A New and Simple Means for Self-Assembled Nanostructure: Facilitated by Buffer Layer

7 AUTHORS, INCLUDING:

Cheng-Liang Hsu
National University of Tainan
108 PUBLICATIONS **2,062** CITATIONS

SEE PROFILE

Yan-Ru Lin
Mingchi University of Technology
38 PUBLICATIONS **989** CITATIONS

SEE PROFILE

Yung-kuan Tseng
National Yunlin University of Science and Tec…
24 PUBLICATIONS **962** CITATIONS

SEE PROFILE

Shoou-Jinn Chang
National Cheng Kung University
992 PUBLICATIONS **11,933** CITATIONS

SEE PROFILE

A New and Simple Means for Self-Assembled Nanostructure: Facilitated by Buffer Layer

Cheng-Liang Hsu,[†,‡] Shang-Shian Yang,[†,§] Yung-Kuan Tseng,[†] I-Cherng Chen,[†] Yan-Ru Lin,*[,†] Shoou-Jinn Chang,[‡] and Shinn-Tyan Wu[§]

Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31040, Taiwan, ROC, Department of Electrical Engineering, Institute of Microelectronics, National Cheng Kung University, Tainan 70101, Taiwan, ROC, and Department of Materials Science & Engineering, National Tsing-Hua University, Hsinchu 30043, Taiwan, ROC

Received: September 25, 2004; In Final Form: October 30, 2004

One-dimensional semiconductor nanomaterials are expected to be important components in future nano-devices. The well-controlled growth of the nanomaterials is the most important aspect of nano-devices production. A new and simple means of growing ZnO nanowire (NW) arrays using a TiN buffer layer, but without using any catalysis or template, was proposed although the crystal structure thus obtained differed entirely from that of ZnO.

Many groups have investigated the mechanisms of growth of atomic-scale structural features, to enable the growth of nanomaterials to be controlled. Some useful techniques for making well-ordered nanowire arrays, such using templates as supports,[1−3] utilizing the characteristic of catalysts in the vapor−liquid−solid (VLS) process,[4−8] being aligned in fluid flows,[9−11] being assembled with electric fields[12] and using homogeneous buffer layers[13−18] or similar crystal structure[19,20] have been investigated. This work shows the use of a TiN(200) buffer layer can help 4-fold symmetric arrays to be formed of ZnO nanowires and to image directly the atomic structure at the interfaces, to understand why such arrays form.

Approximately 80 nm TiN films were deposited by reactive magnetron sputtering on (100)-orientated, 1 cm × 1.5 cm, silicon wafers. To reduce the influence of defects (such as grain boundary) on the subsequent growth, the epitaxial buffer layer should be carefully chosen. The deposition conditions of the buffer layer have been described elsewhere.[21] The base pressure was 1.5×10^{-6} Torr. The total pressure (Ar + N$_2$) was maintained at 3×10^{-3} Torr during sputtering which the nitrogen fractions was 3% and the substrate temperature was kept at 600 °C. The target was titanium (99.9%). The deposition rate was 6 nm/min approximately.

The synthesis of ZnO NWs was performed by vapor phase transport deposition without a metal catalyst or template.[15,22] The zinc vapor source is Zn metal powder with a purity of 99.9% from Strem Chemicals. Two weights, 0.12 g and 0.04 g, of Zn metal powder are used in this study. The substrates and zinc vapor source in an alumina boat were inserted into the quartz tube and put closely in the middle of the furnace. The distance between the Zn source and the substrate is only 20 mm, and the zinc vapor source was placed at the upstream side. And a constant stream of argon flowed through the reaction system. A mechanical pump was used to evacuate the system to maintain the pressure inside the quartz tube at about 10 Torr. The heating ramps were set to be 8, 12, 16, and 20 °C per minute. The experiments lasted for 30 min after the furnace reached the reaction temperature (550 °C).

Parts a−d of Figure 1 show the field emission scanning electron microscopy (FE-SEM) images of ZnO NWs formed at various heating rates (20, 16, 12, and 8 °C/min, respectively). The mass of the Zn powder source in these processes is 0.12 g. Figure 1e presents the cross-sectional transmission electron microscopic (TEM) photograph of the sample, corresponding to Figure 1d. In our previous study, the ZnO NWs can be grown epitaxially, vertically from the surface of the substrates, under the same condition as the sample in Figure 1a on a TiN(111) buffer layer.[23] An important question is as follows. Why should NWs be formed as 4-fold symmetric arrays when the heating is slow? The answer is as follows.

The mass of the Zn powder source is reduced to 0.04 g to generate sparse NWs and facilitate the analysis and thus reduce the disturbance caused by the intersection of the NWs. The FE-SEM images in Figure 2 reveals that two ZnO NWs form a pair that grows with mirror symmetry, and each pair is arranged in parallel or perpendicular to each other, in two vertical directions. Hence, NWs exhibit 4-fold symmetry.

Figure 3a presents the cross-sectional TEM image of the sample that corresponds to Figure 2. Figure 3b shows the high-resolution (HR) image of the ZnO NWs/TiN interface. The HR photographs in Figures 3 and 4 reveal the formation of a new thin layer on the TiN surface. The lattice of the new layer resembles that of TiN, but its lattice constant is about double that of TiN. Figure 5a−c shows the energy-dispersive X-ray (EDX) spectra corresponding to the ZnO, the new layer, and the TiN, respectively. Figure 5b indicates that the new layer comprises zinc, titanium, and oxygen, and the signal of the nitrogen (0.392 keV, Cu Kα) is unrecognizable. This spectrum differs from that of the ZnO and the TiN. According to the JCPDS database, the new layer may be the phase, α-Zn$_2$TiO$_4$ (JCPDS 25-1164, spinel structure), with a lattice constant 8.4602 Å that is almost twice that of TiN (4.2417 Å).

Two factors limit the origin of this 4-fold symmetric structure: one is the coherence between ZnO(0001) and Zn$_2$TiO$_4$(111), and the other is the twin boundary of the ZnO. The ZnO(0001) planes cohere strongly with the Zn$_2$TiO$_4$(111)

* Correspondin author. E-mail: yanrulin@itri.org.tw.
[†] Industrial Technology Research Institute.
[‡] National Cheng Kung University.
[§] National Tsing-Hua University.
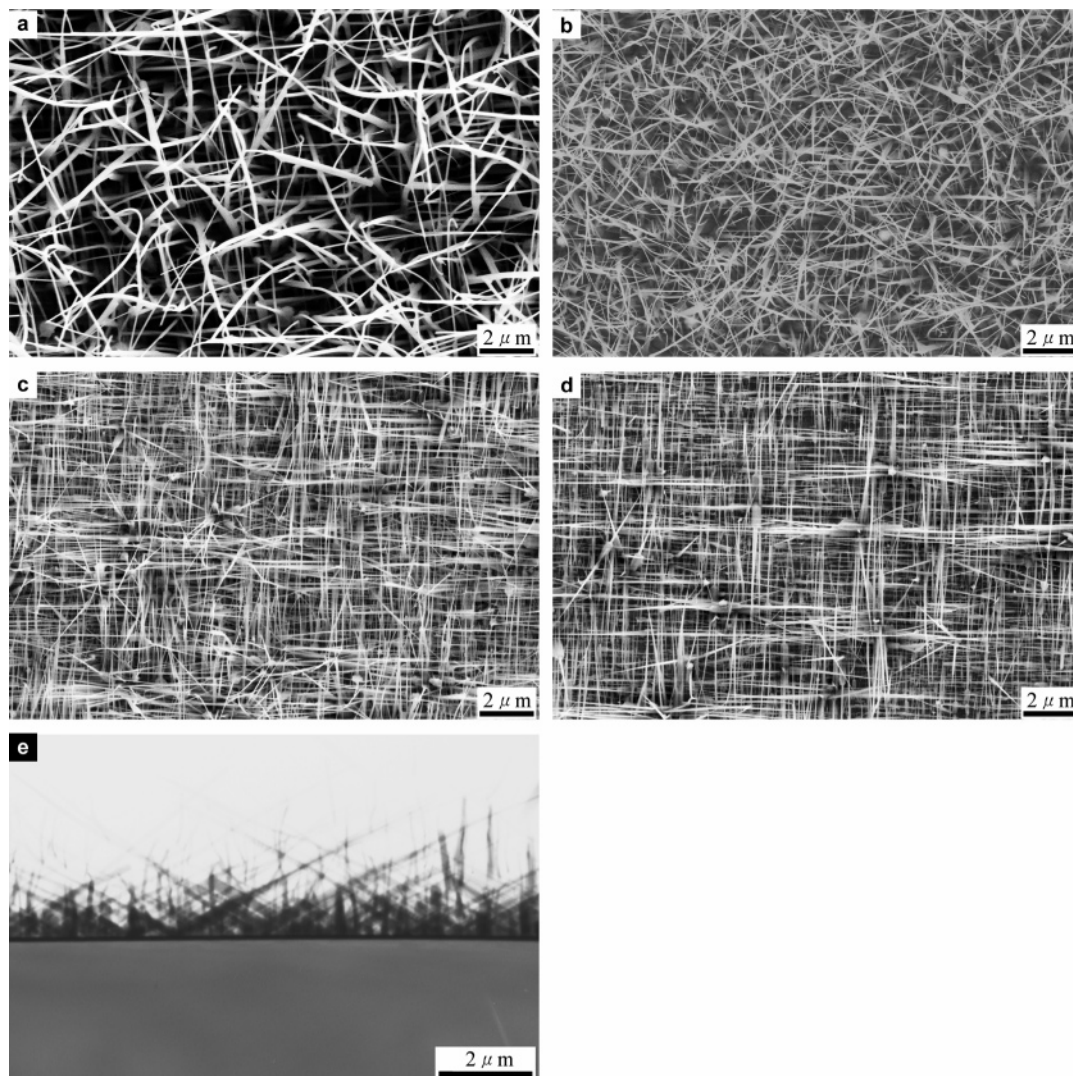
Figure 1. FE-SEM images of ZnO NWs generated at various heating rates: 20, 16, 12 and 8 °C/min, (a)−(d), respectively. The mass of the Zn powder source in these processes is 0.12 g. (e) TEM photograph of the sample that corresponds to (d). NWs grow in a disordered manner at high heating rates, as shown in **a** and (b). NWs are formed as 4-fold symmetric arrays at low heating rates.
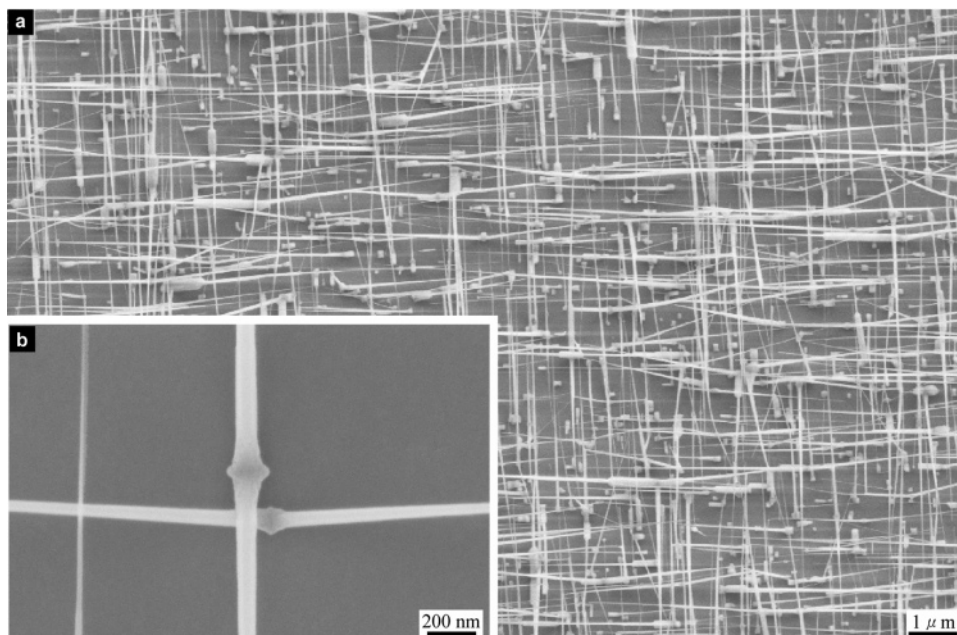
Figure 2. FE-SEM images of ZnO NWs generated at a heating rate of 8 °C/min with a mass of Zn of 0.04 g. Each pair of ZnO NWs was formed in an arrangement parallel or perpendicular to the other pairs, in the two vertical directions.

Letters

J. Phys. Chem. B, Vol. 108, No. 49, 2004 **18801**
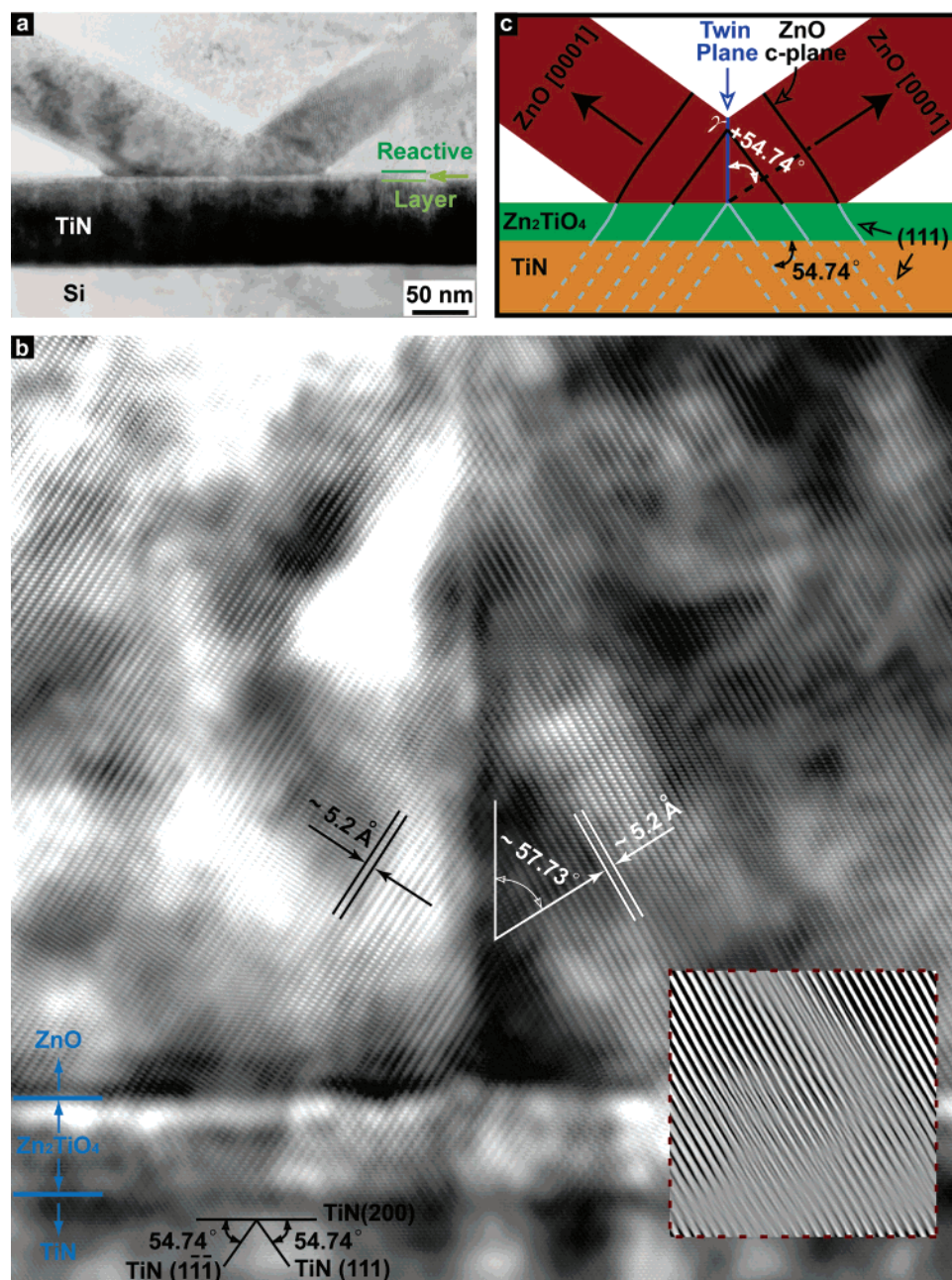
Figure 3. (a) Cross-sectional TEM image of the sample that corresponds to Figure 2. (b) High-resolution TEM photograph of the ZnO NWs/TiN interface. Notably, Fourier filtering was applied to the area outlined by a red dashed line, revealing only ZnO(0001), Zn_2TiO_4(111), and TiN(111). (c) Relationships among the ZnO NWs, Zn_2TiO_4, and TiN.

planes, as shown by the area marked by the red dashed line in Figure 3b. This image underwent Fourier filtering to yield the images of ZnO(0001), Zn_2TiO_4(111), and TiN(111) only. To cohere, an amount of strain exists at the interface because the spacings of the ZnO(0001) and Zn_2TiO_4(111) planes are 5.2 and 4.89 Å, respectively. Two ZnO grains, whose (0001) planes cohere with Zn_2TiO_4(111) and Zn_2TiO_4(1$\bar{1}\bar{1}$) individually, combine to form a twin on the reactive layer. The twin plane is ZnO{$\bar{1}$013}, and its structure and characteristics have been systematically outlined by Ding and Wang.[24] Theoretically, the angle between the *c*-axis and the twin plane (ZnO {$\bar{1}$013}) is 58.34°. Moreover, the angle between the planes (200) and (111) of the cubic structure is 54.74°. A difference of 3.6° exists between the two angles, and the structure must incorporate a rotation for coherence. Although TiN is a hard material, the Zn_2TiO_4 can act as a compliant buffer layer for relaxing the lattice mismatch and rotation. Accordingly, the angle between

the normal to the substrate surface and the ZnO [0001] direction, as illustrated in Figure 3b,c, slightly exceeds 54.74° and is smaller than 58.34°. From the above discussion, the epitaxial relationships among ZnO NW/TiN/Si, as shown in Figure 6a, are resolved easily:

$$[1\bar{2}10]_{ZnO}||[0\bar{1}1]_{TiN}||[0\bar{1}1]_{Si} \quad plus$$
$$(0002)_{ZnO} \, R + \gamma \, ||(111)_{TiN}||(111)_{Si} \quad (1)$$

The $R + \gamma$ in eq 1 means the ZnO(0001) rotates a γ angle clockwise where $\gamma \leq 3.6°$. Furthermore, the diffraction points of the Zn_2TiO_4 are absent in Figure 6. The absence of the diffraction points may result from the distortion that destroys the diffraction conditions.

The role of the Zn_2TiO_4 is very important in this study and the following discusses the formation of the peculiarity thin layer. The relationship between the saturated vapor pressure
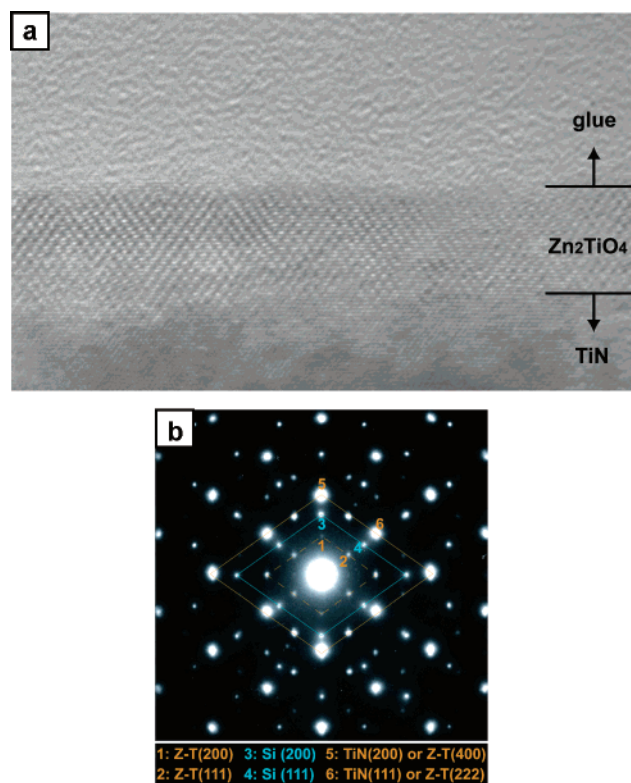
Figure 4. (a) HR image of the substrate surface at the NW-free area. (b) SAD pattern of the $Zn_2TiO_4/TiN/Si$ interface. The SAD pattern clearly shows that the reciprocal lattice vector of the Zn_2TiO_4 (mark as Z−T) has a length almost half that of the TiN. This sample corresponds to Figures 2 and 3.
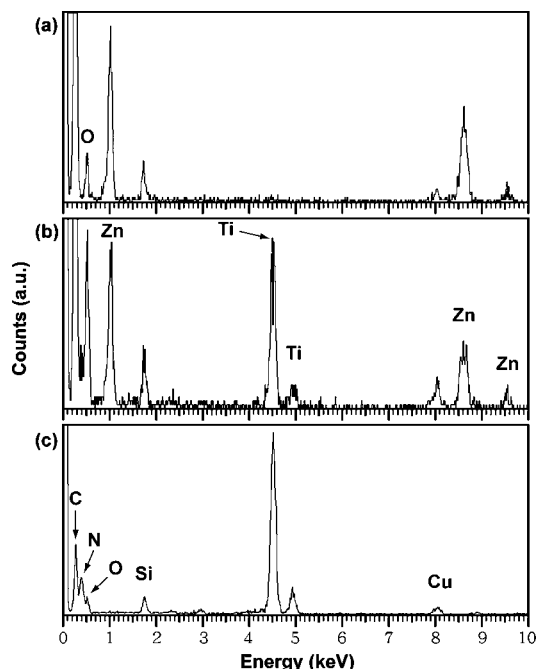
Figure 5. (a)−(c) EDX spectra take from the ZnO, the reactive layer and the TiN, respectively. Signals of C (from glue), Si (from substrate), and Cu (from the sample holder of the Cu ring) may be pollutants caused by ion milling during the making of the TEM sample.

(p, unit with atm) of liquid Zn and absolute temperature (T) follows the equation[25]

$$\ln p \text{ (atm)} = \frac{-15250}{T} - 1.255 \ln T + 21.79 \qquad (2)$$
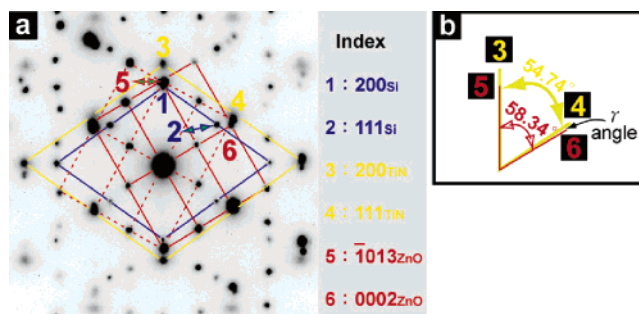
Figure 6. (a) SAD pattern (negative photograph), taken in the area correspondence with Figure 3b, projected along the Si [0$\bar{1}$1], the TiN [0$\bar{1}$1], or the ZnO [1$\bar{2}$10] direction. (b) To cohere, a difference of γ angle exists between the ZnO and TiN, and must be reduced by compliant buffer layer.

TABLE 1: Some Saturated Pressures at Specific Temperatures

temp, K(°C)	saturated pressure, Torr
693 (420) (melting point)	0.1667
723 (450)	0.3940
773 (500)	1.4175
823 (550)	4.3440

Table 1 lists some saturated pressures at specific temperatures. The table clearly shows that certain quantities of Zn vapor can be provided during the heating process. These quantities of Zn vapor can supply sufficient Zn to react with O and the TiN and form thin epitaxial Zn_2TiO_4 on the substrate surface provided there is enough time for the reaction before the nucleation of the ZnO NWs. The growth of epitaxial ZnO NWs on TiN(200) depends on Zn_2TiO_4. NWs can be grown epitaxially on TiN(200) if the epitaxial reactive layer of Zn_2TiO_4 is established before growth of the ZnO NWs begins. The epitaxial growth of this reactive layer takes some time. At high heating rates, epitaxial Zn_2TiO_4 does not have sufficient time to form before the ZnO NWs begin to grow, so the NWs grow in a disordered fashion, as shown in Figure 1a,b.

This work reports an approach to preparing well-ordered, 4-fold symmetric ZnO nanowires arrays. Controlling the growth of nanowires is fundamental to realizing the dream of nanotechnology. The characteristics of the interface can be used to fabricate extended and oriented nanowires. As well as using a catalyst or template, a suitable buffer layer can be chosen to facilitate the control of the productive process, even though the crystal structure of the TiN (or the Zn_2TiO_4) thus obtained differed entirely from that of ZnO in this study.

References and Notes

(1) Martin, C. R. *Science* **1994**, *266*, 1961.

(2) Melosh, N. A.; Boukai, A.; Diana, F.; Gerardot, B.; Badolato, A.; Petroff, P. M.; Heath, J. R. *Science* **2003**, *300*, 112.

(3) Jie, J.; Wang, G.; Wang, Q.; Chen, Y.; Han, X.; Wang, X.; Hou, J. G. *J. Phys. Chem. B* **2004**, *108*, 11976.

(4) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.

(5) Gao, P.; Wang, Z. L. *J. Phys. Chem B* **2002**, *106*, 12653.

(6) Johnson, J. C.; Knutsen, K. P.; Yan, H.; Law, M.; Zhang, Y.; Yang, P.; Saykally, R. J. *Nano Lett.* **2004**, *4*, 197.

(7) Wang, X.; Summers, C. J.; Wang, Z. L. *Nano Lett.* **2004**, *4*, 423.

(8) Gao, P. X.; Wang, Z. L. *J. Phys. Chem. B* **2004**, *108*, 7534.

(9) Messer, B.; Song, J. H.; Yang, P. *J. Am. Chem. Soc.* **2000**, *122*, 10232.

(10) Huang, Y.; Duan, X.; Wei, Q.; Lieber, C. M. *Science* **2001**, *291*, 630.

Letters

J. Phys. Chem. B, Vol. 108, No. 49, 2004 **18803**

(11) Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1255.

(12) Duan, X.; Huang, Y.; Cui, Y.; Wang, J.; Lieber, C. M. *Nature* **2001**, *409*, 66.

(13) Vayssieres, L.; Keis, K.; Lindquist, S. E.; Hagfeldt, A. *J. Phys. Chem. B* **2001**, *105*, 3350.

(14) Park, W. I.; Kim, D. H.; Jung, S. W.; Yi, G. C. *Appl. Phys. Lett.* **2002**, *80*, 4232.

(15) Tseng, Y. K.; Huang, C. J.; Cheng, H. M.; Lin, I. N.; Liu, K. S.; Chen, I. C. *Adv. Funct. Mater.* **2003**, *13*, 811.

(16) Greene, L. E.; Law, M.; Goldberger, J.; Kim, F.; Johnson, J. C.; Zhang, Y.; Saykally, R. J.; Yang, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3031.

(17) Yu, S. F.; Yuen, C.; Lau, S. P.; Park, W. I.; Yi, G. C. *Appl. Phys. Lett.* **2003**, *84*, 3241.

(18) Mikkelsen, A.; Sköld, N.; Ouattara, L.; Borgström, M.; Andersen, J. N.; Samuelson, L.; Seifert, W.; Lundgren, E. *Nature Mater.* **2004**, *3*, 519.

(19) Pauporté, T.; Lincot, D. *Appl. Phys. Lett.* **1999**, *75*, 3817.

(20) Park, W. I.; Yi, G. C. *Adv. Mater.* **2004**, *16*, 87.

(21) Lin, Y. R.; Wu, S. T. *J. Cryst. Growth* **2003**, *252*, 433.

(22) Tseng, Y. K.; Hsu, H. C.; Hsieh, W. F.; Liu, K. S.; Chen, I. C. *J. Mater. Res.* **2003**, *18*, 2837.

(23) Lin, Y. R.; Tseng, Y. K.; Yang, S. S.; Wu, S. T.; Hsu, C. L.; Chang, S. J. Buffer facilitated epitaxial growth of ZnO nanowire. *Cryst. Growth Des.*, in press.

(24) Ding, Y.; Wang, Z. L. *J. Phys. Chem. B* **2004**, *108*, 12280.

(25) Gaskell, D. R. *Introduction to the Thermodynamics of Materials*, 3rd ed.; Taylor & Francis: London, 1995; pp 169 and 548.