

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/224404193>

# Catalyst-free growth of uniform ZnO nanowire arrays on prepatterned substrate

ARTICLE *in* APPLIED PHYSICS LETTERS · JANUARY 2007

Impact Factor: 3.3 · DOI: 10.1063/1.2425036 · Source: IEEE Xplore

---

CITATIONS

23

---

READS

17

4 AUTHORS, INCLUDING:



Yadong Wang

Nanyang Polytechnic

39 PUBLICATIONS 583 CITATIONS

SEE PROFILE



Soo Jin Chua

National University of Singapore

871 PUBLICATIONS 9,542 CITATIONS

SEE PROFILE

# Catalyst-free growth of uniform ZnO nanowire arrays on prepatterned substrate

Y. D. Wang,<sup>a)</sup> K. Y. Zang,<sup>b)</sup> and S. J. Chua<sup>b)</sup>

Singapore-MIT Alliance, E4-04-10, 4 Engineering Drive 3, Singapore 117576, Singapore

C. G. Fonstad

Department of Electrical and Computer Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 3 March 2006; accepted 26 November 2006; published online 29 December 2006)

Uniform and ordered ZnO nanowire arrays have been fabricated on the nanopatterned SiO<sub>2</sub>/GaN substrate without metal catalysts using hydrothermal synthesis. The nanopatterns on SiO<sub>2</sub>/GaN substrate with an average diameter of 65 nm are produced by inductively coupled plasma etching using anodic alumina template as a mask, which provides nucleation sites for the vertical ZnO nanowires growth. High quality of the aligned uniform ZnO nanowire arrays grown on GaN substrate was confirmed by x-ray diffraction, transmission electron microscopy, and photoluminescence. This growth technique provides a cost-effective approach to fabricate ordered nanowire arrays with controlled size, which may benefit the nanowire device applications. © 2006 American Institute of Physics. [DOI: 10.1063/1.2425036]

In recent year, one dimensional ZnO nanostructures have been receiving particular attention due to its direct band gap of 3.37 eV and a large exciton binding energy of 60 meV, which make it a promising candidate for applications in blue-UV light emitting, field emission, and sensing.<sup>1–3</sup> Lots of efforts have been done to fabricate ZnO nanowires and nanorods with average diameters typically ranging over an order of magnitude from 20 to 200 nm, and lengths from hundreds of nanometers up to several micrometers by using catalytic growth via the vapor-liquid-solid mechanism, metal-organic chemical vapor deposition, pulsed laser deposition, and wet chemical methods.<sup>4–13</sup> The ability to fabricate nanomaterials with a high degree of regularity and alignment is important to control the material properties and realize the functional device applications. It is reported that precoated buffer layers or textured seed layers have been used as substrates for improving the alignment of ZnO nanowires.<sup>14,15</sup> These precoated buffer layers or textured seed layers behave as the nucleus for growth of wires. Ordered ZnO nanowires embedded in anodic alumina template also have been fabricated.<sup>16</sup> In the common catalyst-assisted approach, the uniformity and alignment of ZnO nanowires can be improved by spatially selective deposition or pre patterning of catalyst.<sup>17–20</sup> The catalysts which are well defined by lithography or template-based nanopatterning including porous aluminum oxide template, self-assembly nanosphere lithography guided vapor-liquid-solid growth of nanowires. In this letter, we present an efficient technique to fabricate dense uniform ZnO nanowire arrays on prepatterned SiO<sub>2</sub>/GaN substrate without a catalyst via wet chemical method. Similar as patterning of catalyst, the prepatterned GaN substrate provides nucleation sites for the vertical ZnO nanowire growth. Wet chemical method is considered to offer several advantages,

such as large-area applicability, relatively low process temperature, and environmental friendliness. The nanopatterns on the substrate are created by etching substrate using anodic aluminum oxide (AAO) as a mask. AAO produced with ordered nanopores with a narrow distribution of tunable diameter pores ranging from ~10 to 500 nm is a promising template for nanofabrication.<sup>21–24</sup> Furthermore, the use of GaN layer also offers the advantage such as the controllability of electrical conductivity in a broad range, which allows for greater flexibility in device design, and the potential realization of a new class of vertical aligned nanoheterojunction devices.<sup>25–27</sup>

The general procedure to grow uniform ZnO nanowires is described as follows: A thin layer of SiO<sub>2</sub> (~50 nm) is deposited on the top of a 2 μm thick metal-organic chemical vapor deposition grown GaN film by plasma enhanced chemical vapor deposition, followed by evaporation of 1 μm of aluminum onto the substrate. Then the aluminum film is anodized using a two-step anodization process using 0.3M oxalic acid at 40 V. CF<sub>4</sub>-based inductively coupled plasma (ICP) etching is employed to transfer the nanopores from the AAO template to the SiO<sub>2</sub> film. After pattern transfer to the SiO<sub>2</sub> layer, the AAO template is selectively etched away in 5 wt % phosphoric. Then the nanopatterned SiO<sub>2</sub>/GaN substrate is dipped in an autoclave. The details about hydrothermal synthesis of ZnO nanowires are similar to Ref. 28: Zinc acetate was employed as the Zn source, and the pH was adjusted to 10 using NH<sub>4</sub>OH. The temperature was kept at 100 °C. The sample was characterized by field-emission scanning electron microscopy, transmission electron microscopy, x-ray diffraction, and photoluminescence (PL). PL spectra were recorded with a Renishaw 2000 micro-Raman-PL setup. The 325 nm line of the He–Cd laser was used as the source of excitation.

Figure 1(a) shows a SEM image of nanopatterns on SiO<sub>2</sub>/GaN. It is reported that the AAO template is an effective mask for the plasma etching process.<sup>29</sup> The mean diameter of the pores as measured from SEM is ~65 nm with an average interpore distance of 110 nm. The pore density is

<sup>a)</sup>Present address: College of Nanoscale Science and Engineering, UAlbany-State University of New York, NY; electronic mail: ywang@uamail.albany.edu

<sup>b)</sup>Also at Institute of Materials Research and Engineering, 3 Research Link, Singapore 1176, Singapore.

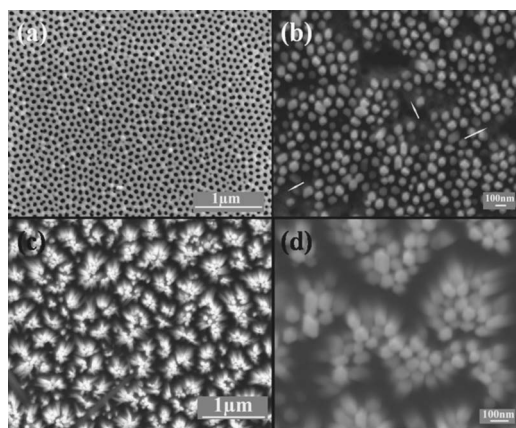


FIG. 1. (a) SEM image of nanopattern in the  $\text{SiO}_2/\text{GaN}$  substrate; (b) SEM image of initial ZnO nanostructure growth indicating the nucleation in the nanopore of  $\text{SiO}_2$ ; [(c) and (d)] SEM images of dense and uniform ZnO nanowire arrays.

about  $10^{10} \text{ cm}^{-2}$ . The diameter and the periodicity of the nanopores in  $\text{SiO}_2$  were directly transferred from the original AAO template due to the anisotropic ICP etching. The pore diameter and density in the AAO film can be easily controlled by tuning the anodization conditions such as applied voltage and electrolyte concentration. Compared to typical lithographic patterning approaches, such nonlithographic patterning based on self-organization processes offers a number of advantages for fabricating arrays of nanostructures, including the ability to pattern nanoscale features over large areas simultaneously, relative process simplicity, and low cost. Figure 1(b) shows the SEM image of the ZnO nanostructures in the initial growth stage. The size distribution of ZnO nanodot arrays mimics that of AAO template. Most of ZnO nanodots extrude out of  $\text{SiO}_2$ , only few still inside the nanopores of  $\text{SiO}_2$  as pointed out by the arrows in Fig. 1(b). It is well known that the net free energy plays an important role in the aqueous system.<sup>30</sup> Initial nucleation will occur at lower net free energy sites. Precoating the substrate with a ZnO buffer layer before the hydrothermal synthesis to lower the energy barrier for nucleation is a well-developed technique to promote high-density nucleation and oriented growth of nanowires in the hydrothermal synthesis.<sup>31</sup> ZnO and GaN have the same wurtzite-type structures with a low lattice mismatch. The net free energy for ZnO nucleus on GaN surface is much smaller than  $\text{SiO}_2$  surface, which will favor the nucleation of ZnO on the patterned GaN surface in our experiment. These uniform ZnO nuclei will guide the growth to form the nanowire arrays, as shown in Figs. 1(c) and 1(d). The growth of ZnO is consistent with the model of ZnO crystal growth proposed by Li *et al.*<sup>32</sup> The hexagonal (0001) plane of ZnO with wurtzite structure is the closest packed plane in the crystal, and stacking along the [0001] direction becomes energetically favorable. The deposition based on GaN (0001) plane and the growth along the normal direction of the substrate surface were faster than the lateral one and resulted in that the crystals had a high aspect ratio shape. The ZnO nanowire arrays are grown over the entire substrate. The average diameter and density of ZnO nanowire arrays are  $\sim 65 \text{ nm}$  and  $10^{10}/\text{cm}^2$  defined by the nanopatterns in the  $\text{SiO}_2$ , which can be easily controlled by the AAO anodization conditions. The ZnO nanowires grown on GaN substrate are hexagonally shaped with flat and smooth surface as shown in the Fig. 1(d), strongly suggesting that

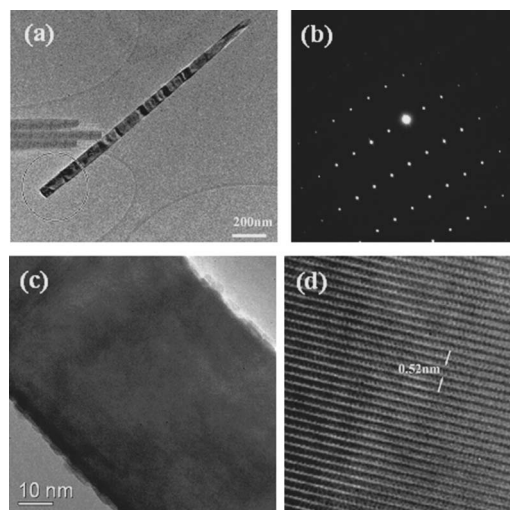


FIG. 2. (a) Low-magnification TEM image of ZnO nanowire grown on GaN substrate; (b) selective area electron diffraction pattern of ZnO nanowire; [(c) and (d)] high-magnification TEM image of a single ZnO nanowire.

these nanowires grow along the  $\langle 001 \rangle$  direction. These nanowires with flat and smooth surfaces may have important implications when they are used as effective laser media.<sup>4</sup> This  $c$ -axis oriented growth was also confirmed by long angle x-ray diffraction (XRD)  $\theta$ - $2\theta$  scan (not shown here). Only two ZnO/GaN (002) and (004) peaks were observed besides sapphire substrate. Since no catalyst was used in our hydrothermal synthesis, there is no metal catalyst detected in the XRD measurement.

TEM images including low-magnification image, high-resolution image, and SAED patterns of individual ZnO nanowire further confirm the structure of ZnO nanowire, as suggested by both SEM and XRD. Figures 2(a) and 2(b) show a low-magnification TEM image of an individual nanowire scratched from the substrate, and its selected area electron diffraction (SAED) pattern reveals the single crystal wurtzite structure of ZnO nanowire. The length and diameter of ZnO nanowire are about  $2 \mu\text{m}$  and  $65 \text{ nm}$ . Figures 2(c) and 2(d) show the high resolution TEM image of a nanowire, indicating that the growth direction of ZnO nanowire is [0001]. No dislocations or stacking faults are observed in areas examined. The lattice spacing of  $2.6 \text{ \AA}$  between adjacent lattice planes corresponded to the distance between two (002) crystal planes.

Room temperature photoluminescence spectroscopy was performed to investigate the optical properties of ZnO nanowire arrays. Strong exciton emission was observed with the peak at  $378 \text{ nm}$  with a FWHM of  $10 \text{ nm}$ , as shown in Fig. 3. The near UV emission is attributed to the excitation transitions in the ZnO material. The narrow FWHM value of PL spectrum and the absence of the broad yellow band in the PL spectrum which is usually due to the recombination of a photogenerated hole with an electron occupying the oxygen vacancy indicate the high optical quality of ZnO nanowires using our method, which is due to lattice match between nanowires and substrate as well as the uniformity of the nanowires.

In summary, we have demonstrated the growth of dense and uniform single crystalline ZnO nanowire arrays on the prepatterned  $\text{SiO}_2/\text{GaN}$  substrate by using hydrothermal synthesis method. The nanopattern on  $\text{SiO}_2/\text{GaN}$  substrate is produced by ICP etching using anodic alumina template as a

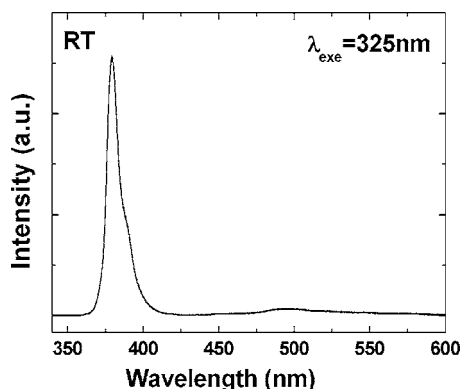


FIG. 3. Room temperature PL spectrum of ZnO nanowire arrays.

mask, which provides the nucleation of the vertical ZnO nanowire growth. The nanowire have uniform hexagonal structure with an average diameter of 65 nm and a length of about 2  $\mu\text{m}$ . The nanowires are of high crystallinity and good optical property. This fabrication process offers a simple and cost-efficient method to fabricate ordered nanowire arrays with controlled size by tuning the AAO template anodization conditions, which may benefit the nanowire device applications.

<sup>1</sup>M. S. Arnold, P. Avouris, Z. W. Pan, and Z. L. Wang, *J. Phys. Chem. B* **107**, 659 (2003).

<sup>2</sup>J. Johnson, H. Yan, P. Yang, and R. Saykally, *J. Phys. Chem. B* **107**, 8816 (2003).

<sup>3</sup>X. D. Bai, E. G. Wang, P. X. Gao, and Z. L. Wang, *Nano Lett.* **3**, 1147 (2003).

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

<sup>5</sup>Y. Zhang, H. B. Jia, R. M. Wang, C. P. Chen, X. H. Luo, D. P. Yu, and C. J. Lee, *Appl. Phys. Lett.* **83**, 4631 (2003).

<sup>6</sup>P. X. Gao, Y. Ding, and Z. L. Wang, *Nano Lett.* **3**, 1315 (2003).

<sup>7</sup>K. Kempa, B. Kimball, J. Rybczynski, Z. P. Huang, P. F. Wu, D. Steeves, M. Sennett, M. Giersig, D. V. G. L. N. Rao, D. L. Carnahan, D. Z. Wang, J. Y. Lao, W. Z. Li, and Z. F. Ren, *Nano Lett.* **3**, 13 (2003).

<sup>8</sup>W. I. Park, J. H. Jun, S. W. Jung, and G. C. Yi, *Appl. Phys. Lett.* **82**, 964

(2003).

<sup>9</sup>M. Yan, H. T. Zhang, E. J. Widjaja, and R. P. H. Chang, *J. Appl. Phys.* **94**, 5240 (2003).

<sup>10</sup>J. Jie, G. Z. Wang, Y. C. Chen, X. H. Han, Q. T. Wang, B. Xu, and J. G. Hou, *Appl. Phys. Lett.* **86**, 031909 (2005).

<sup>11</sup>B. Cheng and E. T. Samulski, *Chem. Commun. (Cambridge)* **3**, 986 (2004).

<sup>12</sup>L. Vayssieres, *Adv. Mater. (Weinheim, Ger.)* **15**, 464 (2003).

<sup>13</sup>Q. Wan, K. Yu, T. H. Wang, and C. L. Lin, *Appl. Phys. Lett.* **83**, 2253 (2003).

<sup>14</sup>L. E. Greene, M. Law, D. H. Tan, M. Montano, J. Goldberger, G. Somorjai, and P. D. Yang, *Nano Lett.* **5**, 1231 (2005).

<sup>15</sup>W. I. Park, G. C. Yi, M. Kim, and S. J. Pennycook, *Adv. Mater. (Weinheim, Ger.)* **14**, 1841 (2002).

<sup>16</sup>C. Liu, J. A. Zapien, Y. Yao, X. Meng, C. S. Lee, S. Fan, Y. Lifshitz, and S. T. Lee, *Adv. Mater. (Weinheim, Ger.)* **15**, 838 (2003).

<sup>17</sup>X. D. Wang, C. J. Summers, and Z. L. Wang, *Nano Lett.* **4**, 423 (2004).

<sup>18</sup>E. C. Greyson, Y. Babayan, and T. W. Odom, *Adv. Mater. (Weinheim, Ger.)* **16**, 1348 (2004).

<sup>19</sup>H. Chik, J. Liang, S. G. Cloutier, N. Kouklin, and J. M. Xu, *Appl. Phys. Lett.* **84**, 3376 (2004).

<sup>20</sup>H. J. Fan, W. Lee, R. Hauschild, M. Alexe, G. L. Rhun, R. Scholz, A. Dadger, K. Nielsch, H. Kalt, A. Krost, M. Zacharias, and U. Gosele, *Small* **2**, 561 (2006).

<sup>21</sup>H. Masuda and K. Fukuda, *Science* **268**, 1466 (1995).

<sup>22</sup>O. Jessensky, F. Muller, and U. Gosele, *Appl. Phys. Lett.* **72**, 1173 (1998).

<sup>23</sup>C. R. Martin, *Science* **266**, 1961 (1994).

<sup>24</sup>M. S. Sander and L. S. Tan, *Adv. Funct. Mater.* **13**, 393 (2003).

<sup>25</sup>X. D. Wang, J. H. Song, P. Li, J. H. Ryou, R. D. Dupuis, C. J. Summers, and Z. L. Wang, *J. Am. Chem. Soc.* **127**, 7920 (2005).

<sup>26</sup>W. Park and G. C. Yi, *Adv. Mater. (Weinheim, Ger.)* **16**, 87 (2004).

<sup>27</sup>H. W. Le, S. J. Chua, Y. W. Koh, K. P. Loh, Z. Chen, C. V. Thompson, and E. A. Fitzgerald, *Appl. Phys. Lett.* **87**, 101908 (2005).

<sup>28</sup>Y. W. Koh, M. Lin, C. K. Tan, Y. L. Foo, and K. P. Loh, *J. Phys. Chem. B* **108**, 11419 (2004).

<sup>29</sup>Y. D. Wang, K. Y. Zang, S. J. Chua, M. S. Sander, S. Tripathy, and C. G. Fonstad, *J. Phys. Chem. B* **110**, 11081 (2006).

<sup>30</sup>B. C. Bunker, P. C. Rieke, B. J. Tarasevich, A. A. Cambell, G. E. Fryxell, G. L. Graff, L. Song, J. W. Virden, and G. L. McVay, *Science* **264**, 48 (1994).

<sup>31</sup>L. E. Greene, M. Law, J. Goldberger, F. Kim, J. C. Johnson, Y. Zhang, R. J. Saykally, and P. Yang, *Angew. Chem., Int. Ed.* **42**, 3031 (2003).

<sup>32</sup>W. J. Li, E. W. Shi, W. Z. Zhong, and Z. W. Yin, *J. Cryst. Growth* **203**, 186 (1999).