Catalyst-Free Surface-Roughness-Assisted Growth of Large-Scale Vertically Aligned Zinc Oxide Nanowires by Thermal Evaporation

Shu-Te Ho, Kuan-Chiao Chen, Hsiang-An Chen, Hsin-Yu Lin, Chun-Yuan Cheng, and Heh-Nan Lin*

Department of Materials Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

Received February 19, 2007. Revised Manuscript Received May 9, 2007

This study reports the successful growth of large-scale vertically aligned ZnO nanowires on sapphire, glass, and Si substrates by direct thermal evaporation without the employment of either metal catalysts or seed layers via a surface-roughness-assisted vapor−solid mechanism. Simple processing steps including mechanical scratching, mechanical polishing, and chemical etching have been utilized to demonstrate the effectiveness of the present approach. The advantages include easy achievement of vertically aligned nanowires and applicability on various types of substrates.

Introduction

Nanostructures of ZnO have attracted a lot of attention in recent years because of their widespread applications in electronics, photonics, mechanics, and chemical sensing.[1−3] Specifically, ZnO nanowires (NWs) or nanorods have been demonstrated for use as light-emitting diodes (LEDs),[4] dye-sensitized solar cells,[5] nanogenerators,[6] nanolasers,[7] nano-photodiodes,[8] and so forth. The growth of large-scale vertically aligned NWs is desirable for realizing the applications of the above-mentioned devices.[9] For devices that implement Schottky junctions or optical resonators, NWs without metal catalysts are also preferred.[10] Obviously, there is a strong need for growth methods that can produce catalyst-free large-scale vertically aligned ZnO NWs.

For the growth of ZnO NWs, methods based on the vapor−liquid−solid (VLS) mechanism have been widely used with the employment of metal catalysts.[11−13] On the other hand, catalyst-free methods have also been reported and are mainly based on the vapor−solid (VS) mechanism.[11,14] For the growth of vertically aligned NWs without catalysts, the deposition of an additional ZnO seed layer with preferred orientation on the substrate prior to growth is often necessary and usually realized by a different method.[15,16] Although some growth methods such as metalorganic vapor-phase epitaxy,[17] thermal evaporation,[18] pulsed laser deposition[19] and aqueous solution synthesis[20] have been demonstrated to produce vertically aligned NWs without the use of either metal catalysts or seed layers, these NWs mostly have a tapered or a needle shape[17−19] and are undesirable for photonic applications.[12]

This study reports that simple processing steps of mechanical scratching, mechanical polishing, and chemical etching are able to produce substrate surfaces well-suited for the effective growth of catalyst-free large-scale vertically aligned ZnO NWs and nanorods by a convenient thermal evaporation method. The growth is based on a surface-roughness-assisted VS mechanism, which has been little explored previously. Although the idea of growing NWs on substrate surfaces with higher corrugation after deliberate processing such as chemical etching[21] is not new, the present results are much improved. It is also found that the chemical etching process is most suitable for the growth of large-scale vertically aligned NWs on sapphire substrates.

Experimental Section

Three different processing steps, namely, mechanical scratching, mechanical polishing, and chemical etching, were employed by

* To whom correspondence should be addressed. E-mail: hnlin@mx.nthu.edu.tw.

(1) Wang, Z. L. *J. Phys.: Condens. Matter* **2004**, *16*, R829.
(2) Heo, Y. W.; Norton, D. P.; Tien, L. C.; Kwon, Y.; Kang, B. S.; Ren, F.; Pearton, S. J.; LaRoche, J. R. *Mater. Sci. Eng.* **2004**, *R47*, 1.
(3) Xia, Y; Yang, P.; Sun, Y.; Wu, Y.; Mayers, B.; Gates, B.; Yin, Y.; Kim, F.; Yan, H. *Adv. Mater.* **2003**, *15*, 353.
(4) Könenkamp, R.; Word, R. C.; Schlegel, C. *Appl. Phys. Lett.* **2004**, *85*, 6004.
(5) Hosono, E.; Fujihara, S.; Honma, I.; Zhou, H. *Adv. Mater.* **2005**, *17*, 2091.
(6) Wang, Z. L.; Song, J. *Science* **2006**, *312*, 242.
(7) Govender, K.; Boyle, D. S.; O'Brien, P.; Binks, D.; West, D.; Coleman, D. *Adv. Mater.* **2002**, *14*, 1221.
(8) He, J. H.; Ho, S. T.; Wu, T. B.; Chen, L. J.; Wang, Z. L. *Chem. Phys. Lett.* **2007**, *435*, 119.
(9) Geng, C.; Jiang, Y.; Yao, Y.; Meng, X.; Zapien, J. A.; Lee, C. S.; Lifshitz, Y.; Lee, S. T. *Adv. Funct. Mater.* **2004**, *14*, 589.
(10) Jeong, J. S.; Lee, J. Y.; Cho, J. H.; Lee, C. J.; An, S.-J.; Yi, G.-C.; Gronsky, R. *Nanotechnology* **2005**, *16*, 2455.
(11) Fan, H. J.; Werner, P.; Zacharias, M. *Small* **2006**, *2*, 700.
(12) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897.
(13) Liu, D. F.; Xiang, Y. J.; Wu, X. C.; Zhang, Z. X.; Liu, L. F.; Song, L.; Zhao, X. W.; Luo, S. D.; Ma, W. J.; Shen, J.; Zhou, W. Y.; Wang, G.; Wang, C. Y.; Xie, S. S. *Nano Lett.* **2006**, *6*, 2375.
(14) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947.
(15) Greene, L. E.; Law, M.; Tan, D. H.; Montano, M.; Goldberger, J.; Somorjai, G.; Yang, P. *Nano Lett.* **2005**, *5*, 1231.
(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) Yuan, H.; Zhang, Y. *J. Cryst. Growth* **2004**, *263*, 119. Park, W. I.; Yi, G. C.; Kim, M.; Pennycook, S. J. *Adv. Mater.* **2002**, *14*, 1841. Park, W. I.; Kim, D. H.; Jung, S.-W.; Yi, G.-C. *Appl. Phys. Lett.* **2002**, *80*, 4232. Wu, J.-J.; Liu, S.-C. *Adv. Mater.* **2002**, *14*, 215.
(18) Ham, H.; Shen, G.; Cho, J. H.; Lee, T. J.; Seo, S. H.; Lee, C. J. *Chem. Phys. Lett.* **2005**, *404*, 69.
(19) Sun, Y.; Fuge, G. M.; Ashfold, M. N. R. *Chem. Phys. Lett.* **2004**, *396*, 21.
(20) Govender, K.; Boyle, D. S.; O' Brien, P.; Binks, D.; West, D.; Coleman, D. *Adv. Mater.* **2002**, *14*, 1221.
(21) Yang, P.; Lieber, C. M. *Science* **1996**, *273*, 1836.

10.1021/cm070474y CCC: $37.00
Published on Web 07/06/2007

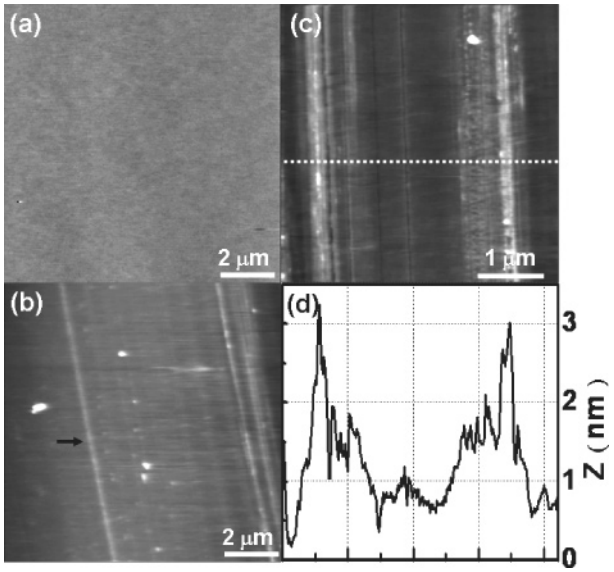

Figure 1. AFM images of (a) a bare sapphire surface (height range 1.8 nm) and (b) the surface (height range 6 nm) showing the presence of a long stripe region indicated by an arrow at a boundary after scratching. (c) Magnified view of the scratched area and (d) the corresponding cross-sectional profile along the dotted line in part c.

using steel needles, silicon carbide abrasive papers (#240, particle diameter 58.5 μm), and sodium hydroxide (concentration 1 M) solution, respectively, to increase surface corrugation on α-plane sapphire (Shinkosha Corp., Japan), non-alkali glass (NA32R, NH Techno Glass Corp., Taiwan), and Si(100) substrates. After surface modification, the substrates were cleaned in an ultrasonic bath of acetone and ethanol and then rinsed in deionized water. It should be noted that the chemical etching was applied to the sapphire substrates only. The etching is widely adopted for refining alumina and can be described by eq 1

$$Al_2O_3 + 3H_2O + 2NaOH \rightarrow 2Na^+ + 2Al(OH)_4^- \qquad (1)$$

The growth of ZnO NWs was preformed in a double-tube furnace. A mixture of zinc (99.9% purity) and graphite powder with a molar ratio of 1:1 was placed in an alumina boat at the high-temperature zone (800 °C), and a substrate was placed downstream at the low-temperature zone (600 °C). The distance between the source boat and the substrate was typically 10 cm. The temperatures at the two zones were elevated at a rate of 4 °C/min to the desired temperatures, held for 30 min, and then cooled to room temperature. During the whole process, the pressure was kept at 800 mtorr with a gas mixture of 90% Ar and 10% O_2 flowing at speed of 80 sccm. An atomic force microscope (AFM; Smena, NT-MDT, Russia) was used to characterize the substrate surfaces. Morphological and structural properties of the NWs were analyzed by a scanning electron microscope (SEM; JSM 6500F, JEOL, Japan) and a transmission electron microscope (TEM; JEM 2010, JEOL, Japan).

Results and Discussion

Figure 1a shows an AFM image of a bare sapphire substrate. The root-mean-square (rms) roughness value was determined to be 0.14 nm and in agreement with the provided specification value. After light scratching with a steel needle, long stripe regions with larger surface corrugation were created, and an AFM image of a scratched area is shown in Figure 1b. A magnified view is shown in Figure 1c along with a cross-section profile plotted in Figure 1d. The rms roughness value of the scratched area increased to 0.77 nm. The glass and the Si substrates were also scratched in a similar way.

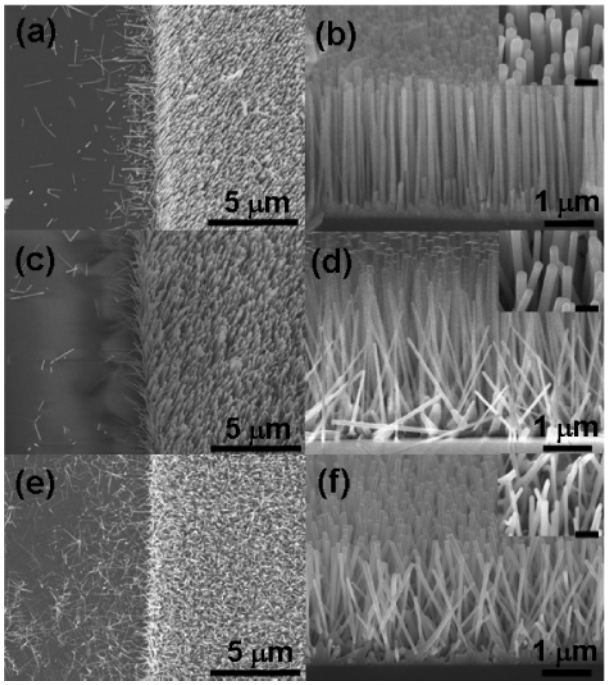

Figure 2. Top-view and side-view SEM images of NWs grown on scratched (a, b) sapphire, (c, d) glass, and (e, f) Si substrates, respectively. The scratched regions are on the right-hand side in the top-view images. The insets in parts b, d, and f are magnified images, and the scale bars are 200 nm long.

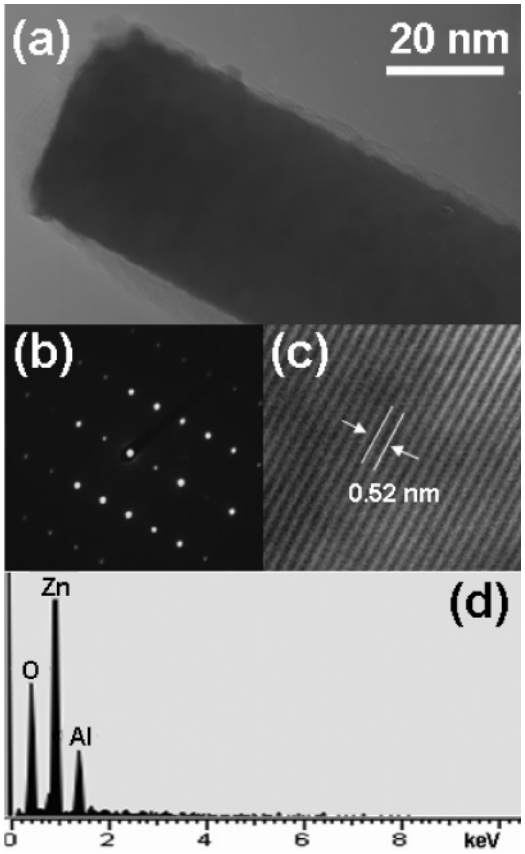

Figure 3. (a) TEM image of a ZnO NW with a diameter of 35 nm, (b) the corresponding selected area electron diffraction pattern, and (c) a high-resolution image exhibiting that the lattice constant *c* is 0.52 nm. (d) EDS spectrum of the ZnO NWs on sapphire.

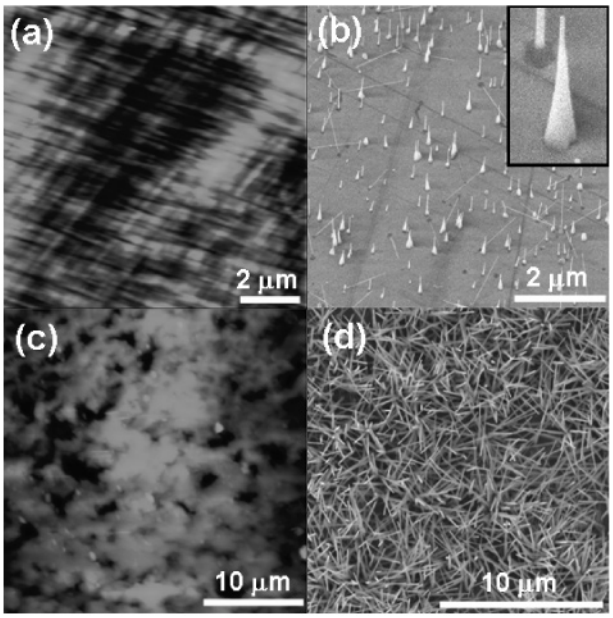

Figure 4. AFM images of sapphire substrates with rms roughness values of (a) 1.2 nm (height range 8 nm) and (c) 60 nm (height range 520 nm). (b, d) SEM images of the ZnO NWs in parts a and c, respectively. The inset is an enlarged view of one ZnO NW with a base diameter of around 150 nm.

The top-view SEM images of the ZnO NWs grown on the scratched sapphire, glass, and Si substrates are shown in Figure 2a,c,e, respectively, along with the side-view images shown in Figure 2b,d,f, respectively. The insets in the side-view images reveal that individual NWs and their diameters are ranging between 50 and 150 nm. As can be seen clearly from the top-view images, the NWs are abundant on the scratched regions (right half) but scarce on the unscratched regions (left half). Apparently, the increased surface roughness after scratching facilitates the NW growth. It is also obvious from the side-view images that the ZnO NWs are vertically aligned on the sapphire substrate and slightly tilted on the other two substrates.

A TEM image of a ZnO NW is presented in Figure 3a and clearly indicates the absence of metal catalysts on the ending and the peripheral facets. Also, the NW top has a flat end and is opposed to tapered or needle-shaped NWs produced from previous growth methods without the use of catalysts and seed layers.[11−13] The corresponding selected area electron diffraction pattern is also shown in Figure 3b and confirms the hexagonal wurtzite structure of the grown NWs. A high-resolution image is shown in Figure 3c and exhibits that the lattice constant *c* is 0.52 nm as expected. To further ascertain that no metal catalysts were introduced during scratching, the energy dispersive spectroscopy (EDS) spectrum of the NWs on sapphire was obtained and is shown in Figure 3d. Again, no trace of other metal components can be observed. Similar results were also found on NWs on other substrates. It can thus be concluded that the growth is indeed governed by the catalyst-free VS mechanism and assisted by surface roughness.

The mechanical polishing, on the other hand, yielded quite different results. Figure 4a shows an AFM image of a sapphire surface with an rms roughness value of 1.2 nm after a soft polishing (i.e., with the use of a small force). Although this value is not far from that of Figure 1c, the NWs grown on the substrate are in strong contrast and shown in Figure 4b. The NWs are still vertically aligned but loosely distributed on the substrate and have a tapered shape as can be seen in the inset. The outcome suggests that the soft polishing produced fewer nucleation sites on the surface for the NW growth in comparison with the scratching. With a hard polishing (i.e., with the use of a large force), the growth result changed again. Figure 4c shows an AFM image of a sapphire surface with an rms roughness value of 60 nm, and the grown NWs are presented in Figure 4d. As can be seen, the NWs are abundant but randomly oriented and highly entangled. The results clearly exemplify the strong influence of the surface corrugation on the NW shape and distribution, at least for the thermal evaporation method.

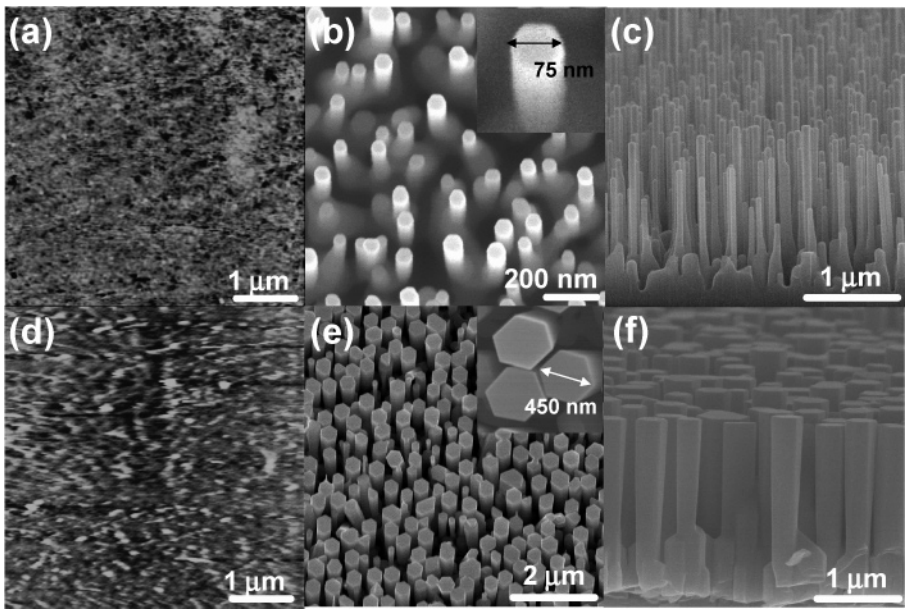

Figure 5. AFM images of sapphire substrates after etching in a 1 M NaOH solution (a) at room temperature for 15 s (height range 2 nm) and (d) at 150 °C for 10 min (height range 3 nm). (b, e) Top-view SEM images of NWs grown on parts a and d, respectively. The insets are magnified images and reveal hexagonal ZnO NWs and nanorods. (c, f) Side-view SEM images of parts b and e, respectively.

With the application of chemical etching on the sapphire substrates, the surface roughness could be controlled within minimal increase. Figure 5a,d shows two sapphire substrates after etching at room temperature for 15 s and at 150 °C for 10 min, respectively. The rms roughness values are measured to be 0.21 and 0.45 nm. The top-view SEM images of the growth results on the two substrates are shown in Figure 5b,e. Despite the small difference in the roughness values, the sizes of the NWs on the two substrates are drastically different. The upper inset reveals that hexagonal NWs of diameters around 75 nm were produced, whereas the lower one indicates that, instead of NWs, nanorods of diameters around 450 nm were produced. The side-view SEM images in Figure 5c,f manifest that both the NWs and the nanorods are vertically aligned. It is not clear at the present time why a small variation in roughness leads to such a large change in the NW size. Nevertheless, the results again demonstrate the strong effect of the substrate roughness. Furthermore, it is apparent that the thermal evaporation in combination with a pre-etching step is an excellent choice for the growth of catalyst-free large-scale vertically aligned ZnO NWs and nanorods on sapphire substrates.

Conclusion

We have successfully produced large-scale vertically aligned ZnO NWs on sapphire, glass, and Si substrates by direct thermal evaporation without the employment of either metal catalysts or seed layers. Simple processing steps including mechanical scratching, mechanical polishing, and chemical etching have been utilized for demonstrating the surface-roughness-assisted VS growth mechanism. The advantages include easy achievement of vertically aligned NWs and applicability on various types of substrates. The present results should have great value for realizing potential industrial applications of ZnO NWs.

Acknowledgment. This work was supported by the National Science Council under Grant 95-2221-E-007-097 and Veterans General Hospital under Grant 96-P6-27.

CM070474Y