The (011) Twin Structure Periodical in Monoclinic ZrO$_2$ Nanofiber

Qing Yang$^*$
Faculty of Material Science and Engineering, Xi’an University of Technology, 5 South Jinhua Road, Xi’an 710048, China

Hirokazu Tatsuoka
Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu 432-8561, Japan

Miyoko Tanaka
National Institute for Materials Science, 3-13 Sakura, Tsukuba 305-0003, Japan
(Received 27 August 2014; Accepted 17 September 2014; Published 4 October 2014)

The twin structure of monoclinic ZrO$_2$ nanofiber was characterized using transmission electron microscopy. The m-ZrO$_2$ nanofiber with diameter $\sim$300 nm was grown by the thermal oxidation of ZrSi$_2$ with gallium. The (011) twinning was observed periodically along the growth direction of m-ZrO$_2$ nanofiber. [DOI: 10.1380/ejssnt.2014.418]

Keywords: Electron microscopy; Crystallization; Oxidation; Twin; Nanofiber; ZrO$_2$

I. INTRODUCTION

One-dimensional oxides have attracted much interest due to their excellent physical, chemical and mechanical properties as compared to those of bulk oxides [1]. As an excellent insulator, ZrO$_2$ provides a new option as structural materials, because it has excellent mechanical characteristics, such as high level of hardness and strength, thermal and chemical stability. Besides the wide investigations on the nano-ZrO$_2$ composite ceramics, the research has been focused on the growth and characterization of one-dimensional nano-ZrO$_2$, which is expect to lead to the development of new applications for nano-scale devices, such as sensors and optical fibers [2-9].

On the other hand, planar defects such as stacking fault and twinning are frequently observed in one-dimensional nanostructures, the characterizations of which are essential to understand the growth mechanism of one-dimensional nanostructures with corresponding physical and chemical properties [10-13]. To the best of our knowledge, the twin structures have been observed in monoclinic ZrO$_2$ films [14] and particles [15, 16]. However, it has been seldom reported on one-dimensional nano-ZrO$_2$. In this paper, we report the periodical twin structure of ZrO$_2$ nanofiber.

II. EXPERIMENTAL

ZrO$_2$ nanofibers were grown by the thermal oxidation of ZrSi$_2$ substrates with gallium for 24 h at a temperature of 900°C with vacuum pressure of $10^{-4}$ Torr. The preparation procedure was described in detail previously [9]. The as-grown nanofibers were characterized using transmission electron microscopy (TEM) with selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM).

FIG. 1. (a) TEM image and (b) SAED pattern of an m-ZrO$_2$ nanofiber that has a (011) twin denoted by normal and dashed lines. (c) HRTEM image of the periodical (011) twin with the incident electron beam along [011] direction. (d) Schematic illustration of crystallographic configuration of twinned m-ZrO$_2$.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the TEM image of a ZrO$_2$ nanofiber with diameter $\sim$300 nm. Figure 1(b) shows the corresponding SAED pattern which is composed of two sets of diffraction spots that have symmetrical geometrical distribution. As indexed in the SAED pattern, the common spot is the twin boundary plane (011) and the incident electron beam direction is [011]. Figure 1(c) shows the HRTEM image recorded from the edge of ZrO$_2$ nanofiber. As shown in the enlarged image in Fig. 1(c), all the fringes clearly observed correspond to the (100) plane. As indexed by the dotted lines, it clearly displays the mirror symmetry between the two parts of the twin which occurs periodically along the nanofiber, namely the growth direction of the ZrO$_2$ nanofiber is normal to the (011) twin plane. It should be mentioned that several ZrO$_2$ nanofibers displaying the same twin structure have been observed. According to the monoclinic structure of ZrO$_2$...
nanofiber revealed by the SAED and HRTEM characterizations, Fig. 1(d) shows the schematic illustration of crystallographic configuration of twinned m-ZrO$_2$.

Pure ZrO$_2$ exists in three phases with temperature increases: monoclinic ($\sim$1205°C), tetragonal ($\sim$2377°C), and cubic ($\sim$2710°C) [17]. It has been reported that the monoclinic ZrO$_2$ twin structure could be formed during the transformation from tetragonal to monoclinic structure [14-16, 18]. The (011) plane was proved to act as twinning plane as transformation as well [14], which has been observed actually in transformed monoclinic ZrO$_2$ particles confined in mullite matrix and was considered to help to minimize the thermal strain on the particle arising due to the different thermal expansion coefficients of particle and matrix [15]. The theory calculation revealed that the twinning on the (011) plane is possible only if the twinning is accompanied by local non-homogeneous deformation due to other mechanisms near the twin planes [18]. In this research, the growth temperature of ZrO$_2$ nanofiber is lower than the formation temperature of tetragonal structure. It is considered that the (011) twin structure in the as-synthesized monoclinic ZrO$_2$ nanofiber may be growth twin rather than transformation twin. However, the twin structure has not been reported in one-dimensional nano-ZrO$_2$ synthesized at low temperatures or by solution phase growth methods [2-8].

Gallium can exist in a liquid state even at a wide temperature range (29.78$^\circ$C~2403$^\circ$C) [17], which means that the gallium can guarantee a suitable supersaturation for the nanostructure growth process which would lead to the periodical formation of planar twin defects to release the stored energy [24]. The fact is that the similar phenomena have been observed in various 1D nanomaterials, such as ZnS, ZnSe, SiC, GaP, GaAs, InAs [11-13, 24-29]. Therefore, it is assumed that the solid-liquid interface between ZrO$_2$ nanofiber and gallium droplet possibly played a key role in the growth of periodical twin structure which was terminated with gallium evaporated.

IV. CONCLUSION

The (011) twin structure periodical in monoclinic ZrO$_2$ nanofiber with diameter $\sim$300 nm was obtained by the thermal oxidation of ZrSi$_2$ with gallium. The synthesis of twinning along the nanofiber may develop a new understanding of twin formation in one-dimensional nano-scale.

[1] J. G. Lu, P. Chang, and Z. Fan, Mater. Sci. Eng. R 52, 49 (2006).
[2] C. Shao, H. Guan, Y. Liu, J. Gong, N. Yu, and X. Yang, J. Cryst. Growth 267, 380 (2004).
[3] M. C. Tsai, G. T. Lin, H. T. Chiu, and C. Y. Lee, J. Nanopart. Res. 10, 863 (2008).
[4] R. E. Cochran, J. J. Shayne, and N. P. Padture, Acta Mater. 55, 3007 (2007).
[5] H. Xu, D. H. Qin, Z. Yang, and H. L. Li, Mater. Chem. Phys. 80, 524 (2003).
[6] W. S. Dong, F. Q. Lin, C. L. Liu, and M. Y. Li, J. Colloid Interface Sci. 333, 734 (2009).
[7] L. Kumari, G. H. Du, W. Z. Li, R. S. Vennila, S. K. Saxena, and D. Z. Wang, Ceram. Int. 35, 2401 (2009).
[8] H. Cao, X. Qu, B. Luo, Y. Liang, Y. H. Zhang, R. Tan, M. Zhao, and Q. Zhu, Adv. Funct. Mater. 14, 243 (2004).
[9] Q. Yang, M. Tanaka, S. Liang, K. Ogino, H. Fujii, A. Ishida, and H. Tatsuoka, Thin Solid Films 519, 8538 (2011).
[10] Y. Ding and Z. L. Wang, Micron 40, 335 (2009).
[11] R. E. Algra, M. A. Verheijen, L. F. Feiner, G. G. W. Immink, R. Theissmann, W. J. P. van Enckevort, E. Vlieg, and E. P. A. M. Bakkers, Nano Lett. 10, 2349 (2010).
[12] J. Bao, D. C. Bell, and F. Capasso, Nano Lett. 8, 836 (2008).
[13] Q. Xiong, J. Wang, and P. C. Eklund, Nano Lett. 6, 2736 (2006).
[14] J. E. Bailey, Proc. R. Soc. A 279, 395 (1964).
[15] E. Bischoff and M. Ruhle, J. Am. Ceram. Soc. 66, 123 (1983).
[16] B. C. Muddle and R. H. J. Hannink, J. Am. Ceram. Soc. 69, 547 (1986).
[17] H. Okamoto, Desk Handbook: Phase Diagrams for Binary Alloys, vol.3, (ASM International, Materials Park, OH, 2000).
[18] K. Y. Lam and J. M. Zhang, Acta Metall. Mater. 40, 1395 (1992).
[19] Z. W. Pan, Z. R. Dai, C. Ma, and Z. L. Wang, J. Am. Chem. Soc. 124, 1817 (2002).
[20] Z. Pan, S. Dai, D. B. Beach, and D. H. Lowndes, Nano Lett. 3, 1279 (2003).
[21] R. E. Honig and D. A. Kramer, RCA Rev. 30, 285 (1969).
[22] Y. Ding, P. X. Gao, and Z. L. Wang, J. Am. Chem. Soc. 126, 2066 (2004).
[23] K. W. Kolasiński, Curr. Opin. Solid State Mater. Sci. 10, 182 (2006).
[24] Y. Hao, G. Meng, Z. L. Wang, C. Ye, and L. Zhang, Nano Lett. 6, 1650 (2006).
[25] Z. H. Zhang, F. F. Wang, and X. F. Duan, J Cryst. Growth 303, 612 (2007).
[26] Y. Q. Wang, U. Philipose, T. Xu, H. E. Ruda, and K. L. Kavanagh, Semicond. Sci. Technol. 22, 175 (2007).
[27] D. H. Wang, D. Xu, Q. Wang, Y. J. Hao, G. Q. Jin, X. Y. Guo, and K. N. Tu, Nanotechnology 19, 215602 (2008).
[28] F. M. Davidson, D. C. Lee, D. D. Fanfair, and B. A. Korgel, J. Phys. Chem. C 111, 2929 (2007).
[29] E. L. Wooda and F. Sansoz, Nanoscale 4, 5268 (2012).