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Self-organized nanocomb of ZnO fabricated by Au-catalyzed vapor-phase transport

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Abstract

Based on a vapor-phase transport process, self-organized nanocomb structures of ZnO were fabricated on Au-coated Si substrate by employing a mixture of ZnO and graphite powders as source materials. The morphology of the product showed a ribbon-like stem and nanorod array aligned evenly along one side of the nanoribbon. It was found that the nanoribbon grew mainly along $[1\ 0\ \bar{1}\ 0]$ direction and the self-assembled branching nanorods grew epitaxially along $[0\ 0\ 0\ 1]$ orientation from the $(0\ 0\ 0\ 2)$ plane of the stem. The growth process was analyzed in detail.

Keywords: B1. Nanocomb; A1. Self-Organized; A2. Vapor-phase transport; A2. Vapor-liquid-solid mechanism

1. Introduction

With the demonstration of room-temperature excitonic nanolaser [1–3] and nanowire based field effect transistor [4,5], nanostructural ZnO has attracted one's great attention because of its wide direct bandgap (3.34 eV), strong excitonic binding energy (60 meV) [6], and its applications in functional optoelectronic nanodevices such as ultraviolet (UV) laser and nanosensors. So far, various ZnO nanostructures, such as nanowire, nanoribbon, nanocable and nanotube, have been fabricated by different methods such as vapor-phase transport (VPT) [1–5,7,8], metal-organic vapor-phase epitaxy (MOVPE) [9], aqueous thermal decomposition [10] and electrochemical deposition [11]. Among these methods, VPT is the simplest, and hence, the most widely utilized method [1–5,7,8]. Besides typical one-dimensional nanostructures, it has been employed to fabricate novel nanostructural ZnO such as nanopins [12], multipod nanorods [13] and hierarchical nanorods [14]. Based on VPT process, Yang and his co-

researchers [15,16] have synthesized comb-like ZnO nanostructures on silicon substrate using metal Zn powder as source materials and oxygen/ argon mixture as carrier gas. The self-organized nanocomb has been successfully employed as a Fabry–Perot optical cavity to obtain UV-laser array [15], however, the growth mechanism of the nanostructure is not clear yet. In this paper, we report the fabrication of ZnO nanocombs by means of gold-catalyzed VPT method using a mixture of ZnO and graphite powders as source materials. The growth process will also be investigated through the analysis of the microstructure.

2. Experimental procedure

ZnO nanostructures were prepared by sintering a mixture of ZnO and graphite powders in air. ZnO and graphite powders with the weight ratio of 1:2 were thoroughly grounded together, and then placed at the bottom of a slender quartz tube. A gold-coated silicon slice was put into the same quartz tube away from the source materials as a collector. Then the slender quartz tube was pushed into a tube furnace. The mixture was heated at 1100 °C for 30min. The temperature of the substrate area was about 750 °C due to the temperature gradient in the tube furnace. After sintering, the samples were taken out from the furnace into air for rapid cooling. A white layer product was observed on the substrate. No gas was introduced into the tube furnace during the entire fabrication process.

The morphology of the product was examined by scanning electron microscopy (SEM). The crystal structure of the samples was characterized by X-ray diffraction (XRD) using copper $K_{\alpha 1}$ radiation. A JEOL 3010 High-resolution transmission electron microscopy (HRTEM) operated at 300 kV was employed to characterize the lattice structure of the products.

3. Result and discussion

Fig. 1 shows the SEM images of the nanostructural ZnO. It is clearly seen that a row of nanorods grow along one side of a nanoribbon to form a comb-like nanostructure. High yield of the nanocomb structural ZnO was obtained. It is noted that the nanorod branches have uniform diameters and are evenly distributed along one side of stem. The ribbon-like stem of the nano-combs is about 100 nm thick and several tens of microns long. The diameter of the branching rods is about 50~100 nm, the length is about several microns and the spacing between two adjacent nanorods is about 400~800 nm. It is also noted that each nanocomb has a trapezoid profile. For each nanocomb, the width of the nanoribbon and the length of the corresponding branching nanorods gradually decrease from one end to another of the nanoribbon. The XRD pattern of the nano-combs is presented in Fig. 2. Every diffraction peak matches with wurtzite ZnO with lattice constants of $a = 3.250\text{\AA}$ and $c = 5.207\text{\AA}$.

Fig. 3 illustrates the TEM images of the nanocomb at low and high magnifications. The HRTEM picture of Fig. 3(b) taken from a branching nanorod clearly shows the lattice planes. The d-spacing between any two adjacent lattice fringes is 0.26 nm which matches that of the (0 0 0 2) planes of the wurtzite ZnO. It demonstrates that the nanorods grew along [0 0 0 1] direction. Fig. 3(c) presents the HRTEM image of the edge of the nanoribbon viewing from zone axis $[\bar{1} 2 \bar{1} 0]$ orientation. As shown in Fig. 3(c), the length direction of the nanoribbon

corresponds to that of $[0\ 0\ 0\ 1]^*$ in reciprocal space, or $[0\ 0\ 0\ 1]$ in real space, and the width direction corresponds to that of $[1\ 0\ \bar{1}\ 0]^*$ in reciprocal space, or $[1\ 0\ \bar{1}\ 0]$ in real space. The lattice structure demonstrates that the nanoribbons grew in the orientation of $[1\ 0\ \bar{1}\ 0]$ along the length direction and in the orientation of $[0\ 0\ 0\ 1]$ along the width direction. This result is consistent with other reports [17–19] on nanoribbons or nanobelts. Under catalyst-free conditions, Pan [17] and Lee et al. [18] achieved a similar morphology by evaporating ZnO powder at 1400 and 1380 °C, respectively. Their TEM and SAED results demonstrated that the nanoribbons grew along $[0\ 0\ 0\ 1]$ direction and were enclosed by $\pm(2\ \bar{1}\ \bar{1}\ 0)$ and $\pm(0\ 1\ \bar{1}\ 0)$ facets, or grew along $[0\ 1\ \bar{1}\ 0]$ direction and were enclosed by $\pm(0\ 0\ 0\ 1)$ and $\pm(2\ \bar{1}\ \bar{1}\ 0)$ facets. By using ZnCl_2 as the source material, ZnO nanoribbons were also obtained by Zhang et al [19]. Their TEM and SAED demonstrated that the nanoribbons grew along $[0\ 1\ \bar{1}\ 0]$ direction.

The growth mechanism of ZnO nanocombs is not clear yet although the hierarchical ZnO nanostructures including nanocombs have been reported recently [14–16,20,21]. It seems, according to the reported results, that the growth process of the self-assembled nanostructures is composed of two steps. The core nanowire or nanoribbon formed first, and then the branching nanorods grew from the new nucleation sites creating at the sides of the core to form 2-, 4- and 6-fold symmetrical hierarchical nanostructures. In the present case, the branches only grew along one side of the nanoribbon. The HRTEM images in Fig. 3 have demonstrated that the $[0\ 0\ 0\ 1]$ orientation is the preferred growth directions for both branching rods and stem ribbons. The width of the nanoribbons grew along $[0\ 0\ 0\ 1]$ orientation and the nanorods self-assembled epitaxially along the same direction.

It is well accepted that the nanostructure growth process of catalyst-assisted vapor-phase transport is based on a vapor–liquid–solid (VLS) mechanism [1]. Based on the VLS mechanism, the initial growth process is very important to the formation of the final morphology. The formation of hierarchical crystal usually results from rapid crystallization under high supersaturation [15], which is satisfied with our present experimental conditions. Due to the high ratio of carbon in the source, ZnO was rapidly reduced into metallic zinc producing a high supersaturation at high temperature, and then quickly condensed and oxidized into ZnO nanocrystals on the substrate surface at lower temperature. Fig. 4 shows the **SEM** images of nanocombs fabricated by reducing the growth time. It can be seen from Fig. 4(a) that the flat nuclei formed in the initial growth stage and the short nanorods grew from one side of the ribbons. With an increase of the growth time, both the branches and the stems grew up, forming comb-like structures, as shown in Figs. 4(b) and 5(c). Consistent with the growth progress, Fig. 5 shows the SEM and TEM images of the intersection part between the branching nanorods and the stem of the nanocomb growing for 30 min. From the SEM of Figs. 1(a) and 5(a), the roots of the nanorods embedding inside the stem (ribbon) can be clearly seen. The TEM image of Fig. 5(b) shows a light contrast rod area between two highlighted lines. It also illustrates a root of the branching nanorod imbedded in the ribbon.

In general, the growth velocity along $[0\ 0\ 0\ 1]$ direction of ZnO is faster than along other directions. However, according to the reported nanoribbons [17–19] and our above TEM results, the nanoribbons formed in high vapor pressure, and grew mainly along $[1\ 0\ \bar{1}\ 0]$ direction and closed by $(0\ 0\ 0\ 2)$ lattice planes. This indicated that the growth velocity along

the $[1\ 0\ \bar{1}\ 0]$ direction was faster than that along $[0\ 0\ 0\ 1]$ direction for nanoribbons. Based on this assumption, a growth model of the nanocomb is proposed in Fig. 6(a). Trapezium ribbons should be observed due to the different growth speed along $[1\ 0\ \bar{1}\ 0]$ and $[0\ 0\ 0\ 1]$ orientations. During the nanoribbon growth, the branching nanorods grew along $[0\ 0\ 0\ 1]$ direction. For a nanocomb, the length of the branching nanorods should become shorter with a decrease in the width of the stem nanoribbon because they were formed later. As shown in Fig. 6(b), the trapezium morphology of the nanocombs fabricated in the present experiment is consistent with the model purposed. It is also noted that some nanocombs have two groups of branches, as shown in Fig. 7(a). As discussed above, the longer nanorods should grow with the nanoribbon stem from the beginning of growth. However, the shorter group of nanorods in Fig. 7(a) might result from new nuclei formed along the side of the stem.

The mechanism of the formation of the evenly distributed branching nanorods is unclear. In Wen's report [21] the three-dimensional self-assembled ZnO-based nanoscale heterostructures have been synthesized through the addition of alloying elements (indium and tin). It was found that the side banding grew only in the presence of alloying elements. The alloying content was continuously segregated to the facets of the central core. The alloy rich layer of the facets became the nucleation sites for the subsequent growth of side branches. In present case, it is assumed that the nuclei of the nanoribbons were formed in the initial growth stage. The Zn–Au alloy droplets condensed spontaneously in order along the $(0\ 0\ 0\ 2)$ plane of the nanoribbons and acted as the nucleation sites, and the branching nanorods grew epitaxially along $[0\ 0\ 0\ 1]$ direction.

The self-organized nanocomb structures imply some applications. By using the similar structures, UV laser array has been observed by Yan et al. [15]. The aligned nanorod arrays are also expected to enable assembled photonic crystals, laser interference/couplers, nanoscaled electromechanical system (NEMS), and crossbar junctions [15]. It can be seen from the SEM images of Figs. 1(c) and 7(a) that the nanorods have sharp tips. This suggests their application in scanning probes or sensor arrays. The two groups of nanorod arrays shown in Fig. 7(a) might have an implication in more functional nanodevices. It is noted from Fig. 7 that the two nanocombs are orthogonal crossed and contacted. These configurations build bridges for communication between the different nanorod arrays, and maybe used in future networks.

4. Conclusion

In summary, the nanocomb structural ZnO arrays have been fabricated by controlling the conditions of the vapor-phase transport. The products show the typical wurtzite crystal structure. The growth process is explained by means of a VLS mechanism. In the initial growth stage, the nucleation of the nanoribbons occurred in the highly supersaturated vapor, and then grew along $[1\ 0\ \bar{1}\ 0]$ in length direction and along $[0\ 0\ 0\ 1]$ in width direction, while the nuclei of the nanorods self-organized evenly in the surface of $(0\ 0\ 0\ 2)$ and grew epitaxially along $[0\ 0\ 0\ 1]$ orientation to form the aligned branch arrays along one side of the nanoribbon stem. This spontaneous ordered nanostructure of ZnO implies some novel applications for nanoscaled optoelectronic devices, sensors and networks.

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References

- [1] M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, *science* 292 (2001) 1897.
- [2] J. Johnson, H. Yan, R. Schaller, L. Haber, R. Saykally, P. Yang, *J. Phys. Chem. B* 105 (2001) 11387.
- [3] X.W. Sun, S.F. Yu, C.X. Xu, C. Yuen, B.J. Chen, S. Li, *Jpn. J. Appl. Phys.* 42 (2003) L1229.
- [4] H. Kind, H. Yan, B. Messer, M. Law, P. Yang, *Adv. Mater.* 14 (2002) 158.
- [5] M.S. Arnlid, P. Avouris, Z.W. Pan, Z.L. Wang, *J. Phys. Chem. B* 107 (2003) 659.
- [6] X.W. Sun, H.S. Kwok, *J. Appl. Phys.* 86 (1999) 408.
- [7] C.X. Xu, X.W. Sun, B.J. Chen, C.Q. Sun, B.K. Tay, S.X. Li, *Chem. Phys. Lett.* 20 (2003) 1319.
- [8] C.X. Xu, X.W. Sun, B.J. Chen, P. Shum, S. Li, X. Hu, *J. Appl. Phys.* 95 (2004) 661.
- [9] W.I. Park, D.H. Kim, S.W. Jung, G.C. Yi, *Appl. Phys. Lett.* 80 (2002) 4323.
- [10] L. Vayssieres, K. Keis, A. Hagfeldt, S.E. Lindquist, *Chem. Mater.* 13 (2002) 4365.
- [11] M.J. Zhang, L.D. Zhang, G.H. Li, W.Z. Shen, *Chem. Phys. Lett.* 363 (2002) 123.
- [12] C.X. Xu, X.W. Sun, *Appl. Phys. Lett.* 83 (2003) 3806.
- [13] V.A.L. Roy, A.B. Djurisic, W.K. Chan, J. Gao, H.F. Liu, C. Surya, *Appl. Phys. Lett.* 83 (2003) 141.
- [14] J.Y. Lao, J.G. Wen, Z.F. Ren, *Nano Lett* 2 (2002) 1287.
- [15] H. Yan, R. He, J. Johnson, M. Law, R.J. Saykally, P. Yang, *J. Am. Chem. Soc.* 125 (2003) 4728.
- [16] H. Yan, R. He, J. Pham, P. Yang, *Adv. Mater.* 15 (2003) 402.
- [17] Z.W. Pan, Z.R. Dai, Z.L. Wang, *Science* 219 (2001) 1947.
- [18] J.S. Lee, K. Park, M.I. Kang, I.W. Park, S.W. Kim, W.K. Cho, H.S. Han, S. Kim, *J. Crystal Growth* 252 (2003) 565.
- [19] J. Zhang, W. Yu, L. Zhang, *Phys. Lett. A* 299 (2002) 276.

- [20] P. Gao, Z.L. Wang, J. Phys. Chem. B 106 (2002) 12653.
- [21] J.G. Wen, J.Y. Lao, D.Z. Wang, T.M. Kyaw, Y.L. Foo, Z.F. Ren, Chem. Phys. Lett. 372 (2003) 717.

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Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7