Network array of zinc oxide whiskers

Chen, B. J.; Yu, M. B.; Zhang, X. H.; Chua, S. J.; Xu, Chunxiang; Sun, Xiaowei; Dong, Zhili

2005

Xu, C., Sun, X., Chen, B. J., Dong, Z. L., Yu, M. B., Zhang, X. H., et al. (2005). Network Array of Zinc Oxide Whiskers. *Nanotechnology*, 16(1), 70-73.

<https://hdl.handle.net/10356/95570>

<https://doi.org/10.1088/0957-4484/16/1/015>

© 2005 Institute of Physics Publishing. This is the author created version of a work that has been peer reviewed and accepted for publication by *Nanotechnology*, Institute of Physics Publishing. It incorporates referee's comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [DOI: <http://dx.doi.org/10.1088/0957-4484/16/1/015>].

Downloaded on 26 Apr 2023 15:00:47 SGT

Network array of zinc oxide whiskers

C X Xu^{1,2}, X W Sun^{1,6}, B J Chen¹, Z L Dong³, M B Yu⁴, X H Zhang⁵ and S J Chua⁵

¹ *School of Electric and Electronic Engineering, Nanyang Technological University, Nanyang Avenue, 639798, Singapore*

² *Department of Electronic Engineering, Southeast University, Nanjing 210096, People's Republic of China*

³ *School of Materials Engineering, Nanyang Technological University, 18 Nanyang Drive, 639798, Singapore*

⁴ *Institute of Microelectronics, 11 Science Park Road, 117684, Singapore*

⁵ *Institute of Materials Research Engineering, 3 Research link, 117602, Singapore*

⁶ *Author to whom any correspondence should be addressed.*

E-mail: exwsun@ntu.edu.sg

Abstract

A zinc oxide (ZnO) whisker network array with sixfold symmetry was fabricated on ZnO-buffered (0001) sapphire substrate by the vapour-phase transport method using a mixture of zinc oxide and graphite powders as source materials and patterned gold as catalyst. From the ZnO buffer layer, hexagonal ZnO nanorods with identical in-plane structure grew epitaxially along the [0001] orientation to form vertical stems. The branches grew horizontally from six side-surfaces of the vertical stem along $[01\bar{1}0]$ and other equivalent directions. Most whiskers were confined along the six preferential orientations and interconnected with each other to form a regular network structure. The growth mechanism is discussed.

One-dimensional nanostructural materials have attracted great interest because of their unique properties and promising applications in electronics, photonics and biochemistry. So far, various one-dimensional nanostructures, such as metal nanowires [1], carbon nanotubes [2] and one-dimensional oxide semiconductors [3], have been fabricated successfully. The remaining challenge is how to organize the nanostructural materials into functional nanodevices, such as nanotransistors, building blocks and nanowebs. Great endeavour has been made to investigate the critical issue of assembling. Self-assembly is an economic and convenient approach to fabricated nanostructural networks. So far, the alternative self-assembling approaches include diffusion-controlled aggregation [4], nanoclusters [5] and template-assisted growth [6], atomic adsorption along stress lines on flat surface [7], dealloying a chemically etched Al-Si thin film [8] and surfactant-induced mesoscopic organization [9]. Very recently, Graham *et al* [10] reported a rapid self-assembly for a two-dimensional network of gallium oxide nanowires and nanotubes using hydrogen/oxygen plasma exposure of gallium-droplet-covered substrate. Although various nanomaterials have been employed in the above reports, all nanowebs were random. To obtain regular structure, Lieber's group [11] has developed a fluidic alignment technology to assemble one-dimensional nanostructures. Electron beam lithography [12] and scanning probe microscopy [13] have

also been utilized to prepare the nanowebs through the so-called top-down approach. Though various desired structures could be fabricated in principle through these advanced tools, the fabrication process is relatively slow and inconvenient.

Recently, nanostructural zinc oxide (ZnO) has been becoming a hot topic because of its fantastic characteristics and its great potential applications to optoelectronic nanodevices, such as nanolasers, nanosensors and nanoscale field effect transistors. So far, various ZnO nanostructures such as nanowires [14], nanotubes [15], nanoribbons [16], nanopins [17] and hierarchical nanorods [18, 19] have been fabricated. In this paper, we shall present a sixfold symmetric network array of ZnO whiskers fabricated on sapphire substrate through vapour-phase transport assisted by an [0001]-oriented ZnO buffer layer and Au-patterned catalyst. To our knowledge, this is the first report on a ZnO whisker network with regular structure. The synthesized ZnO network with regular structure can be used for future electronic or photonic interconnects.

ZnO has been used previously as a buffer layer to grow epitaxially GaN thin film [20, 21], indium tin oxide thin film [22] and aligned ZnO nanorod arrays [23] along the [0001] orientation on various substrates. In the present case, a ZnO thin film was employed as a buffer to prepare a ZnO whisker array with sixfold symmetric network structure. The ZnO buffer layer was fabricated on (0001) sapphire by filtered cathodic vacuum arc (FCVA) [24, 25] technology under an oxygen background pressure of 8×10^{-4} – 2×10^{-3} Torr, using metallic zinc as a target. The substrate temperature was kept at 400 °C, the arc current was 60 A and the toroidal magnetic field is around 40 mT.

Using a copper grid with 400 mesh as the mask, which is often used as a sample holder for transmission electron microscopy (TEM), a patterned array of thin gold film was prepared on the ZnO buffer layer by thermal evaporation. The ZnO whisker network was fabricated on the patterned substrate by the vapour-phase transport method [14, 17]. The growth was carried out in a quartz tube using a mixture of ZnO and graphite powders as source materials. The source temperature was 1100 °C and the growth temperature was about 700 °C. A white layer of product was observed on the collector after sintering in air for 30 min.

Figure 1 shows the scanning electron microscopy images of the product. It can be seen from figure 1(a) that the surface was covered with patterned arrays of ZnO fibres corresponding to the inserted gold pattern (insert of figure 1(a)). This indicates a position-selected growth from the patterned area of Au, which acts as the catalyst. From the enlarged SEM images of figure 1(b), it is clearly seen that all fibres grow along six specific directions parallel to the substrate surface. The size of the fibres is about 500–800 nm in diameter and several tens of microns in length. Each cell is composed of sixfold symmetric branches that interconnect adjacent cells to form a network with regular structure. The morphology of the centre of a cell as circled in figure 1(b) is presented in an enlarged SEM image of figure 1(c). Whiskers are observed and each one of them is composed of a stem with hexagonal cross-section and several branches grown radially around the sides of the stem. It is noted that the stems are perpendicular to the substrate, and the branches from either the same or different stems are parallel to the substrate along the pre-defined sixfold symmetric directions as indicated by the arrows in figure 1(c). Seen from the regular network structure in figure 1, the ZnO stems grown from the ZnO buffer layer must have identical in-plane crystal orientations. So the network array shown in figure 1 demonstrates indirectly the epitaxial growth of the ZnO buffer on the sapphire substrate, and the ZnO vertical stem on the ZnO buffer [23].

Figure 2 shows the high resolution transmission electron microscopy (HRTEM) images taken from different parts of a nanowhisker inset between figures 2(a) and (b). The image of figure 2(a) shows the lattice fringes of the stem. The d -spacing of 0.26 nm matches with that of the (0002) planes of the wurtzite ZnO. The lattice fringes of the branch fibre are presented in figure 2(b), where the d -spacing of 0.28 nm corresponds to the interplane spacing of the (01 $\bar{1}$ 0) facets. The crystal structures of the ZnO

whisker are further confirmed by the selected area electron diffraction (SAED) patterns. Shown as the inset between figures 2(a) and (b), the diffraction spots present the same distribution although they were taken from the above two parts. The two indexed bright diffraction spots in mutually orthogonal directions correspond to the planes of (0002) and (01 $\bar{1}$ 0) and the zone axis is [2 $\bar{1}$ $\bar{1}$ 0]. These results demonstrate that the hexagonal rods grew epitaxially along the [0001] direction from the ZnO buffer layer to form vertically aligned stems with hexagonal structure, and the branch fibres grew epitaxially from the side-surfaces along (01 $\bar{1}$ 0) orientations to form a sixfold symmetric structure.

Figure 3 shows the XRD patterns of the ZnO buffer layer and the whisker network. Only the (0002) peak was observed from the ZnO thin film, which demonstrates that the ZnO buffer layer grow along the [0001] direction with good crystal quality. The XRD spectrum illustrates multi-peaks after the ZnO network structure was fabricated on the buffer layer. As indexed in figure 3, all diffraction peaks match the wurtzite ZnO structure with the lattice constants of $a = 3.250 \text{ \AA}$ and $c = 5.207 \text{ \AA}$.

On symmetric hierarchical nanostructures, Gao *et al* [19, 26] have reported nanopropellers and nanowire–nanoribbon junction arrays of ZnO fabricated by thermal evaporation of a mixture of ZnO and SnO, where metallic tin decomposed from SnO served as catalyst. Lao *et al* [18, 27] have investigated the ZnO–In₂O₃ hetero-structural nanostructures controlled by varying the proportion of In₂O₃ to ZnO powders in the starting material. The individual whiskers in their reports had symmetry; however, the whole whiskers were still distributed randomly on the collector. In the present case, we show a network with regularity constructed by many homogenous ZnO whiskers with sixfold symmetric hierarchical structure. The growth process is determined by means of the vapour–liquid–solid (VLS) mechanism. Vapours of zinc and zinc suboxide are generated in the source region due to reduction of the ZnO powders by graphite powders. The vapour transports to the low temperature region and condenses on the collector surface, and reacts with catalyst Au to form liquid droplets of Zn–Au alloy as nuclei that are favourable to adsorb the incoming vapour; meanwhile, ZnO whisker structures are produced due to the oxidation of Zn and ZnO_x ($x < 1$). According to this mechanism, the initial growth stage is very important for the whole growth process and the nanosized droplets play roles as nucleation seeds. The selected growth position depends on the sites of catalyst. So the patterned ZnO nanofibre arrays were obtained on the Au-patterned substrate as shown in figure 1. Figure 4 shows the SEM image of the sample in the initial growth stage. The morphology illustrates the dispersed nanodots distributed on the Au-patterned sites. It can be seen from the enlarged SEM image (figure 4(b)) that the nanodots have a tendency to grow upwards although they are so small. These nanodots act as nuclei and grow epitaxially up to form ZnO nanorod stems due to the matched lattice constant between the growing ZnO nanorod and the buffer layer. Figure 4 demonstrates the two-step growth process of the hierarchical structures. In other words, the branch fibres grew after the nanorod stem. The nucleation of the branches is not completely clear now. It is assumed that some rough sites appear on the side-surfaces due to the vapour random fluctuation in the growth period of the stem nanorods, which are likely to become nucleation points in the following epitaxial growth due to a self-catalysed process [28]. In other words, the incoming Zn or ZnO_x vapour readily condenses into nano-droplets on the randomly distributed sites on the six side-surfaces of the existing ZnO nanorod stem; therefore, the branches do not always appear on all sides for each whisker. In a Au-patterned cell region, however, all of the branch fibres from either the same or different stems are confined to the six symmetric directions because they grow epitaxially from the self-catalysed positions on the six equivalent side-surfaces.

Figure 5 gives a schematic diagram for the growth process of the ZnO hierarchical structure and the network. The ZnO stem has a hexagonal cross-section bounded by six equivalent crystallographic planes of $\pm(1\bar{1}00)$, $\pm(10\bar{1}0)$ and $\pm(01\bar{1}0)$. While the rod stems grew up, the branch fibres grew around the stem along [10 $\bar{1}$ 0] and the other five equivalent orientations from the above six facets. The intercross angle between any adjacent branches is 60° so the top-view image of the hierarchical whisker has a sixfold symmetric structure although the branches possibly appear at different sites on the side-surfaces, as shown

in figures 5(a) and(b). With a patterned structure of catalyst, the hierarchical whiskers interconnect with each other to form a regular network (figure 5 (c)). It is believed that the epitaxial ZnO buffer layer is very important for the regularity of the network structure. The buffer layer not only provided a lattice-matched substrate for vertical growth of hexagonal ZnO nanorods, but also, more importantly, transferred the crystal structure of the sapphire substrate to the ZnO nanorod stems with identical in-plane orientation, from which sixfold symmetric networks are formed with regularity.

In summary, employing an epitaxial ZnO buffer layer on sapphire, a regular network of ZnO whiskers was fabricated by the vapour-phase transport method using a mixture of ZnO and graphite powders as source materials and patterned Au as catalyst. From the buffer layer, the ZnO nanorod grew epitaxially along the [0001] orientation to form a stem with hexagonal cross-section. During the nanostem growth, the branch nanofibres grew around the stem from its six side surfaces to form a hierarchical structure with sixfold symmetry. The [0001]-oriented ZnO buffer layer provided a lattice-matched substrate and ensured the uniform growth directions. The ZnO network array with regular structure may be used for electronic or photonic interconnects and other advanced applications, such as array waveguides, optical interconnects and optical couplers.

Acknowledgment

Sponsorships from the Research Grant Manpower Fund (RG51/01) of Nanyang Technological University and a Science and Engineering Research Council grant (No 0421010010) from the Agency for Science, Technology and Research (A*STAR), Singapore, are gratefully acknowledged.

References

- [1] Kondok Y and Takayanagi K 2000 *Science* **289** 606
- [2] Vigolo B, Penicaud A, Coulon C, Sauder C, Pailler R, Journet C, Bernier P and Poulin P 2000 *Science* **290** 1331
- [3] Dai Z R, Gole J L, Stout J D and Wang Z L 2002 *J. Phys. Chem. B* **106** 1274
- [4] Roder H, Hahn E, Brune H, Bucher J P and Kern K 1993 *Nature* **366** 141
- [5] Bromann K, Félix C, Brune H, Harbich W, Monot R, Buttet J and Kern K 1996 *Science* **274** 956
- [6] Braun E, Eichen Y, Sivan U and Yoseph G B 1998 *Nature* **391** 775
- [7] Kipp A L, Brandt J, Tarcak L, Traving M, Kreis C and Skibowski M 1999 *Appl. Phys. Lett.* **74** 3053
- [8] Paulose M, Grimes C A, Varghese O K and Dickey E C 2002 *Appl. Phys. Lett.* **81** 153
- [9] Messer B, Song J H, Huang M, Wu Y Y, Kim F and Yang P D 2000 *Adv. Mater.* **12** 1526
- [10] Graham U M, Sharma S, Sunkara M K and Davis B H 2003 *Adv. Funct. Mater.* **13** 567
- [11] Huang Y, Duan X, Wei Q and Leiber C M 2001 *Science* **291** 639
- [12] Cumming D R S, Thoms S, Beaumont S P and Weaver J M R 1996 *Appl. Phys. Lett.* **68** 322
- [13] de Pablo P J, Navarro C G, Gil A, Colchero J, Martinez M T, Benito A M, Maser W K, Herrero J G and Baro A M 2001 *Appl. Phys. Lett.* **79** 2797
- [14] Xu C X, Sun X W, Chen B J, Shum P, Li S and Hu X 2004 *J. Appl. Phys.* **95** 661
- [15] Wu J J, Liu S C, Wu C T, Chen K H and Chen L C 2002 *Appl. Phys. Lett.* **81** 1312
- [16] Arnold M S, Avouris P, Pan Z W and Wang Z L 2003 *J. Phys. Chem. B* **107** 659
- [17] Xu C X and Sun X W 2003 *Appl. Phys. Lett.* **83** 3806
- [18] Lao J Y, Wen J G and Ren Z F 2002 *Nano Lett.* **2** 1287
- [19] Gao P X and Wang Z L 2004 *Appl. Phys. Lett.* **84** 2884
- [20] Sun X W and Kwok H S 1999 *J. Appl. Phys.* **86** 408
- [21] Nanhhas A, Hong K K and Blachere J 2001 *Appl. Phys. Lett.* **78** 1511
- [22] Sun X W, Wang L D and Kwok H S 2000 *Thin Solid Films* **360** 75
- [23] Park W I, Kim D H, Jung S W and Yi G C 2002 *Appl. Phys. Lett.* **80** 4232

- [24] Xu X L, Lau S P and Tay B T 2001 *Thin Solid Films* **398/399** 244
- [25] Chen B J, Sun X W and Tay B K 2004 *Mater. Sci. Eng. B* **106** 300
- [26] Gao P and Wang Z L 2002 *J. Phys. Chem. B* **106** 12653
- [27] Wen J G, Lao J Y, Wang D Z, Kyaw T M, Foo Y L and Ren Z F 2003 *Chem. Phys. Lett.* **372** 717
- [28] Wang Z L, Kong X Y and Zuo J M 2003 *Phys. Rev. Lett.* **91** 185502

List of figures

- Figure 1   The network structure of ZnO whiskers. (a) and (b) SEM images of the network with low and high magnifications respectively. The inset in (a) shows the gold pattern on the ZnO buffer layer. (c) The morphology of the centre area of a pixel circled in (b). The arrows drawn in (c) indicate the growth directions of the branches parallel to the substrate.
- Figure 2   HRTEM images of the inserted stem (a) and the branch (b) and the corresponding SAED pattern.
- Figure 3   XRD patterns of ZnO buffer layer and as-grown ZnO whisker network.
- Figure 4   SEM images of the ZnO network in the initial growth stage with low (a) and high (b) magnifications.
- Figure 5   Schematic diagram of formation and structure of the hierarchical ZnO whisker (a), (b) and the network (c).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5