporting Information) shows that in spite of the structural complexity of the kinked nanostructures there is only a sharp In_2O_3 (111) diffraction peak with a full width at half maximum (FWHM) of only 0.17°. This result indicates that the kinked nanostructures are single crystals and the growth direction of the NC base is [111], confirming the excellent epitaxial relationship between the kinked In_2O_3 nanostructures and the YSZ substrate. Such epitaxial growth is expected because of their matching lattice constants (a_{In2O3} : 1.01170 nm; a_{ysz} : 0.51423 nm).^[47]

The TEM results in Figure 2 and Figure 3 provide more details about the kinked nanostructures. During TEM characterization, we found that it was often challenging to properly align the NCs and NWs to correctly determine their orientation. The complication arises from the fact that the NC base is tapered with an angle of $\approx 10^{\circ}$ and the NW tips are often not positioned flat on the TEM grids. Because the type-I kinked nanostructure is structurally simpler, we take it as an example to explain the geometry of alignment (see Figure S4a-c, Supporting Information). When the nanostructure is not properly aligned, the orientation of NCs and NWs cannot be properly determined from the selected area electron diffraction (SAED) patterns (Figure S4d,e, Supporting Information). As shown in Figure 2 a1-a5, "electron tomography" was used to yield a 3D reconstruction of the NC-NW kinked nanostructure based on a series of 2D projection images with a rotation interval of 2°. A video of the tomographic reconstruction is available in Supporting Information.

In a complementary geometric approach, we developed a procedure to use multiple SAED patterns to determine the

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orientation of the NC and NW segments. First, we took SAED patterns along two different zone axes. Two observed growth directions and two planes which contain those two observed growth directions can be identified from the SAED patterns. Then, as long as these two planes are not parallel, they intersect along a line which is the correct growth direction for each segment. In order to simplify the derivation procedure and find the correct index of the intersecting line between these planes easily, we used the Wulff net, where directions are represented as dots and planes are represented as straight/curve lines.^[48] Here we use the derivation of the growth direction of the NW tip as an example to illustrate our approach. As shown in Figure 2b,c, two SEAD patterns taken along the zone axes [001] and [110] indicate that the observed growth directions of the NW tip are [100] and [-112] respectively. The observed [100] growth direction is in the (010) plane and [-112] growth direction is in the (1–11) plane so that the correct growth direction is the intersecting line of (010) and (1–11) planes. With the help of a Wulff net, we were able to derive that the correct growth direction of the NW tip is [110] (see Figures S6 and S7, Supporting Information for details). Because of the cubic symmetry of In₂O₃, there are three equivalent [110] growth directions: [110], [011], and [101], which are consistent with the observed threefold symmetry of the NW tips observed in the SEM topview images shown in Figure 1d,e. In addition, the obtuse angle between the [111] and [110] directions in a cubic lattice is about 145°, which agrees with the SEM observation in Figure 1c.

The high-magnification TEM image in Figure 2d indicates that the kinked region of the In_2O_3 nanostructure is free of defects (also see Figure S5, Supporting Information), which is different from the kinked nanostructures previously reported.^[23,24,28–32] In previous reports, defects including twin planes and stacking faults were observed and believed to play



Figure 2. a) Tomographic reconstruction of a type-I kinked nanostructure. The five frames (a1-a5) are captured from the video in Supporting Information and separated with a rotation interval of 45°. Scale bar: 200 nm. b,c) TEM images of a kinked nanostructure observed along [001] and [110] zone axes, respectively. The crystallographic directions for the NC and NW segments are denoted. Based on these observations, we concluded that the growth directions of the NC base and NW tip are [111] and [110], receptively. Scale bars: 200 nm. d,e) High-magnification TEM images collected in the kinked region and the catalyst/NW interface. Also shown in b–d) are the SAED patterns. Scale bars: d) 10 nm and e) 5 nm.

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Figure 3. a,b) TEM images of a type-II kinked nanostructure observed along the [110] and [111] zone axes, respectively. Based on the observed crystallographic directions of the different segments, we concluded that the growth directions of the NC base, the connection segment and the NW tip are [111], [110], and [112], respectively. As shown in the insets of a), the identical SAED patterns collected from the three regions confirm the single crystalline nature of the kinked nanostructures. Scale bar: 200 nm. c) Tomographic reconstruction of the type-II kinked NC–NW nanostructure (video is available in Supporting Information). Scale bar: 200 nm. d) HRTEM image collected from yellow rectangular region in (a).

an important role in promoting the formation of kinked structures. The HRTEM image of Figure 2e collected at the interface between the catalyst nanoparticle and the NW tip shows that an ultrathin In_2O_3 shell covers the catalyst nanoparticle, which is consistent with our previous observations on indium tin oxide (ITO) NWs.^[11,46]

Different from the type-I kinked nanostructures, the type-II kinked nanostructures feature a short connection segment between the NC base and the NW tip. Nevertheless, by applying the same geometric method to the SAED patterns collected along different zone axes, we were able to derive the growth directions for every segment (Figure 3a,b). The results show that the growth directions of the NC base, the connection segment and the NW tip are [111], [110], and [112], respectively (see Figures S8-S11, Supporting Information for details). Because of the cubic symmetry, there are three equivalent <110> growth directions: [110], [011], and [101], and six equivalent <112> growth directions: [-112], [-121], [12-1], [21-1], [2-11] and [1-12]. In other words, there are three equivalent growth directions for connection segments and six equivalent growth directions for NW tips, which are consistent with the SEM observations (Figure 1d-f).

The fact that the same [110] growth direction is shared by the connection segments in the type-II nanostructures and the NW tips in the type-I nanostructures indicates that the type-II nanostructure is actually a variant of the type-I nanostructure. As shown in Figure 1f, the six equivalent [112] growth directions of the NW tips in the type-II nanostructures can be divided into three pairs with each pair forming an angle of \approx 19° with one of the three [110] directions. In this particular sample, the percentage of type-II nanostructures is \approx 44%, and the rest are type-I nanostructures. We also counted the number of NW tips for both type-I and type-II kinked nanostructures based on their orientation (see Figure S12, Supporting Information); the statistic results reveal roughly identical numbers for the three [110]-oriented NW tips. The same thing is true for the six [112]-oriented NW tips.

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The identical SAED patterns collected at the NC base, the connection segment and the NW tip (Figure 3a) confirm the single crystal nature of the as-grown kinked NC–NW nano-structure. We also used electron tomography to yield a 3D reconstruction for the type-II kinked nanostructure (Figure 3c); a video of the tomographic reconstruction is available in Supporting Information. The HRTEM image collected at the kinked region further confirms the defect-free transition (Figure 3d).

We carried out time-dependent growth experiments to reveal the evolution of the kinked NC–NW nanostructures during their formation (see Figure S13, Supporting Information). As a result of the VS growth, both the height and size of the NC bases keep increasing during the first few hours of growth (see Figure S14, Supporting Information). We also observed the continuous shrinkage of Au catalyst nanoparticles, which is presumably a result of Au atom migration at high growth temperatures.^[49–51] Importantly, during the transition from NC to kinked NC-NW, as shown in **Figure 4**a,b, the catalyst nanoparticles abruptly move to the NC sidewalls and then initiate the growth of the NW tips. Afterward, the length of the NW tips increases continuously with growth time (see Figure S14b, Supporting Information) until the Au nanoparticles are completely depleted. The process of forming type-I and type-II kinked

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Figure 4. a,b) SEM side-view images of NCs grown at 800 °C for 6 h at a growth pressure of 1 mbar. The catalyst nanoparticles indicated by arrows are pinned to the NC sidewalls. c,d) SEM side-view images of NC–NW nanostructures grown for 7 h under the same conditions. Scale bars: a,c) 1 μ m and b,d) 100 nm. e) Diameter of Au catalyst nanoparticles as a function of time for the growth at a temperature of 800 °C and a pressure of 1 mbar. Due to the Au migration, the catalyst nanoparticles shrink during growth. f,g) Schematics illustrating the free energies of growing [111]-, [110]-, and [112]-oriented NWs as a function of the NW diameter (equivalent to the Au nanoparticle diameter) at low (i.e., 1 mbar) and high (i.e., 30 mbar) growth pressures, respectively.

nanostructures is illustrated schematically in Figure S15, Supporting Information.

Clearly, the relocation of the Au nanoparticles from the NC apex to the sidewalls triggers the growth of tilted NW segments. It is well known that the growth direction of NWs is correlated with the conditions of the catalyst nanoparticles.^[52] Particularly, the NW growth direction can be manipulated by engineering the composition of the catalyst droplet during VLS growth. For example, the growth direction of InP NWs could be switched reversibly between [100] and [111] by varying the indium concentration in the catalyst droplets;^[21] similar observations were also reported for GaN NWs^[53] and InAs NWs.^[54] However, in our experiments, different from these reports, the growth conditions and the catalyst composition were not intentionally modified.

Besides composition engineering, the size of catalyst particles was also reported to influence the growth direction of the NWs. It was previously reported for Si NWs that smaller catalyst particles stimulate the growth of [110]-oriented Si NWs, whereas bigger ones stimulate the growth of [111]-oriented Si NWs.^[55–58] The similar results have also been observed in ZnSe nanowires.^[59] Such a size effect is a result of the size-dependent free energy of growing NWs with different orientation.^[56] However, this size effect has not been exploited so far to synthesize kinked nanostructures.

In our experiments, the size of the Au nanoparticles actually shrinks from ≈ 200 to ≈ 100 nm (Figure 4e) when the transition from conventional NC to a kinked NC–NW nanostructure occurs. The higher free energy of smaller nanoparticles, as a result of the conventional Gibbs-Thomson effect, increases their instability at the NC apex. In fact, the instability of the catalyst droplets at the liquid/solid interfaces has been associated

with some fascinating phenomena observed in NWs such as periodic sidewall facets^[60] and twining.^[4] Recently, Schwartz and co-workers proposed a kinetic model to explain the oscillation of catalyst droplets in the growth of Si NWs,^[61] and using in situ TEM they directly observed jumping of droplets induced by the mismatch between catalyst size and NW diameter.^[62] Besides Si, such dynamics of catalyst droplets during the VLS growth have been observed in other NW materials like Al_2O_3 ,^[63] Ge,^[64,65] and GaP.^[66] In our experiments, when the Au catalyst particles are smaller than 100 nm, they might become unstable at the high growth temperature of 800 °C (see Figure S13c–f, Supporting Information), and their migration and pinning to the NC sidewall could initiate the growth of NW tips (Figure 4a–d).

From the thermodynamic point of view, both the NW surface energy and the liquid/solid interfacial energy should be dependent on the growth direction and the NW diameter. In order to provide further insights on the observed switching of growth direction, we adapt the model of Schmidt et al., where the free energy per circumference is a linear function of the NW diameter.^[56] Figure 4f shows a schematic of the catalyst-size-dependent free energies of growing NWs with different orientations. For the growth of [111]-oriented NWs, the free energy of interface per circumference is given by

$$f_{111} = \Delta z \sigma_{s,111} + a_{111} \sigma_{1s,111} r \tag{1}$$

where Δz is the interfacial thickness, $\sigma_{s,111}$ is the surface energy of [111]-oriented NWs, a_{111} is the geometrical parameter of [111]-oriented NWs, $\sigma_{is,111}$ is the liquid/solid interfacial energy of [111]-oriented NWs, and r is the radius of [111]-oriented

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$$f_{112} = \Delta z \sigma_{s,112} + a_{112} \sigma_{ls,112} r$$
⁽²⁾

$$f_{110} = \Delta z \sigma_{s,110} + a_{110} \sigma_{1s,110} r \tag{3}$$

The plot of free energies of growing [111]-, [110]-, and [112]-oriented NWs in Figure 4f actually assumes that $\sigma_{s,111} > \sigma_{s,112} > \sigma_{s,110}$ and $a_{111}\sigma_{ls,111} < a_{112}\sigma_{ls,112} < a_{110}\sigma_{ls,110}$. Our observations imply that above the critical NW diameter of 100 nm, $f_{110} > f_{112} > f_{111}$, or the [111] growth direction is energetically favored for NCs, while below the critical diameter, the order is reversed with f_{110} being the lowest, triggering the growth direction switching. Furthermore, the frequently observed coexistence of type-I and type-II nanostructures indicates that the free energies of growing [110]- and [112]-oriented NWs are quite close. Interestingly, a similar case was previously reported for Si NWs: when the size of the catalyst particles falls in a certain range, [110]- and [112]-oriented NWs grow concurrently due to the proximity of their free energies.^{55,56}



By systematically exploring the impact of the growth parameters, i.e., growth temperature (from 750 °C to 950 °C) and pressure (1 mbar and 30 mbar), we observed rich growth behavior of the In₂O₃ NWs. The detailed results are shown in Figure S16 (Supporting Information). Apart from the mixed type-I and type-II kinked nanostructures, three typical nanostructures are shown in Figure 5a-f. With a growth temperature of 800 °C and high growth pressure, [110]-oriented NWs are grown (Figure 5a,b), which is consistent with the previous reports.^[67,68] When the growth temperature is increased to 850 °C, both type-I kinked NC-NW nanostructures and [110]-oriented NWs are grown (Figure 5c,d). When the growth temperature is further increased to 900 °C, vertical NWs terminated by (100) and (111) facets are formed (see Figure 5e,f and Figure S17, Supporting Information). The disappearance of catalyst nanoparticles at the NW apexes is due to the enhanced migration and solubility of Au atoms at high growth temperatures.^[50,51,69]

More importantly, by fine-tuning the growth pressure, i.e., increasing the growth pressure to 30 mbar after growing the NCs at 1 mbar (see Figure S18, Supporting Information), we exclusively obtained type-I NC–NW nanostructures at the



Figure 5. Temperature- and pressure-dependent growth behavior of In_2O_3 nanostructures. a,b) SEM top-view and tilted-view (20°) images of In_2O_3 NWs grown on (111) YSZ substrate at 800 °C with a growth pressure of 30 mbar. [110], [101], and [011]-oriented NWs were grown on the substrate with an inclined angle of 55°. c,d) SEM top-view and tilted-view (20°) images of the kinked nanostructures grown at 850 °C with a growth pressure of 30 mbar. Both type-I kinked NC-NW nanostructures and [110]-oriented NWs were obtained. The arrows highlight the [110]-oriented NWs grown directly on the substrate. e,f) SEM top-view and tilted-view (20°) images of vertical In_2O_3 NWs grown at 900 °C with a growth pressure of 30 mbar. The [111]-oriented NWs are terminated by (100) and (111) facets. g,h) SEM top-view and tilted-view (20°) images of exclusive type-I kinked NC–NW nanostructures achieved by changing the growth pressure, i.e., first grown at 1 mbar for 6 h and then at 30 mbar for 4 h. Scale bars are a–h) 1 µm.



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growth temperature of 800 °C (Figure 5g,h). This result suggests that at a relatively high growth pressure of 30 mbar the [110]-oriented NWs might possess a lower free energy than the [112] ones within a wide diameter range (Figure 4g), thereby eliminating the growth of [112] transition segment in the kinked regions. Remarkably, in comparison to Figure 4f, only some slight changes of the y-axis intercepts, i.e., the surface energies of f_{112} and f_{110} , in Figure 4g are sufficient to account for the experimental observation that the [110]-oriented NWs are energetically favored than the [112] ones during the whole growth process. More knowledge on the surface and interface energies, which could be achieved via future measurements and theoretical calculations, may help further reveal the dependence of the NW morphology on parameters such as growth orientation, temperature, and pressure, which is however out of the scope of this experimental work. Down the same line, it should be noted that we cannot completely exclude the change of In content in the Au nanoparticles during the NW growth and its role in the switching of NW growth direction. Apparently, the free energies in Figure 4f,g depend on both the size and In content of the catalyst nanoparticles, and if the In content does change during the NW growth it is likely that both parameters reach the critical values when the switching of NW growth direction occurs.

Figure 6 summarizes the temperature- and pressuredependent growth behavior of the In_2O_3 nanostructures. Four representative nanostructures denoted as a–d have been obtained and discussed in detail here, while fine tuning the growth parameters in future works is expected to lead to an even richer growth behavior. The formation of these nanostructures is induced by the sensitive dependence of the catalyst nanoparticle dynamics and the free energy of the In_2O_3 NW orientation on the growth temperature and pressure. Furthermore,

3. Conclusions

In summary, our experiments revealed an unprecedented, rich growth behavior of In2O3 NWs. In particular, novel kinked NC-NW nanostructures were identified and characterized in detail, and their well-controlled morphology is different from previously reported oxide nanostructures. Our data unambiguously suggest that the switching of the growth direction of In₂O₃ NWs from [111] to [110] and [112] is induced by the sensitive dependence of the NW free energy on the size of the catalyst nanoparticles, which dynamically evolves during the growth process. This size-dominated mechanism distinguished our works from the previous ones, which underlies the observed reliable control of the nanostructure morphology. Such kinked oxide nanostructures may hold great promise for applications in electronic and sensing nanodevices. More importantly, the insights on the VLS growth mechanism of kinked nanostructures may be extended to other functional materials.

4. Experimental Section

Growth of In_2O_3 Nanostructure: The typical mixed type-I and type-II kinked NC-NW In_2O_3 nanostructures were grown on [111]-oriented YSZ substrates using the vapor transfer method in a horizontal furnace with controlled gas delivery and pumping.^[70,71] A mixture of In_2O_3 and graphite powder with weight ratio of 1:1 was used as the source and put at the center of the furnace quartz tube. The YSZ substrate was coated



Figure 6. Schematic summarizing the rich growth behavior of In_2O_3 nanostructures under tailored growth conditions. a) [110]-oriented NWs grow on a [111]-oriented YSZ substrate at a growth temperature of 800 °C and a growth pressure of 30 mbar. b) Vertical NWs terminated by (100) and (111) facets grow at a growth temperature of 900 °C and a growth pressure of 30 mbar. c) An exclusive type-I kinked NC–NW nanostructure can be obtained by increasing the growth pressure from 1 mbar to 30 mbar during the growth of NW tips. d) Mixed type-I and type-II kinked NC–NW structures are grown at a growth temperature of 800 °C and a growth pressure of 1 mbar.



with 1 nm Au films by sputtering and located 9 cm downstream from the source. Argon gas with a fixed gas flow of 10 sccm (standard cubic centimeters per minutes) was introduced as the carrier gas to transfer the In vapor from the source to the substrate. The pressure inside the tube was fixed at 1 mbar during the growth process. The furnace was heated up to 800 °C at a ramping rate of 50 °C min⁻¹. After growth, the argon gas was shut down and the furnace was cooled down naturally.

Characterization: The morphology of as-grown In₂O₃ nanostructures was examined by field emission scanning electron microscopy (FESEM, JEOL JSM-6700F). The conventional θ -2 θ XRD investigation was done in an X-ray diffractometer (Bruker D8, λ = 1.54184 Å). The high-resolution TEM (HRTEM) and electron diffraction experiments were carried out on a FEI Tecnai G2 30 UT transmission electron microscope operated at 300 kV. Data for tomographic reconstruction were acquired using a FEI Tecnai microscope, operated in HAADF-STEM mode at 200 kV acceleration voltage. Images were acquired at a 2° interval, from a +70° to -76° tilt angle for the type-I structure, and from +74° to 56° tilt angle for the type-II structure. Tomographic reconstruction was performed in the FEI inspect 3D software using 50 SIRT iterations. Visualization was performed using the Amira software package.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

S.T. gratefully acknowledges the FWO Flanders for a post-doctoral scholarship. This research was partially supported by King Abdullah University of Science and Technology (KAUST). The authors acknowledge Maria Meledina for her help with the tomographic reconstruction.

Received: January 10, 2016 Revised: February 26, 2016 Published online: April 25, 2016

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