J|A|C|S
ARTICLES
Published on Web 05/07/2005

Growth of Uniformly Aligned ZnO Nanowire Heterojunction Arrays on GaN, AlN, and $Al_{0.5}Ga_{0.5}N$ Substrates

Xudong Wang,[†] Jinhui Song,[†] Peng Li,[‡] Jae Hyun Ryou,[‡] Russell D. Dupuis,[‡] Christopher J. Summers,[†] and Zhong L. Wang*,[†]

Contribution from the School of Materials Science and Engineering and the School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332

Received February 8, 2005; E-mail: zhong.wang@mse.gatech.edu

Abstract: Vertically aligned single-crystal ZnO nanorods have been successfully fabricated on semiconducting GaN, $Al_{0.5}Ga_{0.5}N$, and AlN substrates through a vapor−liquid−solid process. Near-perfect alignment was observed for all substrates without lateral growth. Room-temperature photoluminescence measurements revealed a strong luminescence peak at ~378 nm. This work demonstrates the possibility of growing heterojunction arrays of ZnO nanorods on $Al_xGa_{1-x}N$, which has a tunable band gap from 3.44 to 6.20 eV by changing the Al composition from 0 to 1, and opens a new channel for building vertically aligned heterojunction device arrays with tunable optical properties and the realization of a new class of nanoheterojunction devices.

Introduction

Zinc oxide, a direct wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 meV), is considered to be one of the most important semiconductor materials for applications in optoelectronics, sensors, and actuators.[1,2] ZnO is also a material that is biocompatible and biosafe for applications as implantable biosensors. In recent years, quasi-one-dimensional (1D) ZnO nanostructures,[3] such as nanobelts,[4] nanorods, and nanowires,[5] have attracted a great research interest for applications in sensing,[6] optoelectronics,[7] field emission,[8] and piezoelectricity.[9] The growth of aligned ZnO nanorods is considered to be a good candidate for light emitting[10] and field emission.[11]

For the growth of aligned ZnO nanowires/nanorods, *a*-plane-oriented Al_2O_3 (sapphire) single crystals have been used as substrates with the assistance of gold particles as catalysts, in which the growth is initiated and guided by the Au particle, and the epitaxial orientation relationship between ZnO and Al_2O_3 leads to the alignment.[10,12] Two intrinsic problems are, however, associated with this technique, possibly limiting its application to devices. Al_2O_3 is a nonconductive material, making it difficult to utilize the aligned ZnO nanorods for electronic and optoelectronic devices. A lateral growth of side branches close to the substrate surface is almost inevitable during the early stages of growth. For technological applications, it is highly desirable to grow ZnO nanorods on a conductive or semiconductive substrate in order to fabricate heterostructure devices and to make electronic measurements. GaN, an important optoelectronic material with the same crystal structure as ZnO, has been used as a substrate for growing aligned ZnO nanorods by the metal−organic chemical vapor deposition (MOCVD) technique[13] and the carbon−thermal evaporation process[14] due to their very close lattice match. MOCVD can achieve a perfect alignment of ZnO nanowires on GaN substrate but lacks the control over the nanowires' site distribution and density since no catalyst was used.

Although GaN can electrically connect to the aligned ZnO nanowires, due to the very close band gaps of GaN (3.44 eV) and ZnO (3.37 eV), the heterojunction effect is fairly weak, thus limiting their applications in semiconductor devices. As a result, it is important to achieve a reasonably large band gap difference between the substrate and the ZnO nanowires while still maintaining good electrical conductivity and aligned morphology. In this paper, we present perfectly aligned ZnO

[†] School of Materials Science and Engineering.
[‡] School of Electrical and Computer Engineering.

(1) Look, D. C. *Mater. Sci. Eng. B* **2001**, *80*, 383−387.
(2) Cao, H.; Xu, J. Y.; Zhang, D. Z.; Chang, S. H.; Ho, S. T.; Seelig, E. W.; Liu, X.; Chang, R. P. H. *Phys. Rev. Lett.* **2000**, *84*, 5584−5587.
(3) Wang, Z. L. *Mater. Today* **2004**, *7*, 26−33.
(4) (a) Pan, Z. W.; Dai, Z. R.; Wang, Z. L. *Science* **2001**, *291*, 1947−1949. (b) Wang, Z. L.; Kong, X. Y.; Ding, Y.; Gao, P. X.; Hughes, W. L.; Yang, R. S.; Zhang, Y. *Adv. Func. Mater.* **2004**, *14*, 944−956.
(5) Huang, M.; Wu, Y.; Feick, H.; Tran, N.; Weber, E.; Yang, P. *Adv. Mater.* **2001**, *13*, 113−116.
(6) Arnold, M. S.; Avouris, P.; Pan, Z. W.; Wang, Z. L. *J. Phys. Chem. B* **2003**, *107*, 659−663.
(7) Johnson, J.; Yan, H.; Yang, P.; Saykally, R. *J. Phys. Chem. B* **2003**, *107*, 8816−8828.
(8) Bai, X. D.; Wang, E. G.; Gao, P. X.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1147−1150.
(9) Kong X. Y.; Wang, Z. L. *Nano Lett.* **2003**, *3*, 1625−1631.
(10) Wang, X. D.; Summers, C. J.; Wang, Z. L. *Nano Lett.* **2004**, *4*, 423−426.
(11) Li, S. Y.; Lin, P.; Lee, C. Y.; Tseng, T. Y. *J. Appl. Phys.* **2004**, *95*, 3711−3716.
(12) Huang, M. H.; Mao, S.; Feick, H.; Yan, H.; Wu, Y.; Kind, H.; Weber, E.; Russo, R.; Yang, P. *Science* **2001**, *292*, 1897−1899.
(13) (a) Park, W. I.; Kim, D. H.; Jung, S. W.; Yi, G. C. *Appl. Phys. Lett.* **2002**, *80*, 4232−4234. (b) Park, W. I.; Yi, G. C. *Adv. Mater.* **2004**, *16*, 87−90.
(14) (a) Fan, H. J.; Bertram, F.; Dadgar, A.; Christen, J.; Krost, A.; Zacharias, M. *Nanotechnology* **2004**, *15*, 1401−1404. (b) Fan, H. J.; Fleischer, F.; Lee, W.; Nielsch, K.; Scholz, R.; Zacharias, M.; Gosele, U.; Dadgar, A.; Krost, A. *Superlattices Microstruct.* **2004**, *36*, 95−105. (c) Tseng, Y. K.; Chia, C. T.; Tsay, C. Y.; Lin, L. J.; Cheng, H. M.; Kwo, C. Y.; Chen, I. C. *J. Electrochem. Soc.* **2005**, *152*, G95−G98.

10.1021/ja050807x CCC: $30.25

nanorods grown on semiconducting GaN, $Al_{0.5}Ga_{0.5}N$, and AlN thin-film substrates by a vapor−liquid−solid (VLS) phase process using gold as a catalyst. The as-grown nanorods show no lateral growth but are vertically aligned on the substrate surface. Our results prove that ZnO nanorods can be epitaxially grown on $Al_xGa_{1-x}N$ thin-film layers with any Al alloy composition ratio. Since the band gap of $Al_xGa_{1-x}N$ is tunable from 3.44 to 6.20 eV by changing the Al composition from 0 to 1, a band gap tunable heterojunction array of ZnO nanorods on a thin-film substrate can be achieved, thus making them an ideal candidate structure for light-emitting diode arrays.

Experiments

In our experiments, the MOCVD technique was employed for growing GaN, AlN, and AlGaN epilayers,[15,16] which served as the substrate for the subsequent growth of ZnO nanorods. Undoped *c*-plane-oriented GaN and AlN thin films were grown on one-side-polished *a*-plane sapphire substrates to thicknesses of 2 μm and 500 nm, respectively. $Al_{0.5}Ga_{0.5}N$ epitaxial layers with a thickness ∼205 nm were grown on a 500 nm thick AlN buffer layer grown on a one-side-polished *c*-plane-oriented sapphire substrate. A 7−8 nm thick ∼5 × 5 mm^2 gold catalyst layer was then deposited by plasma sputtering onto the epitaxial nitride substrates. The ZnO nanorods were grown through a vapor−liquid−solid process using a mixture of equal amounts (by weight) of ZnO and graphite powders (0.6 g each) that were loaded in an alumina boat located at the center of an alumina tube, which was placed in a single-zone tube furnace. Argon was used as carrier gas at a flow rate of 49 sccm with additional 2% (1 sccm) oxygen to facilitate the reaction. The substrates were placed 10 cm downstream from the source materials. The source materials were heated to 950 °C at a rate of 50 °C/min, and the temperature was held at the peak temperature for 30 min under a pressure of 30 mbar, while the local temperature of the substrates was ∼880 °C. Then the furnace was turned off, and the tube was cooled in air to room temperature within ∼2 h under an argon flow.

Results and Discussion

The as-synthesized aligned ZnO nanorods were first examined under a LEO 1530 field emission gun (FEG) scanning electron microscope (SEM) operated at 10 kV. A typical low-magnification SEM image of ZnO nanorods grown on GaN is shown in Figure 1a. All of the ZnO nanorods are straight and perpendicular to the substrate with a high uniformity across the entire substrate, indicating that this technique can be scaled up for large-area production. As shown from a higher-magnification SEM image in Figure 1b, the ZnO nanorods exhibit uniform diameter. Figure 1c shows a top view of the aligned ZnO nanorods, where only the very bright gold catalyst tips can be observed. It also confirms that almost every single nanorod is perpendicular to the substrate, and that there are no side branches, which is generally unavoidable when sapphire is used as substrate.

Highly aligned ZnO nanorods were also grown on $Al_{0.5}Ga_{0.5}N$ and AlN substrates under the same growth conditions, even though the lattice mismatch for these materials is larger than that for GaN. Figure 2a−c gives the X-ray diffraction (XRD) spectra of the aligned ZnO nanorod samples grown on GaN, $Al_{0.5}Ga_{0.5}N$, and AlN substrates, respectively. In all three spectra, only diffraction from (0002) and (0004) atomic planes of ZnO

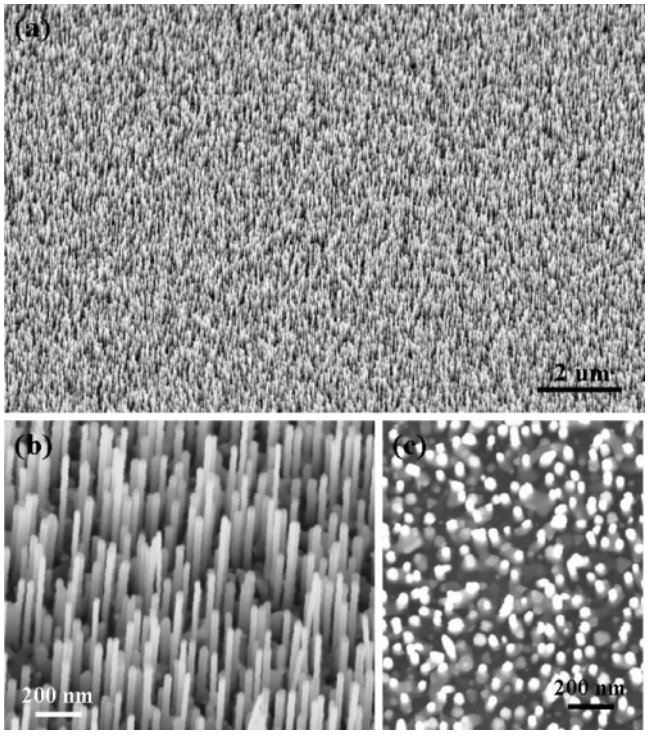

Figure 1. SEM images of aligned ZnO nanorods grown on a GaN substrate. (a) Low-magnification 30° side view image. (b) High-magnification 30° side view image. (c) High-magnification top view image.

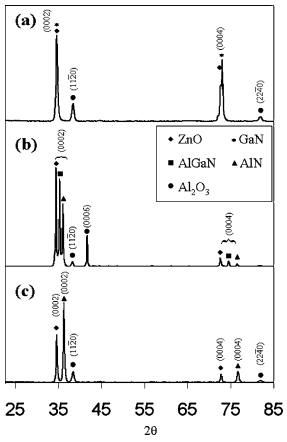

Figure 2. XRD spectra of aligned ZnO nanorods growing on GaN (a), $Al_{0.5}Ga_{0.5}N$ (b), and AlN (c) substrates.

is observed at 34.63 and 72.76°, respectively, indicating the high degree of nanorod alignment and their epitaxial relationship with the substrate. From the lattice constants of wurtzite GaN (a = 3.190 Å and c = 5.189 Å) and wurtzite ZnO (a = 3.249 Å and c = 5.207 Å), the lattice mismatch between the (0001) planes is 1.9%. Thus, in the XRD spectrum (Figure 2a), the peak from the GaN (0002) plane overlaps that of ZnO, while a double shoulder is observed on the (0004) peak. The epitaxial relationship between the ZnO nanorods and the GaN substrate layer is $(0001)_{ZnO} \parallel (0001)_{GaN}$, $[01\bar{1}0]_{ZnO} \parallel [01\bar{1}0]_{GaN}$. Although the lattice constant decreases from 3.190 (GaN) to 3.15 ($Al_{0.5}Ga_{0.5}N$) and to 3.110 (AlN) Å, and their lattice mismatch correspondingly increases from 1.8 to 3.0 to 4.3%, the epitaxial relationship is preserved as supported by the XRD spectra shown in Figure 2b and c. This figure also shows that the diffraction peaks of $Al_{0.5}Ga_{0.5}N$ and AlN are gradually separated from ZnO peaks

(15) Chowdhury, U.; Wong, M. M.; Collins, C. J.; Yang, B.; Denyszyn, J. C.; Campbell, J. C.; Dupuis, R. D. *J. Cryst. Growth* **2003**, *248*, 552−555.
(16) Zhu, T. G.; Chowdhury, U.; Wong, M. M.; Denyszyn, J. C.; Dupuis, R. D. *J. Cryst. Growth* **2003**, *248*, 548−551.

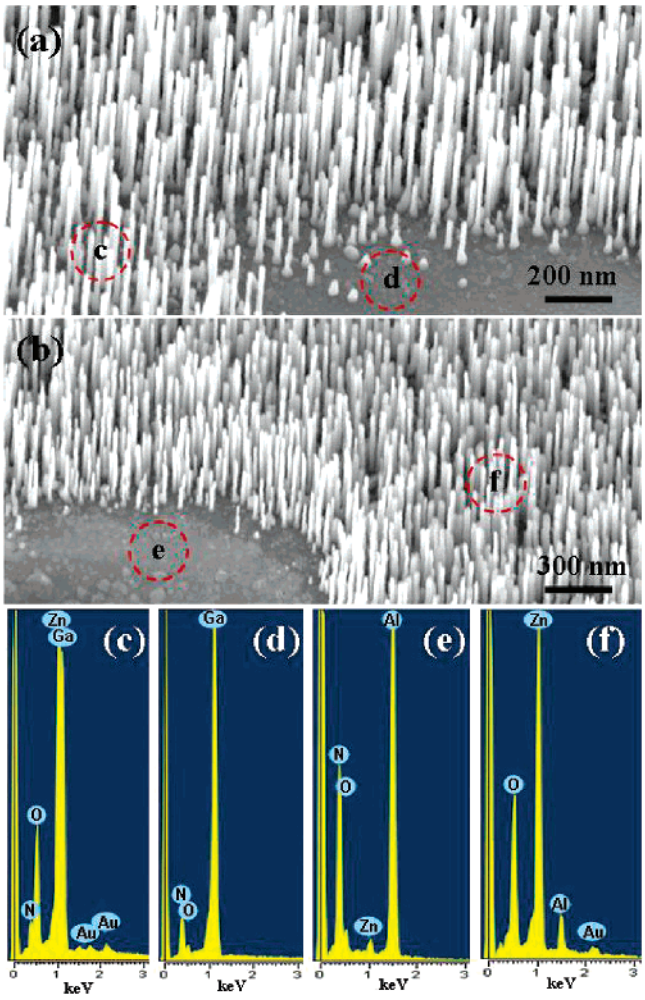

Figure 3. SEM images of ZnO nanorods growing on GaN (a) and AlN (b) substrates at the edge of catalyst layer. (c−f) EDS spectra of the corresponding circled region in (a) and (b).

due to the increased lattice mismatch, whereas the ZnO (0002) and (0004) peaks remain sharp and clear.

Because both ZnO and the substrates have the same wurtzite structure, the deposited ZnO nanorods are confined in their six equivalent <01$\bar{1}$0> directions and only grow along the [0001] direction exactly following the substrate's crystal orientation. As a result, the possibility for ZnO nanorods to undergo lateral growth is rare, even around the catalyst where conditions are favorable for lateral growth, as shown in Figure 3a and b. Therefore, *c*-plane-oriented $Al_xGa_{1-x}N$ substrates are ideal for the growth of aligned ZnO nanorods. On the other hand, the epitaxial relationship between ZnO and *a*-plane sapphire substrate is $(0001)_{ZnO} \parallel (11\bar{2}0)_{Al_2O_3}$, $[01\bar{1}0]_{ZnO} \parallel [0001]_{Al_2O_3}$. Although the lattice mismatch between $4[01\bar{1}0]_{ZnO}$ ($4 \times 3.249 = 12.996$ Å) and $[0001]_{Al_2O_3}$ (12.99 Å) is almost zero, there is only one direction that is defined by this epitaxial relationship because the $(11\bar{2}0)$ plane of Al_2O_3 is a rectangular lattice but the (0001) plane of ZnO is a hexagonal lattice. As a result, the lateral growth of ZnO side branches was always observed for *a*-plane sapphire substrates.[17]

The properties of catalytic particle initiated growth were further investigated using energy-dispersive X-ray spectroscopy

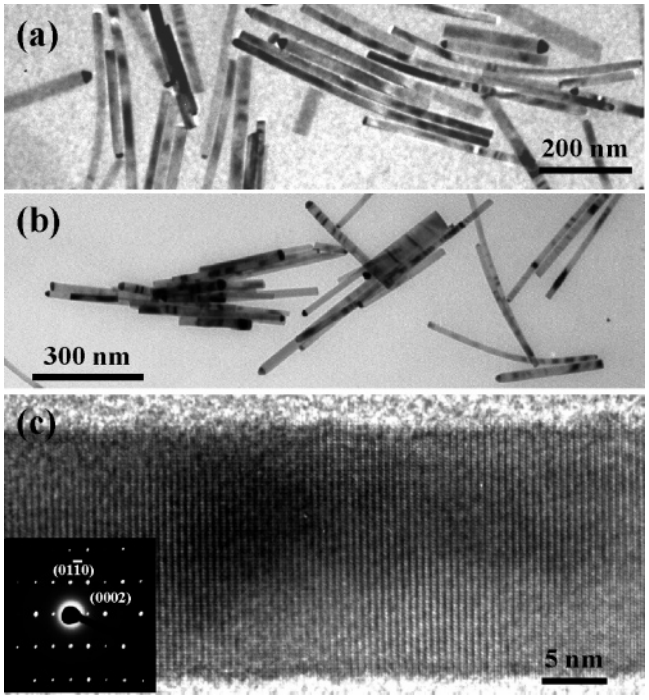

Figure 4. Low-magnification TEM image of ZnO nanorods grown on GaN (a) and AlN (b) substrates. (c) High-magnification TEM image of a single ZnO nanorod; (inset) the corresponding electron diffraction pattern of the ZnO nanorod shown in (c).

(EDS) during the SEM measurements. Panels a and b of Figure 3 are SEM images of ZnO nanorods grown around the edge of the gold catalyst on GaN and AlN substrates, respectively, in which the catalyst boundary is clearly marked by the growth of aligned ZnO nanorods. EDS measurements were performed on the nanorod regions and the exposed substrate regions. Within the nanorod regions (Figure 3c and f), strong signals from zinc and oxygen were detected with a small gold signal originating from the Au film which acted as the catalyst and a portion of which remained at the tip of ZnO nanorods. Signals from the GaN and AlN substrates were also found. However, on the exposed substrate (Figure 3d and e), only strong signals from the substrate materials were detected. Therefore, unlike the noncatalyst technique, such as MOCVD, which lacks of control over the growth position, the VLS process can precisely position the aligned ZnO nanorods by patterning the gold catalyst, where the uncovered substrate area remains chemically and structurally unchanged. Moreover, an almost perfect vertical alignment of ZnO nanorods without lateral growth can be achieved using the VLS technique demonstrated here.

Transmission electron microscopy (TEM) was also performed for size and crystal structure analysis using a Hitachi HF2000 TEM operated at 200 kV. The lower-magnification TEM images obtained for ZnO nanorods grown on GaN and AlN substrates are shown in Figure 4a and b, respectively. All of the nanorods exhibit fairly uniform thickness along their entire length with gold catalysts at the tips. By measuring ~200 nanorods recorded on TEM images, we found that the average length of ZnO nanorods grown on GaN was 434 nm, while the ZnO nanorods grown on AlN substrate were a little longer, ~500 nm. However, their length distributions are very close (±118 and ±120 nm for ZnO nanorods grown on GaN and AlN substrates, respectively). The average diameter was 28 ± 6 nm for ZnO nanorods grown on GaN and 22 ± 2 nm for those deposited on AlN.

(17) Yang, P.; Yan, H.; Mao, S.; Russo, R.; Johnson, J.; Saykally, R.; Morris, N.; Pham, J.; He, R.; Choi, H. *Adv. Funct. Mater.* **2002**, *12*, 323−331.

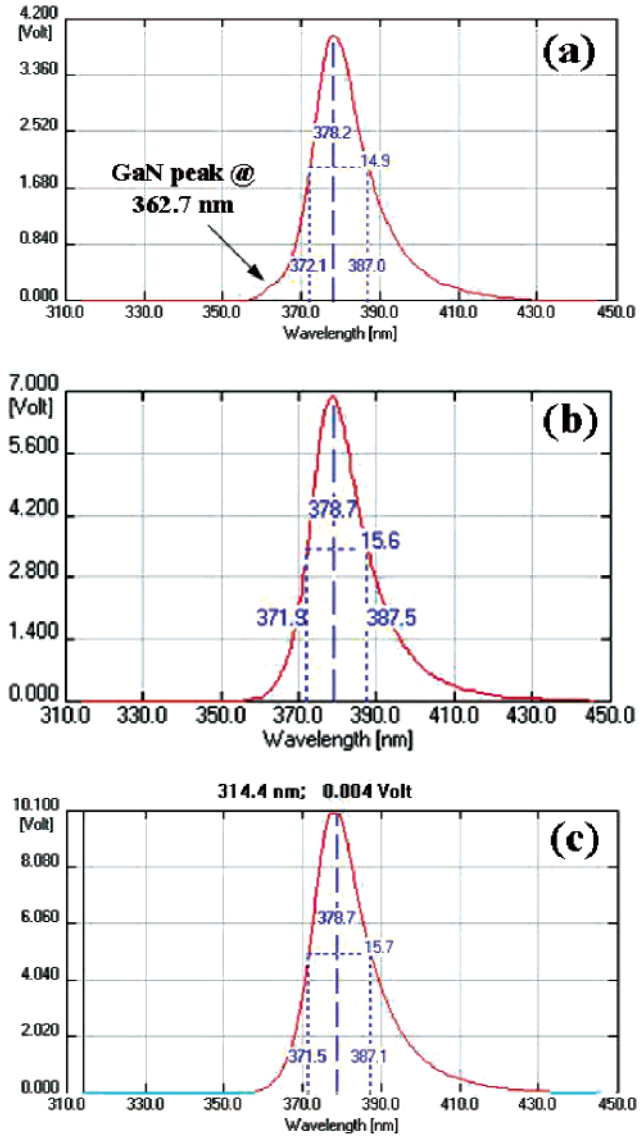

Figure 5. Photoluminescence spectra (300 K) of aligned ZnO nanorods grown on GaN (a), $Al_{0.5}Ga_{0.5}N$ (b), and AlN (c) substrates.

The smaller size of the ZnO nanorods on AlN is possibly due to the larger lattice mismatch between ZnO with AlN. The ZnO nanorods are single crystal (Figure 4c), the growth direction is [0001], and the six side facets are $\{11\bar{2}0\}$.

Room-temperature photoluminescence (PL) properties were measured for ZnO nanorod arrays grown under same conditions on GaN, AlGaN, and AlN substrates (Figure 5a−c) using a 266 nm Nd:YAG Q-switched laser with an average power of 1.9 mW as the excitation light source. A Si photodetector is used to measure the PL. All of the samples exhibited a strong luminescence peak at ∼378 nm, corresponding to the near band gap emission of ZnO, an identical peak shape with a peak width at half intensity of ∼15 nm. For the PL spectrum of ZnO nanorods on GaN, a small peak at 362.7 nm was also detected, which corresponds to the band gap of GaN (3.44 eV). Due to the increased band gap when Al is introduced into the GaN lattice, the PL peaks from the substrate are blue shifted and thus no additional substrate-related peaks were observed from ZnO nanorods grown on AlGaN and AlN substrates.

Although the PL peaks have an identical shape, their peak intensity varies significantly. The highest PL signal intensity, which was more than 10 V, was measured from ZnO nanorods grown on AlN (Figure 5c) and the lowest from ZnO nanorods grown on GaN, only ∼4 V, as shown in Figure 5a. The PL peak intensity from ZnO nanorods grown on AlGaN exhibited an intermediate peak intensity of ∼7 V (Figure 5b). Since the density of nanorods grown on GaN, AlGaN, and AlN substrates is calculated from the SEM images to be 146, 70, and 157 per μm^2, respectively, these relative PL intensities are not linearly related to the nanorod density. Therefore, the measured PL intensity of ZnO is likely to be affected by the absorption of GaN substrate. Due to the wide band gap of AlN (6.20 eV), the luminescence at 378 nm from ZnO is not absorbed by AlN substrate, but the band gap of GaN is very close to that of ZnO, thus the PL of ZnO is likely to be absorbed by the GaN substrate for the nanorods grown on GaN.

Conclusion

Vertically aligned single-crystal ZnO nanorods have been successfully fabricated on semiconducting GaN, $Al_{0.5}Ga_{0.5}N$, and AlN substrates through a vapor−liquid−solid process. This alignment is almost perfect on the three types of substrates without lateral growth. The as-synthesized ZnO nanorods also showed a reasonable size distribution and high crystal quality. Room-temperature PL measurements revealed a strong luminescence peak at ∼378 nm whose intensity depends on the substrate material, possibly due to the different absorption properties of AlN, $Al_{0.5}Ga_{0.5}N$, and GaN. This work demonstrates the possibility of growing heterojunction arrays of ZnO nanorods on $Al_xGa_{1-x}N$ substrates with x values ranging from 0 to 1. If the AlGaN alloy composition can be designed laterally using a combinatorial approach,[18] this could possibly open a new channel for building vertically aligned heterojunction device arrays with tunable optical properties and the realization of a new class of nanoheterojunction devices.

Acknowledgment. The research was partially supported by Georgia Institute of Technology Nanoscience/Nanoengineering Research Program, by the DARPA SUVOS program, NASA Vehicle Systems Program and Department of Defense Research and Engineering (DDR&E), and MURI program from ARO (Grant DAAD19-01-1-0603). In addition, R.D.D. gratefully acknowledges the support of the Steve W. Chaddick Endowed Chair in Electro-Optics.

JA050807X

(18) Xiang, X. D.; Sun, X. D.; Briceno, G.; Lou, Y. L.; Wang, K. A.; Chang, H. Y.; Wallacefreedman, W. G.; Chen, S. W.; Schultz, P. G. *Science* **1995**, *268*, 1738−1740.