AIP Applied Physics Letters

Controlled selective growth of ZnO nanorod and microrod arrays on Si substrates by a wet chemical method

Yong-Jin Kim, Chul-Ho Lee, Young Joon Hong, Gyu-Chul Yi, Sung Soo Kim, and Hyeonsik Cheong

Citation: Applied Physics Letters **89**, 163128 (2006); doi: 10.1063/1.2364162
View online: http://dx.doi.org/10.1063/1.2364162
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/89/16?ver=pdfcov
Published by the AIP Publishing

Controlled selective growth of ZnO nanorod and microrod arrays on Si substrates by a wet chemical method

Yong-Jin Kim, Chul-Ho Lee, Young Joon Hong, and Gyu-Chul Yi[a)]
National CRI Center for Semiconductor Nanorods, Department of Materials Science and Engineering, and School of Environmental Science and Engineering, POSTECH, Pohang, Gyeongbuk 790-784, Korea

Sung Soo Kim and Hyeonsik Cheong
Department of Physics, Sogang University, Seoul 121-742, Korea

(Received 5 July 2006; accepted 4 September 2006; published online 20 October 2006)

The use of a wet chemical method to selectively grow ZnO microrod and nanorod arrays on Si substrates is described. To control the size and position of the ZnO microrods and nanorods, polymethylmethacrylate (PMMA) submicron patterns were prepared on the Si substrates with an intermediate ZnO layer using e-beam lithography. Selective growth of the ZnO structures was achieved by the absence of ZnO nucleation sites on the PMMA mask, resulting in position-controlled growth of ZnO structures only on patterned holes where the ZnO layer was exposed. In addition, the diameters of the ZnO microrods were determined by the patterned hole size, and the diameters as small as 250 nm were obtained when a hole diameter of 250 nm was employed. The structural and optical characteristics of the ZnO microrods were further investigated using x-ray diffraction, transmission electron microscopy, and photoluminescence spectroscopy. [DOI: 10.1063/1.2364162]

Considerable interest has developed in the preparation of semiconductor microstructures and nanostructures on Si substrates for use in Si-based electronic and photonic device applications.[1,2] Despite the progress in heteroepitaxial growth and etching technology, differences in the crystal structures and chemical properties between Si and the other semiconductor films make it very difficult to grow high quality single crystalline films on Si substrates. For example, ZnO films are polycrystalline when grown on Si substrates, because Si surfaces are easily oxidized and form an amorphous silicon oxide layer during the film growth process.[3] In addition, many of the commonly used etching techniques result in surface damage as well as contamination. The difficulties associated with such top-down methods may be solved using a bottom-up approach, i.e., utilizing methods of self-organization at the molecular and nanocrystalline levels. Among the numerous nanomaterial preparation methods, catalyst-assisted vapor-liquid-solid (VLS) methods and catalyst-free metal-organic chemical vapor deposition (MOCVD) have been developed for the growth of semiconductor nanowires and nanorods on Si substrates.[4–6] Meanwhile, selective growth which permits the position, size, and morphology of semiconductor microstructures and nanostructures on many types of substrates to be controlled is prerequisite for the integration of nanodevices. Although the position and size controls of the nanowires and nanorods have been obtained using selective area MOCVD and catalyst-assisted VLS techniques,[7,8] these methods require high growth temperatures and expensive single crystalline substrates that satisfy the epitaxial growth conditions. In addition, position control of individual ZnO nanorods has not been achieved although ZnO nanorods were vertically grown on patterned substrates.[9,10] On the contrary, for the wet chemical process,[11] the growth temperature can be as low as 80–100 °C. As a result, many kinds of substrates, including amorphous oxide on silicon, glass, and polymers, can be employed. Here, we report on the size- and position-controlled selective growth of ZnO nanorods and microrods on Si substrates at 95 °C using a solution method.

Our approach to fabricating ZnO nanorod and microrod arrays at specific positions was to selectively grow them on prepatterned substrates using a wet chemical solution method. In this solution method, the nanorod and microrod growth temperature was as low as 80–100 °C, so that an organic mask layer, which is rarely used in other methods, could be employed for the selective growth. As a seed layer, for growing ZnO nanostructures on Si substrates, ZnO thin films were coated on Si substrates with a native oxide layer using pulsed laser deposition or MOCVD.[12,13] The as-grown ZnO films were polycrystalline, as determined by x-ray diffraction analysis. After spin coating an e-beam resist organic layer on the ZnO-coated Si substrates, circular hole array patterns were made on the organic layer using e-beam lithography. The patterned substrates were then treated with an oxygen plasma to remove organic residues on the patterned holes. The plasma-treated patterned substrates were then immersed in a nutrient solution for the growth of ZnO nanorods and microrods.[11,14] The nutrient solution was prepared from an equimolar aqueous solution (0.1*M*) of zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot 6H_2O]$ and hexamethylenetetramine in a Teflon-lined autoclave. Since ZnO is not grown on the mask area due to the lack of ZnO nucleation sites on the organic resist layer, it grows only on the patterned sites. In addition to position control, diameter and length of ZnO micro- and nanostructures were controlled using controlled pattern sizes and growth conditions such as growth time and temperature. The average growth rate of the ZnO nanorods and microrods at the growth temperature of 95 °C was in the range of 0.15–0.30 μm/h. After the growth, the ZnO struc-

[a)]Electronic mail: gcyi@postech.ac.kr

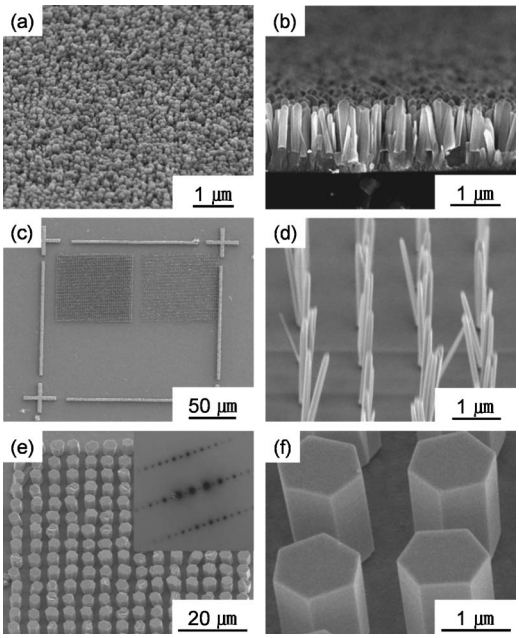

FIG. 1. Scanning electron microscopic images of ZnO nanorod and microrod arrays grown on ZnO thin films without and with a prepatterned mask. (a) Tilted and (b) cross-sectional FE-SEM images of ZnO nanorods grown on the substrate without any patterned mask. (c) Low magnification and (d) high magnification FE-SEM images of ZnO nanorod arrays selectively grown on the substrate with a prepatterned polymer mask. (e) Low magnification and (f) high magnification FE-SEM images of ZnO microrod arrays selectively grown on the substrate with a prepatterned polymer mask. The inset is the selective area electron diffraction pattern measured using TEM, indicating the high crystallinity of the ZnO microrods.

tures on substrates were immersed in acetone to dissolve the e-beam resist mask layers, and the residual material was removed.

Structural and optical characteristics of as-grown ZnO nanorod and microrod arrays were investigated using x-ray diffraction, field emission gun scanning electron microscopy (FE-SEM), tunneling electron microscopy (TEM), and microphotoluminescence (micro-PL) measurements. The micro-PL measurements were performed at room temperature with the 325 nm line of a He–Cd laser. The average pumping power was 670 μW and the focused laser beam size was 2 μm.

FE-SEM clearly revealed the general morphology of ZnO nanorods and microrods on ZnO/Si substrates grown without patterns and on prepatterned ZnO/Si substrates. As shown in Figs. 1(a) and 1(b), ZnO nanorods without patterns exhibited vertical arrays over the entire surface of the thin films. Furthermore, the SEM images in Figs. 1(c) and 1(d) show that all of the ZnO nanorods were selectively grown only on the patterned sites, when prepatterned substrates were used. The average diameter of the ZnO nanorods was 100 nm, much smaller than ZnO nanorods grown without patterns, presumably due to selective growth in the confined holes of the mask. Although some of the nanorods showed a little poor vertical alignment, excellent vertical alignment was observed for microrod arrays prepared on larger sized hole arrays, as shown in Figs. 1(e) and 1(f). The vertically well aligned ZnO microrods exhibited a hexagonal rod shape, implying that the growth direction of the ZnO microrods was ZnO(0001). The growth direction was confirmed using TEM. In addition, as shown in the inset in Fig. 1(e), electron diffraction patterns of ZnO microrods clearly showed diffraction spots without any hollow ring patterns, indicating that the ZnO microrods were highly crystalline.

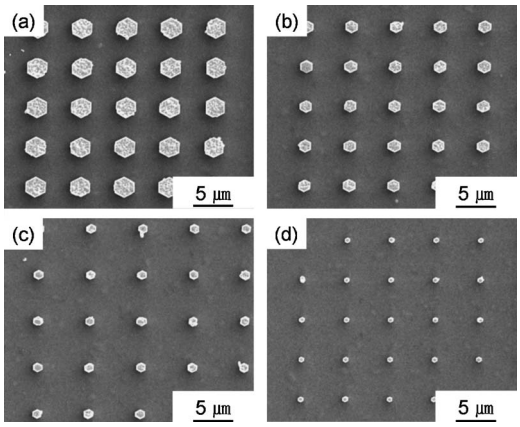

FIG. 2. FE-SEM images of ZnO microrod arrays grown in hole arrays with diameters of (a) 2, (b) 1, (c) 0.5, and (d) 0.25 μm. The microrod diameters can be controlled by changing the hole size of the pattern.

In addition to the position control of the microrods, their diameters were precisely determined by controlled pattern size. Figures 2(a)–2(d) show SEM images of ZnO microrod arrays that were simultaneously grown on the same ZnO/Si substrates with different diameters of prepatterned holes, 2, 1, 0.5, and 0.25 μm, respectively. The interdistance between the circular holes was fixed at 5 μm. The diameters of the as-grown ZnO microrod arrays were almost identical to those of the defined circular holes. When ZnO microrods were grown on 3 μm sized hole patterns, the diameter and length of the ZnO microrod arrays were 3 ± 0.21 and 3 ± 0.18 μm, respectively. Without regard to hole size, the ZnO microrods exhibited vertical alignment and uniform distribution in their diameters and lengths. Consequently, it was possible to fabricate different sized ZnO microrod arrays at specific sites on the same Si substrates.

The crystal structure and orientation of the selectively grown ZnO microrod arrays were also investigated by x-ray diffraction (XRD) measurements. From the XRD θ-2θ scan results of selectively grown ZnO microrod arrays, two strong peaks were observed at 34.24° and 72.40°, attributed to the ZnO(0002) and ZnO(0004) planes, respectively, indicating that the growth direction along the *c* axis of ZnO is normal to the substrate plane. In addition, XRD θ-rocking curves of ZnO microrod arrays in Fig. 3(b) show a full width at half maximum (FWHM) value of 1.3° for the selectively grown ZnO microrod arrays, much smaller than that (2.46°) of as-grown ZnO microrods without patterns and comparable to that (1.1°) of as-grown ZnO thin films. The small FWHM value from the XRD rocking curves of ZnO microrods prepared on the patterned substrates indicates that the *c* axes of the microrods are well aligned with the growth direction perpendicular to the substrate surface.

Figure 4 shows a typical micro-PL spectrum measured at room temperature. As shown in Fig. 4(a), a single ZnO microrod in the array shows a strong free-exciton emission at 3.23 eV and a weak deep level emission at 2.2 eV. Meanwhile, the excitonic PL emission exhibited much higher intensity than that of a ZnO thin film prepared on the same substrate and also a small FWHM value of 140 meV. The

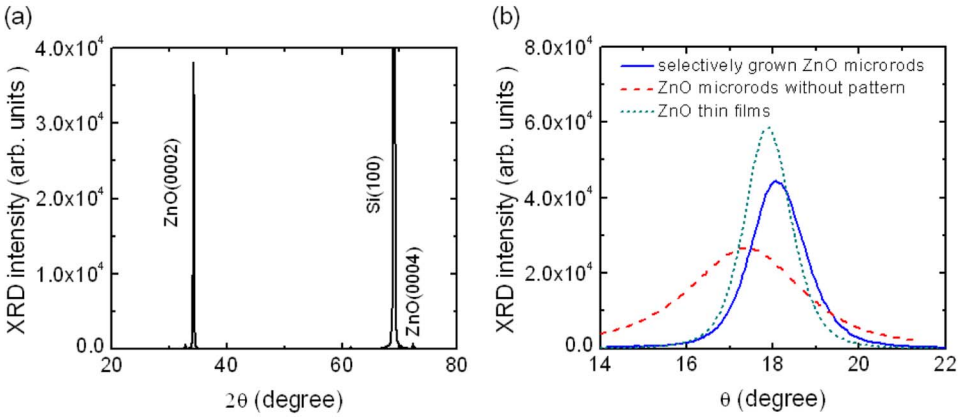

FIG. 3. (Color online) XRD (a) θ-2θ scan and (b) rocking curve measurement results of ZnO microrods. From the XRD θ-2θ scan data, only two peaks were observed at 34.24° and 72.40°, which correspond to ZnO(0002) and (0004) peaks, respectively. The rocking curve of ZnO microrods show a FWHM value of 1.3°.

FWHM value is comparable to that of metal-organic vapor phase epitaxy grown ZnO nanorods on an Al_2O_3 substrate.[15] These results indicate that the ZnO microrods produced in this study are of high optical quality.

We demonstrated the size and position controlled growth of ZnO nanorod and microrod arrays by a wet chemical process. In particular, the diameter of the ZnO nanorod and microrod arrays could be determined by the pattern size. Furthermore, the nanorod and microrod arrays are highly crystalline and are of excellent optical quality. More generally, we believe that this simple "bottom-up" chemical solution approach might readily be expanded to create many other semiconductor microstructure arrays on many types of substrates and will eventually contribute to the fabrication of vertical nanorod and microrod devices.

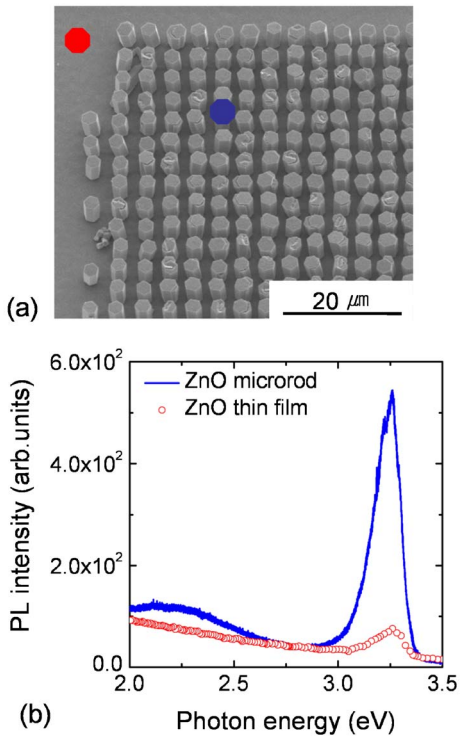

FIG. 4. (Color online) Micro-PL spectrum of selectively grown ZnO microrods measured at room temperature. The PL spectrum of ZnO microrod array shows a strong UV emission with a weak deep level emission.

This work was financially supported under the National Creative Research Initiative Project by the KOSEF. One of the authors (H.C.) was supported by the KOSEF through the Quantum Photonic Science Research Center.

[1]R. A. Beckman, E. Johnston-Halperin, N. A. Melosh, Y. Luo, J. E. Green, and J. R. Heath, J. Appl. Phys. **96**, 5921 (2004).
[2]A. Blanco, E. Chomski, S. Grabtchak, M. Ibisate, S. John, S. W. Leonard, C. Lopez, F. Meseguer, H. Miguez, J. P. Mondia, G. A. Ozin, O. Toader, and H. M. von Driel, Nature (London) **405**, 437 (2000).
[3]W. I. Park and G.-C. Yi, J. Electron. Mater. **30**, L32 (2001).
[4]R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).
[5]A. M. Morales and C. M. Lieber, Science **279**, 208 (1998).
[6]W. I. Park, G.-C. Yi, M. Kim, and S. J. Pennycook, Adv. Mater. (Weinheim, Ger.) **14**, 1841 (2002).
[7]T. Mårtensson, P. Carlberg, M. Borgstro, L. Montelius, W. Seifert, and L. Samuelson, Nano Lett. **4**, 699 (2004).
[8]J. Noborisaka, J. Motohisa, and T. Fukui, Appl. Phys. Lett. **86**, 213102 (2005).
[9]P. Yang, H. Yan, S. Mao, R. Russo, J. Johnson, R. Saykally, N. Morris, J. Pham, R. He, and H.-J. Choi, Adv. Funct. Mater. **12**, 323 (2002).
[10]X. Wang, C. J. Summers, and Z. L. Wang, Nano Lett. **4**, 423 (2004).
[11]L. Vayssieres, Adv. Mater. (Weinheim, Ger.) **15**, 464 (2003).
[12]S.-J. An, W. I. Park, G.-C. Yi, and S. Cho, Appl. Phys. A: Mater. Sci. Process. **74**, 509 (2002).
[13]W. I. Park, G.-C. Yi, and H. M. Jang, Appl. Phys. Lett. **79**, 2022 (2001).
[14]Y. Tack and K. Yong, J. Phys. Chem. B **109**, 19263 (2005).
[15]W. I. Park, D. H. Kim, S.-W. Jung, and G.-C. Yi, Appl. Phys. Lett. **80**, 4232 (2002).