

Tower-like structure of ZnO nanocolumns

Ping'an Hu, Yunqi Liu,* Xianbiao Wang, Lei Fu and Daoben Zhu*

Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, P. R. China. E-mail: liuyq@iccas.ac.cn; Fax: 86-10-62559373

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The tower-like structure of ZnO nanocolumns grows normal to alumina substrates *via* pyrolysis and oxidation of ZnS, and is formed by stacking of ZnO nanocrystals layer upon layer.

Since the discovery of carbon nanotubes,¹ one-dimensional (1-D) nanomaterials have stimulated wide interest due to the fundamental effect of their size and dimensionality on physical and chemical properties as well as their application in nanoelectronics and optics.² Many efforts have been made to synthesise one-dimensional materials with various structures and compositions *via* templates using carbon nanotubes³ or porous alumina,⁴ a vapor–liquid–solid (VLS) process,⁵ kinetic control solution growth⁶ and self-assembly.⁷ ZnO is a versatile material with excellent properties in applications such as transparent conductive films,⁸ varistors,⁹ piezoelectric devices¹⁰ and electronic transducers.¹¹ Moreover, ZnO exhibits a wide direct bandgap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV, which is suitable for application in short-wave optics. Owing to their promising applications in optical nanodevices, one-dimensional ZnO nanostructures with various morphologies including nanowires,¹² nanobelts,¹³ and nanotubes¹⁴ have been prepared. Here, we report a new nanostructure of ZnO that has a stacking structure, which is different from the 1-D nanostructures previously reported.

The tower-like ZnO nanocolumns grew in a gas flow reactor consisting of a high temperature tube furnace with a quartz tube and an independent temperature controller. The substrate used for growth of ZnO nanocolumns is a single crystalline (110) sapphire polished with a miscut value within $\pm 0.5^\circ$. A quartz boat with 0.5 g ZnS powder was placed in the region where the temperature was about 850 °C, and the substrate was placed downstream at a distance of 15 cm from the ZnS powder. Under a constant flow of a mixed gas composed of 200 ml min⁻¹ Ar and 5 ml min⁻¹ O₂, the furnace was heated to 950 °C, and held at this temperature for 4 h. The wool-like white products were found on the substrate.

The products were structurally characterized by X-ray diffraction (XRD, Rigaku Dmax2000, CuK α). Fig. 1 shows a typical XRD pattern of well aligned ZnO tower-like nano-

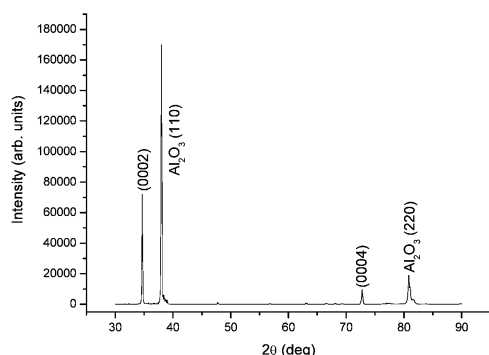


Fig. 1 A typical X-ray diffraction pattern of the as-prepared products, showing a preferred growth direction along the *c*-axis.

columns grown on the (110) plane of a single crystalline sapphire. Two peaks are indexed as (0002) and (0004) of the wurtzite structure of ZnO, revealing that the nanocolumns are preferentially oriented along the *c*-axis. No characteristic peaks from impurities, such as ZnS and Zn, were detected.

The morphologies and chemical composition of the products were characterized using a scanning electron microscope (SEM, JSM-6700F) equipped with an Oxford energy dispersive X-ray detector (EDX, INCA300). The as-prepared products were determined to be composed of zinc and oxygen with the atomic ratio of about 1 : 1 by EDX analysis. As shown in Fig. 2a, which is a low magnification SEM image of the tower-like ZnO nanocolumn arrays, these novel ZnO nanocolumns with lengths of 2–3 μm grew along the direction perpendicular to the substrate in the well distributed mode, and their morphologies are irregular. Each nanocolumn becomes gradually thinner to form a circular nanorod showing impressive layered structures. More distinct layered structures are seen at the top segments where the structure is transformed from a stacking structure to a thinner nanorod. These nanorods, with uniform diameters of 100–150 nm and a length of 500 nm, grew from the centre of the (0002) plane of hexagonal ZnO nanocrystals. An individual top segment is shown in Fig. 2b; the impressive layered structure seems to be formed by piling up nanocrystals with gradually decreased areas layer upon layer in a determinate mode. Interestingly, a very small crystal exhibiting white due to contrast grew out from the top of the nanorod. A similar phenomenon can also be seen in some of the products (Fig. 2a and Fig. 3).

Higher magnification SEM images shown in Fig. 3 reveal various morphologies of the ZnO nanocolumns. Fig. 3a indicates that the nanocolumns grew by themselves normal to the substrate. The lower segments of the nanocolumns with no clear layered structure exhibit an irregular elliptic cylinder structure, while the upper ones possess a distinct stair structure. More distinct layered structures are seen in Fig. 3b; these ZnO nanotowers were formed from stacking of very uniform hexagonal ZnO nanocrystals with an average thickness of 100 nm, showing a tower structure. And the united structures are shown in Fig. 3c: two nanotowers are joined by a nanosheet, which was formed during their growth process.

Due to the good epitaxial interface between the (0001) plane of the ZnO nanocolumns and the (110) plane of the alumina

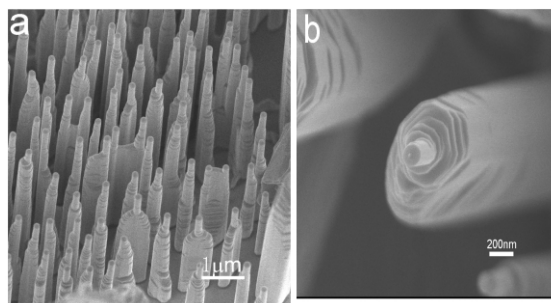


Fig. 2 (a) A low magnification SEM image of ZnO nanocolumn arrays normal to the substrate; (b) an individual top segment shows clear stacking structure.

substrate,¹⁵ the nanocolumns grow vertically from the substrate. The *a*-plane (110) of sapphire is two-fold symmetric while the *c*-plane (0001) of ZnO is six-fold symmetric. The two planes are essentially incommensurate with the exception that the *a*-axis of ZnO and the *c*-axis of sapphire are related by a factor of 4 with a mismatch less than 0.08% at room temperature. This coincidental match up along the sapphire (0001) direction, the strong tendency of ZnO to grow in the *c*-axis direction and the incoherence of the interface in directions other than sapphire (0001), lead to the unique vertical epitaxial growth configuration. Therefore, the anisotropy of the *a*-plane of sapphire is essential for growing highly *c*-oriented ZnO nanocolumns.

The product was further characterized by transmission electron microscopy (TEM, Hitachi-800, JEOL-2010F), accompanied by selected-area electronic diffraction (SAED). As shown in Fig. 4a, this ZnO nanocolumn exhibits clear stacking structure along its length. But this ZnO nanocolumn has no

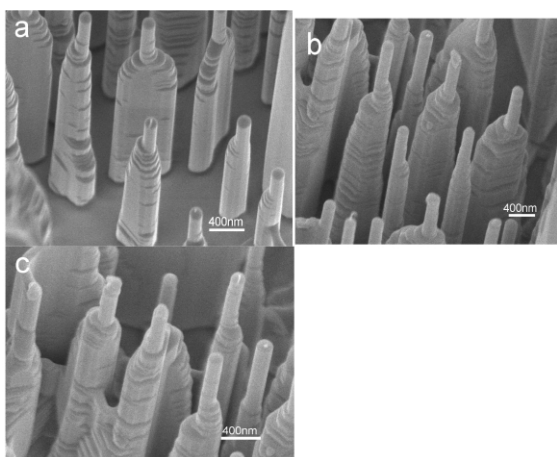


Fig. 3 SEM images of ZnO nanocolumns with different morphologies: (a) irregular elliptic cylinder structure; (b) the nanocolumn seems to be formed from stacking uniform hexagonal nanocrystals, indicating a tower structure; (c) twin growth of two nanotowers joined by a nanosheet.

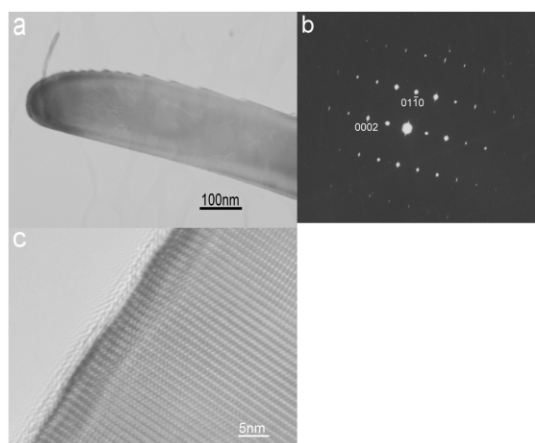


Fig. 4 (a) A ZnO nanocolumn shows stacking structure; (b) the SAED pattern suggests that the ZnO nanocolumn grew along the (0001) direction; (c) the high-resolution TEM image reveals that the ZnO nanocolumn is highly crystalline and has a preferred growth direction.

smaller nanorods grown on the (0002) plane. The SAED pattern (Fig. 4b) suggests that the ZnO nanocolumn grew along the (0001) direction. The high-resolution TEM image (Fig. 4c) clearly shows that the ZnO nanocolumn is highly crystalline and has a preferred growth direction. No stacking defaults were found in the whole nanocolumn under the observation of high-resolution TEM.

Since no additional metal catalysts were introduced into the reaction, it is presumed that the ZnO nanocolumn growth was governed by a vapor–solid (VS) process.¹⁶ During the heating process, ZnS was evaporated and decomposed into Zn and S. Vapor Zn reacted with O₂ to form ZnO vapor, which was deposited on the alumina substrate at low temperature where ZnO nanotowers nucleated and grew along the (0001) direction. The formation of the tower-like structure of ZnO nanocolumns resulted from a gradually decreasing supply of ZnO vapor. Compared with the former state, the ZnO vapor content decreased owing to rapid evaporation of ZnS, and it gradually reached a low and stable level. Accordingly, the parts formed later were thinner, which resulted in production of a layered structure, and finally a thinner nanorod with uniform structure was formed.

In conclusion, a novel one-dimensional nanostructure of ZnO is demonstrated, in which the highly oriented ZnO nanotowers are normal to the alumina substrate and grow along the (0001) direction. These novel one-dimensional ZnO nanomaterials may well be used in nanoelectronics and optics.

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Notes and references

- S. Iijima, *Nature*, 1991, **354**, 56.
- J. Hu, T. Odom and C. M. Lieber, *Acc. Chem. Res.*, 1999, **32**, 435.
- (a) W. Han, S. Fan, Q. Li and Y. Hu, *Science*, 1997, **277**, 1287; (b) H. Huu, N. Keller, C. Estourn, G. Ehret and M. Ledoux, *Chem. Commun.*, 2002, **17**, 1882.
- (a) J. Sha, J. Niu, X. Ma, J. Xu, X. Zhang, Q. Yang and D. Yang, *Adv. Mater.*, 2002, **14**, 1219; (b) M. Fu, Y. Zhu, R. Tan and G. Shi, *Adv. Mater.*, 2001, **13**, 1874.
- (a) X. Wang and Y. Li, *J. Am. Chem. Soc.*, 2002, **124**, 2880; (b) D. Zhue, H. Zhu and Y. Zhang, *Appl. Phys. Lett.*, 2002, **80**, 1634.
- A. M. Morales and C. M. Lieber, *Science*, 1998, **279**, 208.
- (a) M. Remskar, A. Mrzel, A. Jesih and F. Lévy, *Adv. Mater.*, 2002, **4**, 680; (b) P. Terech, A. Geyer, B. Struth and Y. Talmon, *Adv. Mater.*, 2002, **14**, 495.
- T. Minami, *MRS Bull.*, 2000, **25**, 38.
- V. C. Sousa, A. M. Segadaes, M. R. Morelli and R. H. G. A. Kiminami, *Int. J. Inorg. Chem.*, 1999, **1**, 235.
- G. Agarwal and R. F. Speyer, *J. Electrochem. Soc.*, 1998, **145**, 2920.
- F. Quaranta, A. Valentini, F. R. Rizzi and G. Casamassima, *J. Appl. Phys.*, 1993, **74**, 244.
- (a) M. Huang, H. Y. Wu, H. Feick, N. Tran, E. Weber and P. Yang, *Adv. Mater.*, 2001, **13**, 113; (b) M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, *Science*, 2001, **292**, 1897.
- Z. W. Pan, Z. R. Dai and Z. L. Wang, *Science*, 2001, **291**, 1947.
- (a) J.-J. Wu, S.-C. Liu, C. T. Wu, K.-H. Chen and L.-C. Chen, *Appl. Phys. Lett.*, 2002, **81**, 312; (b) J. Zhang, L. Sun, C. Liao and C. Yan, *Chem. Commun.*, 2002, **3**, 262.
- P. Fons, K. Iwata, A. Yamada, K. Matsubara, S. Niki, K. Nakahara, T. Tanabe and H. Takasu, *Appl. Phys. Lett.*, 2000, **77**, 1801.
- P. Yang and C. M. Lieber, *J. Mater. Res.*, 1997, **12**, 2.