

Growth of GaN Nanowires on Si Substrate Using Ni Catalyst in Vertical Chemical Vapor Deposition Reactor

Tae Yun Kim, Sang Hyun Lee**, Young Hwan Mo, Hyun Wook Shim*, Kee Suk Nahm†, Eun-Kyung Suh* and Gyung Soo Park**

School of Chemical Engineering and Technology, *Department of Semiconductor Science and Technology, Chonbuk National University, Chonju 561-756, Republic of Korea

**FED Project Team, Samsung Advanced Institute of Technology, P.O. Box 111, Suwon 440-600, Republic of Korea
(Received 15 April 2003 • accepted 2 September 2003)

Abstract—GaN nanowires were successfully grown on Ni-coated Si substrate by direct reaction of gallium with ammonia gas in a home-made vertical tubular chemical vapor deposition reactor. The growth of GaN nanowires was uniformly observed across the Si substrate surface, but the density and average diameter of the nanowires varied along the position of the substrate surface. At the position of 5 cm above Ga source surface, the growth of GaN crystal grains was observed with few nanowires. The length of the nanowires reached several micrometers. The clear lattice fringes in HRTEM image revealed the growth of good quality hexagonal single-crystal GaN nanowires. Photoluminescence of the GaN nanowires showed a strong band edge emission at the energy position of ~ 3.4 eV with negligible deep level yellow emission. Field emission characteristics of the GaN nanowires showed that the turn-on field of GaN nanowires was ~ 7.4 V/ μm with a field enhancing factor β of ~ 555 . The catalytic growth mechanism of the GaN nanowires was discussed on the basis of experimental results in this work.

Key words: GaN Nanowires, Ammonia, Ni Catalyst, Si Substrate, Vertical CVD Reactor

INTRODUCTION

Semiconductor nanowires and carbon nanotubes have recently been drawing a great attention as potentially ideal building blocks for nanoscale electronics and optoelectronics [Dekker, 1999; Suh et al., 2002]. Carbon nanotubes have already been employed as active channel of field-effect and single electron transistors [Tans et al., 1998; Deryche et al., 2001]. However, practical application of carbon nanotubes for nanodevices is still limited because of the difficulty of selective growth of semiconducting or metallic nanotubes [Odom et al., 1998; Wildoer et al., 1998]. GaN is an important semiconductor for this aim due to its exceptional physical properties [Yang et al., 2000; Nahm et al., 2002]. A number of techniques have been proposed for the growth of 1-dimensional semiconducting GaN nanowires. Chen et al. reported the synthesis of high purity and quality GaN nanowires by the catalytic reaction of gallium and ammonia using transition metals [Chen et al., 2001]. A carbon nanotubes-confined reaction has been also employed to synthesize GaN nanorods [Han et al., 1997]. He et al. succeeded in growing large-scale GaN nanowires and tubes by a direct reaction of metal Ga vapor with ammonia [He et al., 2000]. Kim et al. also synthesized high-quality GaN nanowires using a Ni catalyst by thermal CVD [Kim et al., 2002]. In particular, a number of high-yield crystalline GaN were obtained by using a catalytic growth based on a vapor-liquid-solid (VLS) mechanism [Duan and Lieber, 2000].

In this work, GaN nanowires were grown by a direct reaction of

molten Ga and ammonia gas over Ni catalyst supported by Si substrate in a vertical chemical vapor deposition (CVD) reactor. The GaN nanowires were characterized by using various techniques to investigate structural, optical, and electrical properties.

EXPERIMENTS

GaN nanowires were synthesized in a vertical CVD reactor depicted in Fig. 1 [Ahn et al., 2002]. The reactor consists of two quartz inner and outer tubes. A mixed solution was prepared by dissolving 0.5 M $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in DI water and was used to coat Ni catalyst on the surface of Si substrate. Si (100) substrate (1.0 cm \times 8 cm) was sonicated in acetone and the solution was dropped on the cleaned Si surface to load Ni catalyst. The catalyst coated Si substrate was dried in an oven for 24 hrs. Metallic Ga (2 g) and GaN powder (0.5 g) were first put together in the inner reactor for Ga source and then

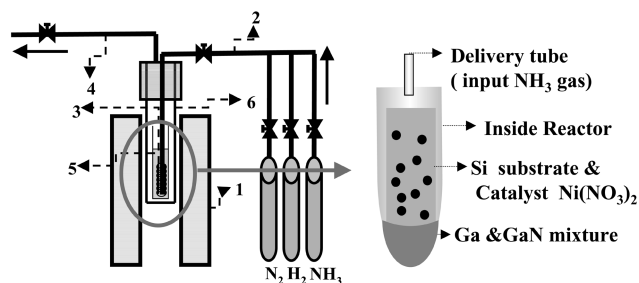


Fig. 1. A schematic diagram of the vertical chemical vapor deposition system for the growth of GaN nanowires.

- | | |
|-----------------------|--------------------|
| 1. Electrical furnace | 4. Output gas line |
| 2. Input gas line | 5. Outer reactor |
| 3. Silicon substrate | 6. Inner reactor |

†To whom correspondence should be addressed.

E-mail: nahmks@moak.chonbuk.ac.kr

†This paper is dedicated to Professor Hyun-Ku Rhee on the occasion of his retirement from Seoul National University.

the Ni-coated Si substrate was vertically set up over the Ga source mixture. Hydrogen gas was introduced into the outer quartz tube to minimize any other side reactions while the reactor temperature was increased. At 700 °C, the H₂ flow was shut off and then ammonia gas flowed into the inner reactor through a delivery tube with a flow rate of 20 sccm. The gas pressure remained under 40 torr during the growth reaction of GaN nanowires. The flow of ammonia gas was only maintained during the reaction and was replaced by nitrogen gas when the reactor was cooled down to room temperature. After GaN nanowires were grown, the Si substrate was cut into three pieces with two centimeters in length for the characterization of the GaN nanowires.

The grown GaN nanowires were characterized by X-ray diffraction (XRD), Raman spectroscopy, field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The room-temperature Raman spectra were measured with 514.5 nm photons from an Ar⁺ laser. Photoluminescence (PL) was also measured with He-Cd laser with 325 nm excitation to study optical properties of the nanowires. Field emission characteristics were examined by using a parallel-plate configuration of I-V mea-

surement under a base pressure of 5×10^{-7} Torr at room temperature. A Keithly 237 electrometer was employed for supplying the voltage and measuring the current. The measurements were performed by collecting electrons emitted from the sample while applying a positive voltage on an indium-tin-oxide-coated (ITO) glass electrode, which was placed 145 μm above the sample.

RESULTS AND DISCUSSION

Fig. 2 shows FE-SEM images of nanowires grown on Si substrate using Ni catalyst. The images were taken at three different positions of Ni-loaded Si surface: 1, 3, and 5 cm above from the Ga source surface, which are denoted as P1, P2, and P3, respectively. The nanowires were grown for 3 hrs at 910 °C with 20 sccm NH₃. The growth of high density nanowires was observed at P1 and P2, and the length of the nanowires reached several micrometers. The average diameter of the nanowires grown at P2 (~26 nm) is smaller than that of P1 (~70 nm). It seems that the nanowires are denser at P2. But the growth of crystal-like grains was mainly seen at P3 with few nanowires. The nanowires grown at P1 and P2 are uniformly distributed over the Si substrate surface and metal tips are observed at the top of the nanowires, as shown in Fig. 2(b).

Shown in Fig. 3 are XRD spectra for the nanowires measured at P1, P2, P3, respectively. The spectra show the growth of a typical hexagonal GaN structure. The XRD patterns are consistent with the characteristic peaks of the hexagonal GaN structure reported in the X-ray powder data file of JCPDS, as well as in other previous works [Ahn et al., 2002; Zhang et al., 1999; Kumar and Kumar, 2002]. The Miller indices are indicated on each diffracted peak. The relative intensities of the XRD peaks are slightly different from that of bulk GaN, which may be due to the size effect and disorder arising from the formation of nano-sized structures [Zhang et al., 1999]. The spectrum measured at P3 shows low intensities of GaN related peaks, whereas the intensity of Si related peak is very strong. This is consistent with SEM observation, indicating that a small amount

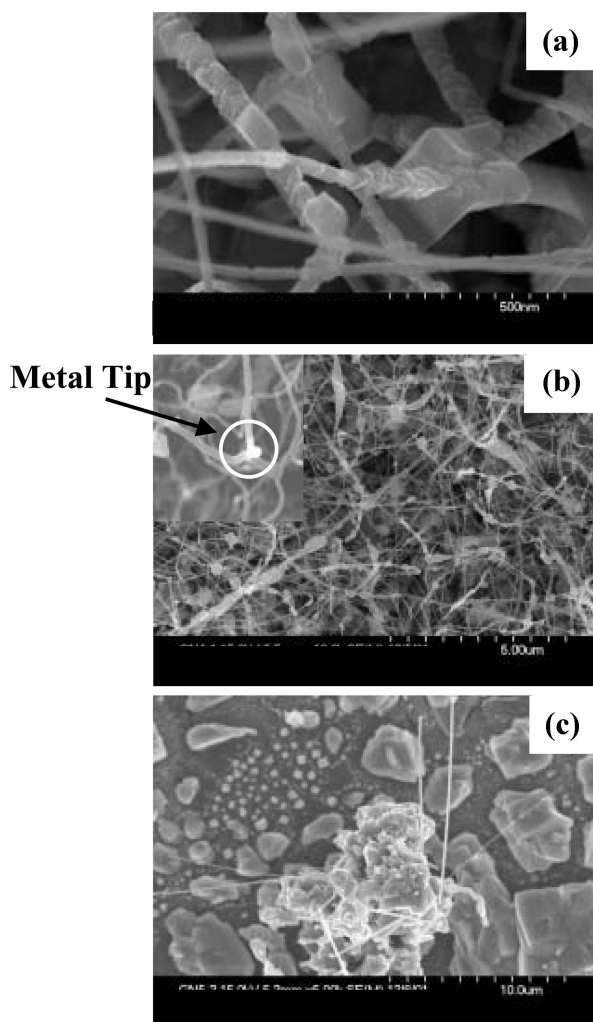


Fig. 2. FE-SEM images for GaN nanowires grown at different substrate surface positions from Ga source.
(a) 1 cm, (b) 3 cm, and (c) 5 cm

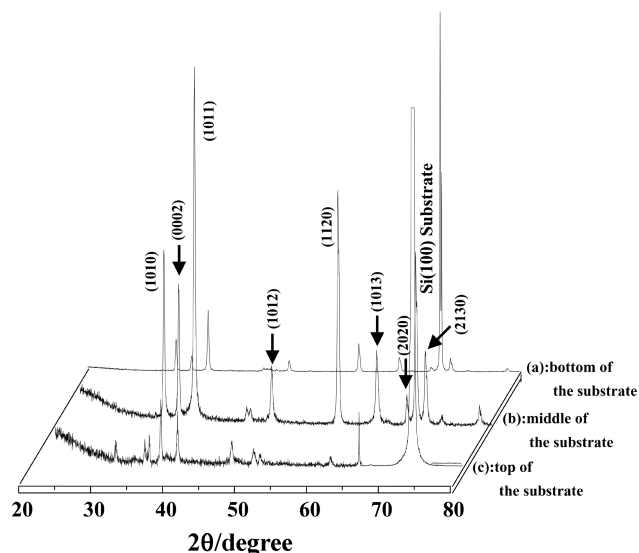


Fig. 3. XRD spectra for GaN nanowires grown at different substrate surface positions from Ga source.
(a) 1 cm, (b) 3 cm, and (c) 5 cm

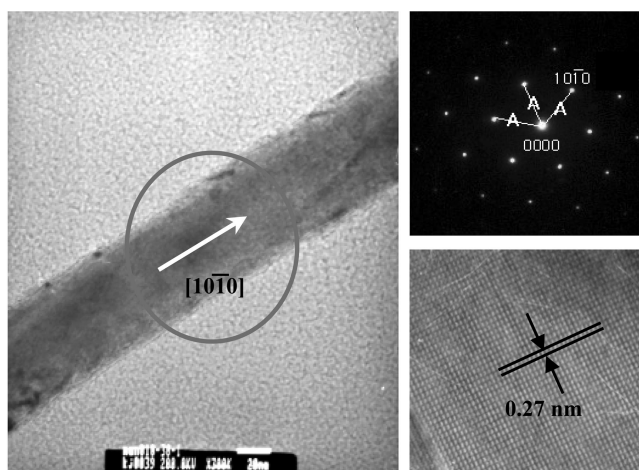


Fig. 4. TEM and HRTEM images for GaN nanowires grown at 3 cm with SAED pattern.

of GaN grows at P3 when the substrate position is far from the Ga source. The relative intensity ratio of GaN to Si peak is stronger at P2 than at P1, indicating growth of high density GaN nanowires at P2. This means that the traveling distance of Ga from its source is a decisive factor to control the growth of GaN nanowires.

For further characterization of structural and optical properties of the GaN nanowires, TEM, Raman, and PL measurements were carried out for the nanowires grown at the center of the substrate (P2). Fig. 4 shows the TEM image of a GaN nanowire with a diameter of 50 nm approximately. The upper right inset of the figure presents a selected area diffraction pattern (SAED), which reveals that the GaN nanowires are grown along $[1010]$ direction and have hexagonal structures. The lattice image of the GaN nanowires was also observed by using high resolution TEM (HRTEM) and is presented in the lower right inset of the figure. The HRTEM image and SADP (selected area diffraction pattern) for the GaN nanowires show no defects between contrast bands. The lattice constant of GaN nanowire is estimated to be 0.27 nm from the image. The clear lattice fringes in this image identify the growth of good quality single-crystal GaN nanowires.

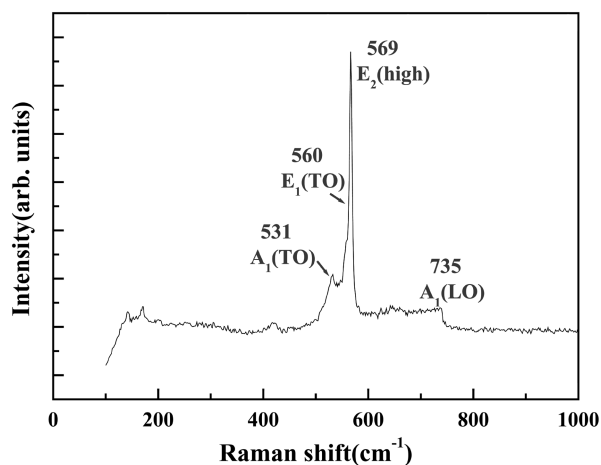


Fig. 5. Raman spectrum for GaN nanowires grown at 3 cm apart from Ga source.

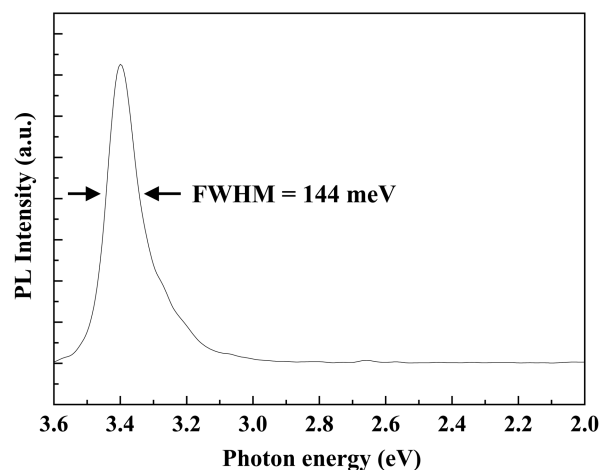


Fig. 6. PL spectrum for GaN nanowires grown at 3 cm apart from Ga source.

Shown in Fig. 5 is the Raman spectrum for the nanowires. The spectrum was recorded in a $z(yu)z$ configuration with the z -direction along the c -axis of GaN. The E_2 peak is observed at 569 cm^{-1} from the sample, as we expected from the selection rule for the scattering configuration employed. It has been reported that the wurtzite GaN E_2 mode is attributed to the deformation potential scattering [Demangeot et al., 1996]. The spectrum of bulk hexagonal GaN gives main three phonon bands at 142 cm^{-1} (E_2 low), 569 cm^{-1} (E_2 high), and 734 cm^{-1} (A_1 [LO] high) and the signal at 569 cm^{-1} (E_2 high) is very strong [Yu et al., 1988], which are all observed from Fig. 5. The Raman spectrum exhibits additional weak peaks at 170, 421, 498, 531, 560, 645 cm^{-1} . It is thought that the peaks are due to various crystalline defects (or imperfections) or size effects [Chen et al., 2001]. Crystal Si peak appearing at the frequency of 520 cm^{-1} seems to be buried in the shoulder of the lower frequency side of 569 cm^{-1} , consistent with XRD spectrum [Fig. 3(b)].

Fig. 6 shows a typical PL spectrum for the GaN nanowires. PL is one of the powerful and non-destructive tools for characterizing the intrinsic processes like band-to-band recombination. It can also be used to detect and identify impurities in semiconductor materials particularly for the detection of shallow-level impurities [Kumar and Kumar, 2002]. Photoluminescence of the GaN nanowires shows a strong band edge emission at $\sim 3.4\text{ eV}$ with negligible deep level yellow emission, which confirms the growth of good quality GaN nanowires [Kumar and Kumar, 2002]. FWHM of the band is about 144 meV, possibly due to the size effect and unintentionally doped shallow impurity [Seo et al., 2002].

The growth mechanism of nanowires and carbon nanotubes has been widely discussed [Chen et al., 2001; He et al., 2000; Duan and Lieber, 2000; Peng et al., 2002; Sen et al., 1997; Hernadi et al., 2002]. Fig. 2(b) showed that the GaN nanowires are terminated with metal catalyst nanoparticles on their tips. Similar observation was reported from literature, which proposed the VLS (vapor-liquid-solid) mechanism for the growth of nanowires [Chen et al., 2001; Duan and Lieber, 2000]. They suggested a mechanism in which a liquid metal cluster or catalyst acts as the energetically favorable site for absorption of gas-phase reactants. At the reaction temperature, it is thought that gallium first evaporates and transports from Ga source to the

Si surface, where the catalytic reaction takes place. The Ni catalyst and Ga form Ni-Ga-N alloy in the presence of NH_3 gas. N participating in the reaction is the catalytically decomposed product from NH_3 gas [Nahm et al., 2003]. The Ni-Ga-N transition alloy is a liquid phase during the catalytic reaction process and presumably an intermediate product in the production of GaN nanowires. Additionally, the fluidization temperature of nano-sized catalytic metal particles is considerably lower than the melting point of either eutectic mixture or pure metal [Krivoruchko et al., 1993]. When the concentration of Ga-N exceeds a saturation point in the liquid phase alloy droplets, the GaN begins to diffuse through the liquid phase to the bottom of the droplet and condenses as a GaN nanowire, which grows along a certain direction. Consequently, our GaN nanowires seem to be produced on Si substrate by the catalytic action of Ni through the VLS mechanism from the direct reaction between Ga melt and NH_3 gas. We think that further experimental studies are necessary to clearly explain the growth mechanism of the GaN nanowires. The diameters of resulting GaN nanowires seem to be dependent on the sizes of the miscible liquid alloys of Ga-N-catalyst as well as the amount of gallium transported from the source, which is influenced by the growth temperature and the distance of the substrate from the Ga source.

Fig. 7 shows the field emission characteristics of the GaN nanowires and the corresponding Fowler-Nordheim (F-N) plot. This figure illustrates that 1 μA of the emission current is obtained at an applied voltage 1,200 V. Thus, the turn-on field for GaN nanowires is 7.4 V/ μm (The gap between the GaN nanowires and the anode plate is 150 μm , and the emission area is 7 mm^2). The straight line behavior of the F-N plot indicates that the measured electron current of GaN nanowires results from field emission. Due to the band bending in the semiconducting nanowires together with the intrinsic high n-doping of GaN [Kim et al., 2002], most electrons are assumed to be emitted from the conduction band [Wang et al., 2002]. Consequently, in order to estimate the field enhancement factor ($\beta' =$

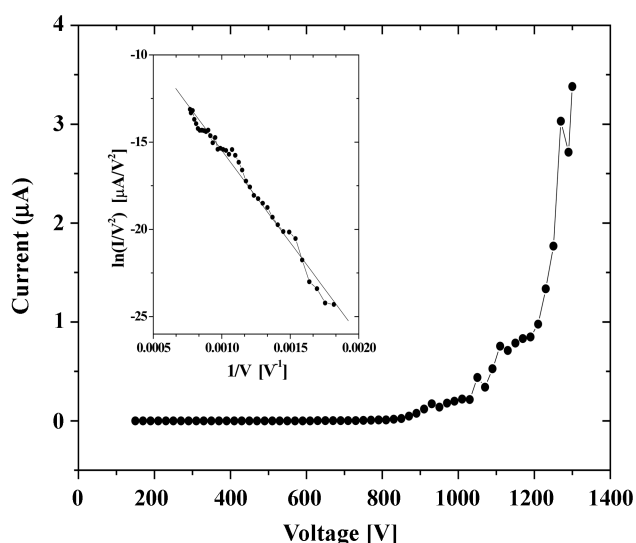


Fig. 7. Typical field emission characteristic of GaN nanowires grown at 3 cm apart from Ga source. The F-N plot at the inset indicates field emission character of the GaN nanowires.

βd , β and d are field conversion factor, and the distance between the emitter and the anode, respectively), we use the electron affinity (3.3 eV) of GaN instead of the work function. The field enhancement factor β' was found to be 555 from the slope of the F-N plot. This field enhancement factor is the highest value among reported GaN data as far as the authors know [Sugino et al., 2001; Berishev et al., 1998; Underwood et al., 1997]. In addition, the turn-on field is lower than that previously reported [Chen et al., 2001; Sugino et al., 2001; Berishev et al., 1998; Underwood et al., 1997]. The good electrical contact between the nanowires and the underlying substrate in our cases is expected to be formed due to intrinsic growth of nanowires on the conducting substrate. Whereas, other nanowires were moved for field emission measurement from the insulating substrate to the conducting one by dispersing nanowires. Therefore, this relatively good contact may contribute to good field emission characteristics of our nanowires together with the good crystallinity of protrusion-like nanowires from the underlying large GaN clusters.

CONCLUSION

GaN nanowires were grown on Ni-coated Si substrate at 910 °C for 3 hr under NH_3 flow rate of 20 sccm in a vertical CVD reactor. The GaN nanowires were uniformly grown on Si substrate surface when the distance of the Si substrate from Ga source was in the range of 0-4 cm. The growth of high density GaN nanowires was observed at a distance of 3 cm above the Ga source surface. At 5 cm apart from the source, GaN crystal grains were grown with few nanowires. The average diameter of the nanowires varied from 70 to 26 nm in the distance range of 0-4 cm, and the length of the nanowires reached several micrometers. The GaN nanowires were grown along [1010] direction and had a hexagonal structure. The clear lattice fringes in HRTEM image indicated the growth of good quality single-crystal GaN nanowires. Photoluminescence of the GaN nanowires showed a strong band edge emission at ~ 3.4 eV with a negligible deep level yellow emission. From field emission characteristic measurements, it was determined that the turn-on field of GaN nanowires was ~ 7.4 V/ μm and a field enhancing factor β was about ~ 555 . The growth mechanism of the GaN nanowires was suggested in this work.

ACKNOWLEDGMENTS

This work was supported by the Brain Korea 21 Project in 2003.

REFERENCES

- Ahn, S. H., Lee, S. H., Nahm, K. S., Suh, E. K. and Hong, M. H., "Catalytic Growth of High Quality GaN Micro-crystals," *J. of Crystal Growth*, **234**, 70 (2002).
- Berishev, I., Bensaoula, A., Rusakova, I., Karabutov, A., Ugarov, M. and Ageev, V. P., "Field Emission Properties of GaN Films on Si (111)," *Appl. Phys. Lett.*, **73**, 1808 (1998).
- Chen, C. C., Yeh, C. C., Chen, C. H., Yu, M. Y., Liu, H. L., Wu, J. J., Chen, K. H., Chen, L. C., Peng, J. Y. and Chen, Y. F., "Catalytic Growth and Characterization of Gallium Nitride Nanowires," *J. Am. Chem. Soc.*, **12**, 2791 (2001).

- Dekker, C., "Carbon Nanotubes as Molecular Quantum Wires," *Phys. Today*, **52**, 22 (1999).
- Demangeot, F., Frandon, J., Renucci, M. A., Briot, O., Gil, B. and Aulombard, R. I., "Raman Determination of Phonon Deformation Potentials in α -GaN," *Solid State Comm.*, **100**, 207 (1996).
- Derycke, V., Martel, R., Appenzeller, J. and Ph. Avouris, "Carbon Nanotube Inter- and Intramolecular Logic Gates," *Nano Lett.*, **1**, 453 (2001).
- Duan, X. F. and Lieber, C. M., "Laser-Assisted Catalytic Growth of Single Crystal GaN Nanowires," *J. Am. Chem. Soc.*, **122**, 188 (2000).
- Han, W., Fan, S., Li, Q. and Hu, Y., "Synthesis of Gallium Nitride Nanorods Through a Carbon Nanotube-Confined Reaction," *Science*, **277**, 1287 (1997).
- He, M., Minus, I., Zhou, P., Mohammed, S. N., Halpern, J. B., Jacobs, R., Samey, W. L., Riba, L. S. and Vispute, R. D., "Growth of Large-scale GaN Nanowires and Tubes by Direct Reaction of Ga with NH_3 ," *Appl. Phys. Lett.*, **77**, 3731 (2000).
- Hernadi, K., Konya, Z., Siska, A., Kiss, J., Oszko, A., Nagy, J. B. and Kiricsi, I., "On the Role of Catalyst, Catalyst Support and Their Interaction in Synthesis of Carbon Nanotubes by CCVD," *Mater. Chem. Phys.*, **77**, 536 (2002).
- Kim, J. R., So, H. M., Park, J. W. and Kim, J. J., "Electrical Transport Properties of Individual Gallium Nitride Nanowires Synthesized by Chemical-Vapor-Deposition," *Appl. Phys. Lett.*, **80**, 3548 (2002).
- Krivoruchko, O. P., Zaikovskij, V. I. and Zamaraev, K. I., *Doklady RAN*, **329**, 744 (1993).
- Kumar, M. S. and Kumar, J., "XRD, XPS, SEM, PL and Raman Scattering Analysis of Synthesised GaN Powder," *Mater. Chem. Phys.*, **77**, 341 (2002).
- Nahm, K. S., Kim, T. Y. and Lee, S. H., "Catalytic Effect of Metal Elements on the Growth of GaN and Mg-doped GaN Micro-Crystals," *Korean J. Chem. Eng.*, **20**, 623 (2003).
- Nahm, K. S., Mo, Y. H., Shajahan, M. and Lee, S. H., "Catalytic Growth of Semiconductor Micro- and Nano-crystals using Transition Metal Catalysts," *Korean J. Chem. Eng.*, **19**, 510 (2002).
- Odom, T. W., Huang, I.-L., Kim, P. and Lieber, C. M., "Atomic Structure and Electronic Properties of Single-walled Carbon Nanotubes," *Nature*, **391**, 62 (1998).
- Peng, H. Y., Wanf, N., Zhou, X. T., Zheng, Y. F., Lee, C. S. and Lee, S. T., "Control of Growth Orientation of GaN Nanowires," *Chem. Phys. Lett.*, **359**, 241 (2002).
- Sen, R., Govindaraj, A. and Rao, C. N. R., "Carbon Nanotubes by the Metallocene Route," *Chem. Phys. Lett.*, **267**, 276 (1997).
- Seo, H. W., Bae, S. Y., Park, J. H., Yang, H. I., Park, K. S. and Kim, S. S., "Strained Gallium Nitride Nanowires," *J. of Chem. Phys.*, **116**, 9492 (2002).
- Sugino, T., Hori, T., Kimura, C. and Yamamoto, T., "Field Emission from GaN Surfaces Roughened by Hydrogen Plasma Treatment," *Appl. Phys. Lett.*, **78**, 3229 (2001).
- Suh, D. J., Park, O. O., Jung, H. T. and Kwon, M. H., "Fabrication of a Graded-index Polymer Optical Fiber Preform by Using a Centrifugal Force," *Korean J. Chem. Eng.*, **19**, 529 (2002).
- Tans, S. J., Verschuere, A. R. M. and Dekker, C., "Room-temperature Transistor Based on a Single Carbon Nanotube," *Nature*, **393**, 49 (1998).
- Underwood, R. D., Kapolnek, D., Keller, B. P., Keller, S., Denbaars, S. P. and Mishra, U. K., "Selective-area Regrowth of GaN Field Emission Tips," *Solid-State Electronics*, **41**, 243 (1997).
- Wang, R. Z., Wang, B., Wang, H., Zhou, H., Huang, A. P., Zhu, M. K., Yana, H. and Yan, X. H., "Band Bending Mechanism for Field Emission in Wide-band Gap Semiconductors," *Appl. Phys. Lett.*, **81**, 2782 (2002).
- Wildoer, J. W. G., Venema, I. C., Rinzler, A. G., Smalley, R. E. and Dekker, C., "Electronic Structure of Atomically Resolved Carbon Nanotubes," *Nature*, **391**, 59 (1998).
- Yang, S. H., Ahn, S. H., Lee, W. H., Nahm, K. S., Suh, E.-K. and Lim, K. Y., "Structural and Optical Properties of GaN Films Grown by the Direct Reaction of Ga and NH_3 in a CVD Reactor," *Solid-State Electronics*, **44**, 1655 (2000).
- Yu, V., Davydov, Kitaev, Yu. E., Goncharuk, I. N., Smirnov, A. N., Graul, J., Semchinova, O., Uffmann, D., Smirnov, M. B., Mirgorodsky, A. P. and Evarestov, R. A., "Phonon Dispersion and Raman Scattering in Hexagonal GaN and AlN," *Phys. Rev. B*, **58**, 12899 (1988).
- Zhang, H. Z., Kong, Y. C., Wang, Y. Z., Du, X., Bai, Z. G., Wang, J. J., Yu, D. P., Ding, Y., Hang, Q. L. and Feng, S. Q., " Ga_2O_3 Nanowires Prepared by Physical Evaporation," *Solid State Commun.*, **109**, 677 (1999).