Effects on Optical Characteristics of GaN Polarity Controlled by Substrate

Sang Won Kang*, Hyun Wook Shim*, Dong-Yul Lee*, Sang-Heon Han*, Dong Joon Kim*, Je Won Kim*, Bang Won Oh*, Olga Kryliouk, and Timothy J. Anderson****

Abstract—**N-polar, Ga-polar, and non-polar GaN was grown by MBE and MOVPE using various substrates and influence of polarity has been investigated. The GaN growth by MOVPE is along c-plane (0001), c-plane (0001), and a-plane (11-20) direction on c-plane (0001), a-plane (11-20) and r-plane (1-102) sapphire substrate respectively. The polarity of the film has a strong influence on the morphology and the optical properties of PA-MBE grown As-doped GaN layers. Strong blue emission from As-doped GaN was observed only in the case of N-polarity (000-1) layers, which was attributed to the highest concentration of Ga dangling bonds for this polarity of a GaN surface.**

Index Terms—**GaN, polarity, non-polar, MOCVD, MBE**

I. INTRODUCTION

The group III-nitrides have been actively investigated for the past decade, because of their importance in short-wavelength photonics and high temperature, high frequency electronic device structures. To date most of the group III-nitride based device structures were grown parallel to the (0001) c-axis of their wurtzite structure. The unique feature of wurtzite group III-nitrides in comparison with the standard III-V compounds is the existence of strong polarity effects inside the crystal layer structure. For wurtzite group III-nitrides, the built-in electric fields arising due to the piezo- and spontaneous polarizations are very strong [1]. The existence of the built-in electric fields inside the group III-nitrides structures is an advantage for some device applications, but play a negative role for others. For example, a high density two-dimensional electron gas can be created at GaN/AlGaN interfaces without doping, which is now strongly exploited for high mobility transistors [2]. A strong red shift of the photo-emission is observed in GaN/AlGaN and GaN/InGaN quantum well structures due to the quantum confined Stark effect, which allows one to change and control the emission wave-length [3]. However, the quantum confined Stark effect significantly reduces the optical emission intensity due to charge separation within the quantum wells [4] and the resulting red shift is undesirable in UV emitters. The strong piezoelectric and spontaneous polarization effects led to current instabilities and charge trapping in GaN/AlGaN double barrier resonant tunneling structures [5]. All the above led to highly active studies of non-polar growth of group III-nitride layers and structures. The polarization effects can be eliminated by growing zinc-blende (cubic) GaN layers or wurtzite GaN layers of non-polar orientations such as (11-20) or (1-100) GaN on r-plane (1-102) sapphire and $LiAlO_2$ (100) substrates respectively [6,7].

Arsenic doped GaN films grown by plasma-assisted molecular beam epitaxy (PA-MBE) on sapphire substrates show very strong blue emission at room temperature [8], which is more than one order of magnitude stronger than the band edge emission in undoped GaN films. There is theoretical and experimental evidence to suggest that the blue emission is caused by recombination involving an arsenic anti-

Manuscript received Apr. 15 2006; revised Jun. 1, 2006.
* Samsung Electro-Mechanics Co. LTD., 314 Metan3-Dong, Yeoungtong-Gu, Suwon, Korea 443-743
** Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, U.S.A.
E-mail : sang1.kang@samsung.com

site deep level defect [6]. However, the mechanism responsible for the blue emission has not been definitively established. Previous results demonstrate that the growth conditions have a strong influence on the intensity of the blue emission from As-doped GaN grown by PA-MBE [9]. It has been shown that the incorporation of As into the GaN lattice is strongly influenced by the choice of substrate polarity [9]. For the growth of As-doped GaN on sapphire (N-polarity (000-1)) and on GaN MOVPE templates (Ga-polarity (0001)) growth under Ga-rich conditions is needed to obtain blue emission from the layers. However, in the case of MBE growth of Ga-polarity GaN layers on MOVPE GaN templates, the Ga:N ratio must be significantly higher in comparison with growth of N-polarity layers on sapphire substrates to achieve the same intensity of the blue emission.

In this study the influence of the polarity of the layer on the blue emission from As-doped GaN layers grown by PA-MBE was investigated further by extending the study to non-polar directions.

II. EXPERIMENTS

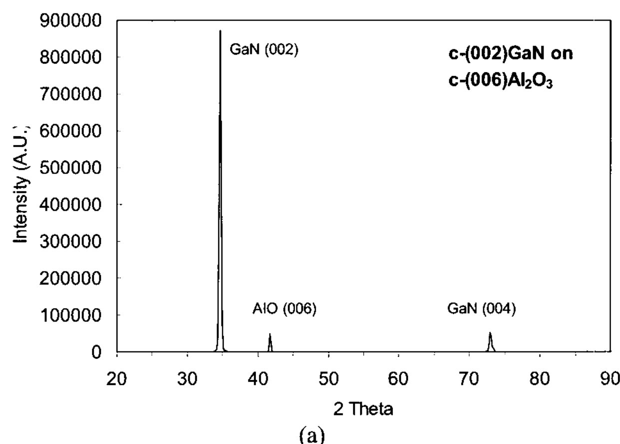
Arsenic doped GaN layers were grown under identical PA-MBE conditions on several types of substrates including c-plane (0001) sapphire and polar and non-polar GaN layers grown by MOVPE. Ga-polarity GaN layer was grown on (0001) sapphire. Non-polar a-plane (11-20) GaN was grown on r-plane (1-102) sapphire substrate and m-plane(1-100) GaN was grown on (100) $LiAlO_2$. Gallium nitride epitaxial layers about 0.3 μm thick were grown by low-pressure horizontal cold wall MOVPE reactor under following conditions: T ~850°C, V/III ratio = 3600, and reactor pressure 100 Torr. Triethylgallium (TEGa) and ammonia were used as the precursors and nitrogen was a carrier gas. Every substrate was nitrided by flowing ammonia at ~850°C for 15 minutes and low temperature buffer layer was grown at ~560°C for 15 minutes prior epitaxial film growth.

Arsenic doped GaN layers were grown on all different types of substrates by PA-MBE at a temperatures of ~800°C in a reactor, which has been described in detail elsewhere [8]. Ga-rich conditions were established from the growth on sapphire substrates and the same Ga:N ratio was used through the whole set of the growths. The active nitrogen for the growth of the group III-nitrides was provided by a CARS25 RF activated plasma source. Arsenic in the form of dimers (As_2) was produced using a two-zone cell.

Samples were studied in-situ using the reflection high-energy electron diffraction (RHEED) and after growth ex-situ measurements were performed using atomic force microscopy (AFM), Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), X-ray diffraction, transmission electron microscopy (TEM) and photoluminescence (PL).

III. CHARACTERISTICS OF GAN ON C-, A, -R-SAPPHIRE AND LAO BY MOVPE

Gallium nitride epitaxial layers about 0.3 μm thick were grown by MOVPE on c-plane (0001), a-plane (11-20), and r-plane (1-102) sapphire and (100) γ-$LiAlO_2$. X-ray diffraction measurement indicates that the GaN growth by MOVPE is along c-plane (0001), c-plane (0001), and a-plane (11-20) direction on c-plane (0001), a-plane (11-20) and r-plane (1-102) sapphire substrate respectively. These orientation relationships are also found in references [10, 11, 12]. GaN grows along m-plane (1-100) on (100) γ-$LiAlO_2$. Fig. 1 shows these relationships well. Also, crystallographic relationship between grown GaN film and substrate revealed by X-ray diffraction is summarized in Table 1.



(a)

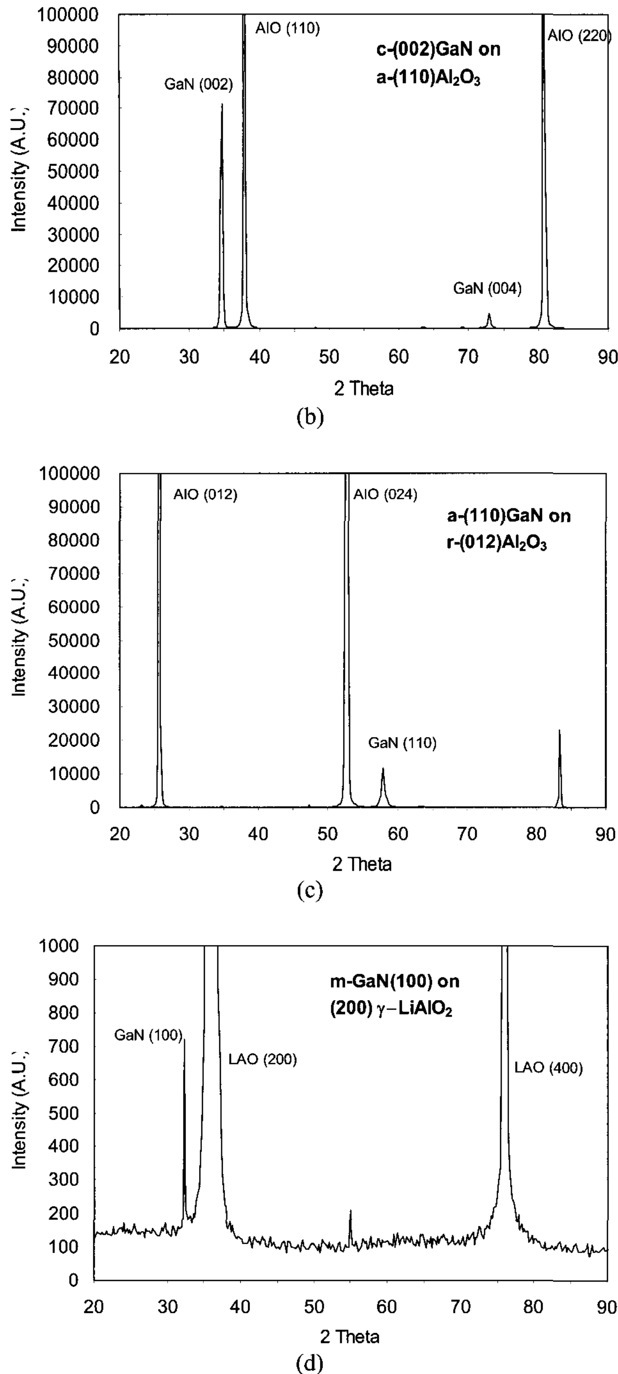


Fig. 1. X-ray diffraction of GaN on various substrate planes; (a) c-plane (0001), (b) a-plane (11-20), (c) r-plane (1-102) sapphire and (100) γ-$LiAlO_2$ substrate.

Table 1. Crystallographic relationship between film and substrate

Substrate	Film (w-GaN)
c-plane (0001) α-Al_2O_3	c-plane (0001) w-GaN
a-plane (11-20) α-Al_2O_3	c-plane (0001) w-GaN
r-plane (1-102) α-Al_2O_3	a-plane (11-20) w-GaN
(100) γ-$LiAlO_2$	m-plane (1-100) w-GaN

A strong GaN (002) peak can be seen in Fig. 1 (a) and a relatively strong GaN (002) peak in Fig. 1 (b). However, a-GaN (110) peak in Fig. 1 (c) is weak.

In the hexagonal structure, 4 indices system [uvtw] and 3 indices system [UVW] is converted to each other by following relations:

$$U=u-t \quad V=v-t \quad W=w \qquad u=(2U-V)/3 \quad v=(2V-U)/3 \quad t=-(U+V)/3 \quad w=W \tag{Eq.1}$$

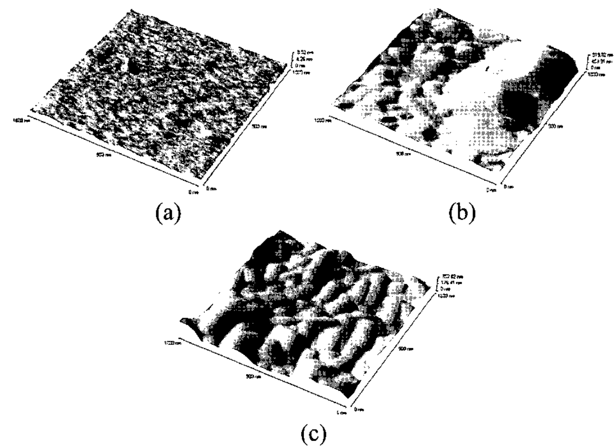


Fig. 2. AFM images of the surface of GaN layers. GaN MOVPE templates grown on (a) c-plane sapphire, (b) r-plane sapphire, (c) (100) γ-$LiAlO_2$.

Fig. 2 shows AFM images of the surface of MOVPE templates. The GaN surface grown on c-plane sapphire is smooth and flat and GaN grown on r-plane exhibited worse morphology than that of GaN grown on c-plane sapphire. The MOVPE grown GaN on $LiAlO_2$ (Fig. 2 (b)) has very rough surface morphology and consisted of large grains, but the shape of the grains are very different for this m-plane orientation.

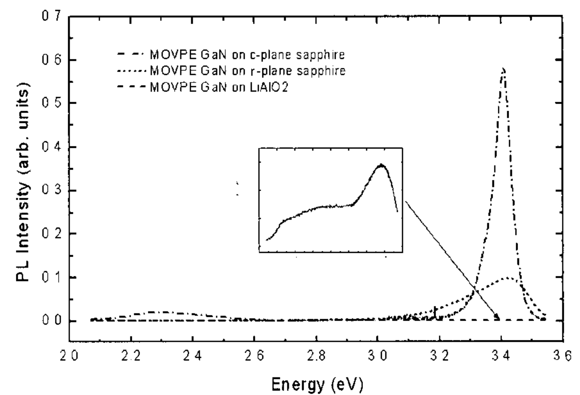


Fig. 3. PL from GaN on c-, r- sapphire, and $LiAlO_2$ by MOVPE.

Fig. 3 shows room temperature PL from GaN on different plane of sapphire and $LiAlO_2$. The PL spectra of the GaN layers are dominated by excitonic band-edge emission at ~3.4 eV. The strongest band-edge emission was observed from the Ga-polarity GaN layer and weakest and broadest was from the GaN grown on $LiAlO_2$. This tendency is dominantly due to the crystalline quality of the samples.

It is well known that MOVPE grown a-GaN on r-sapphire and m-GaN on (100) $LiAlO_2$ is non-polar and c-GaN on c-sapphire is Ga-polarity [Wal00, Tri99]. As-doped GaN was grown on MOVPE grown GaN and the effect of the polarity controlled by substrate direction will be investigated in next section.

IV. THE INFLUENCE OF SUBSTRATE POLARITY ON THE MBE GROWN GAN

For the As-doped GaN sample grown at ~800°C directly on sapphire under Ga-rich conditions [16, 10] the RHEED pattern is intense and streaky and shows a (2 × 2) reconstruction immediately on termination of growth. However, for growth of GaN with an As flux on all polar and non-polar MOVPE GaN templates, only a (1 × 1) unreconstructed RHEED pattern was observed both during and after growth and it was weak for MBE on non-polar GaN templates.

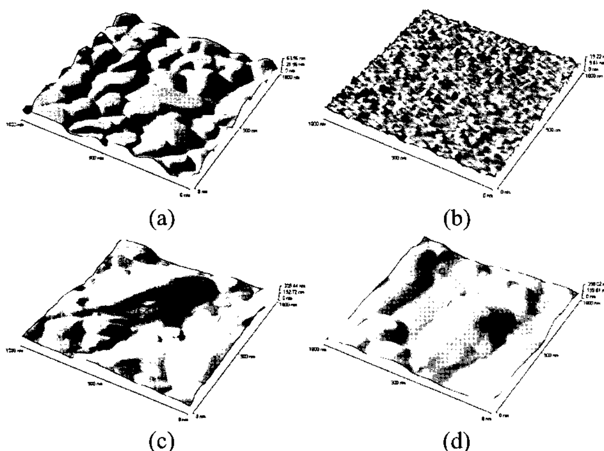


Fig. 4. AFM images of the surface of GaN layers. (a) Arsenic-doped GaN MBE layers grown on c-plane sapphire and on different GaN templates, (b) on GaN MOVPE template on c-plane sapphire, (c) on GaN MOVPE template on r-plane sapphire and (d) on GaN MOVPE template on $LiAlO_2$ (100) substrates.

Fig. 4 shows AFM images of the surface of MBE layers grown on these templates respectively. It is obvious from Fig. 4 that the surface morphologies of the GaN layers are very strongly dependent on the polarity of template. In general the surface morphology of MBE layers follows the morphology of underlying templates. In the case of the MBE growth directly on sapphire, the GaN layer has N-polarity as shown recently by convergent beam electron diffraction (CBED) [9] and consists of a single crystal film with relatively large sub-grains (Fig. 4 (a)). In the case of growth on the very smooth Ga-polarity (0001) GaN MOVPE layer, the As-doped GaN layer the sub-grain size is smaller (Fig. 4 (b)) due to the underlying MOVPE template. The As-doped GaN MBE layers on the non-polar templates (GaN MOVPE layer on r-plane sapphire and (d) on GaN MOVPE layer on $LiAlO_2$ (100) substrates) follow to some extent the morphology of underlying template, but demonstrated some improvement in the surface roughness and flattening of the surfaces.

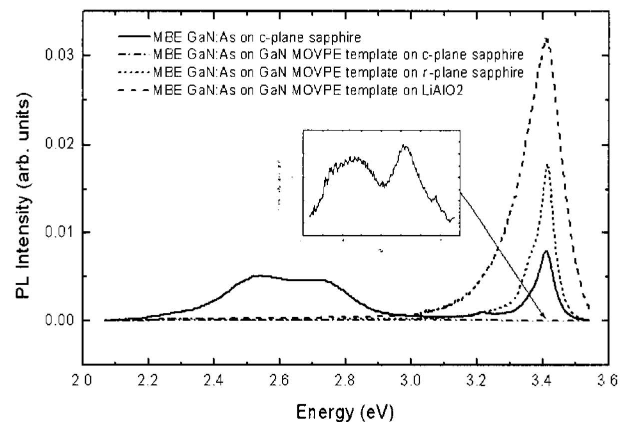


Fig. 5. PL spectra from MBE grown As-doped GaN layers.

Fig. 5 shows the PL for the As-doped GaN MBE layers. It is obvious from Fig. 5 that PL spectra of As-doped GaN MBE layers grown under same conditions are very different and strongly depend on the polarity of underlying template. The PL from the N-polarity (000-1) As-doped GaN layers grown directly on sapphire consists of three main features: excitonic band-edge emission around 3.4 eV, emission at 3.2 eV and strong blue luminescence centered around 2.6 eV. By contrast, the PL from the Ga-polarity (0001) As-doped GaN (0001) layers was very weak and rather broad. The PL from As-doped GaN layers grown on the non-polar

templates demonstrate only strong band-edge peaks with no trace of any blue emission. Curiously the strongest PL intensity for the band-edge emission from the MBE grown GaN films come from the layers grown on the $LiAlO_2$ MOVPE template, which shows the weakest band edge emission. Analysis of the results from Fig. 5 is leading to the conclusion that for identical MBE growth conditions the strong blue emission from As-doped GaN can be observed only in the case of N-polarity (000-1) layers grown directly on sapphire.

For the case of Ga-polarity (0001) GaN, at the surface of the layer there is only one free Ga dangling bond towards the surface for each Ga atom. By contrast for the case of N-polarity (000-1) GaN there are 3 dangling bonds at the surface for each Ga atom. As a result (000-1) surface is generally more chemically active for impurity adsorption. It follows that in the growth by MBE of N-polarity As-doped GaN, there is a higher probability for As atoms to be incorporated into the GaN lattice. In the case of Ga-polarity As-doped GaN layers, it is possible to achieve blue emission from the layers grown with a very high excess Ga adatom population on the surface [9], which again will produce a high density of the Ga dangling bonds at the surface. Finally for the growth of N-polarity As-doped GaN layers, the blue emission intensity increased for the layers grown under high Ga:N ratios [5]. All this evidence suggests that the concentration of Ga dangling bonds on the surface is crucial for achieving strong blue emission and that the polarity of the GaN growth strongly influences the concentration of Ga dangling bonds.

There are two possible explanations of the above results on the PL from As-doped GaN layers. The first possibility is that As incorporation into the GaN film during MBE is influenced by polarity of the growth and as a result the total concentration of As atoms incorporated into the GaN layer is different for different polarities of the growth. The second possible explanation is that the polarity of the growth influences the location of the As in the GaN lattice.

Fig. 6 shows SIMS profiles of the As distribution in two As-doped GaN layers grown with the same As flux and under the same MBE conditions. Fig. 6 (a) is SIMS data for an N-polarity GaN layer, which was grown directly on c-plane (0001) sapphire and Fig. 6 (b) is SIMS data for a Ga-polarity GaN film, which was grown on GaN MOVPE template on c-plane (0001) sapphire. In each case, the As concentration was calculated using different secondary ions – CsAs+ and As-. A CAMECA IMS-4f ion microprobe was used and a GaN layer implanted with As was employed as the SIMS standard. The As concentrations estimated from different secondary ions are different in the case of N-polarity GaN, but they are almost identical for the Ga-polarity layers. It is clear that the total concentrations of As inside the GaN layers of the different polarity are comparable ~ (5-10) $10^{20}cm^{-3}$. The difference in the arsenic SIMS concentrations estimated using different CsAs+ and As- secondary ions for two As-doped GaN layers of different polarity suggests that the

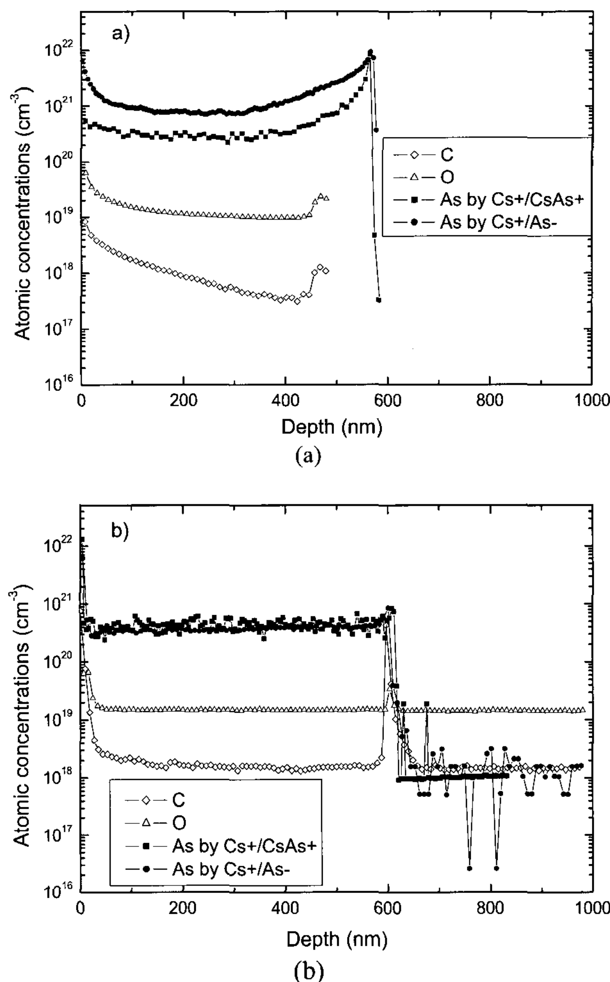


Fig. 6. SIMS profiles of the As concentration in two As-doped GaN layers grown under the same MBE conditions. (a) A GaN layer grown directly on c-plane (0001) sapphire and (b) the equivalent GaN layer grown on a GaN MOVPE template on c-plane (0001) sapphire.

microstructure and the position of the As inside the GaN lattice must be different. This perhaps allows one to conclude that, the main reason for the strong difference in the intensity of the blue emission in As-doped GaN films of different polarity does not relate to the any difference in the concentration of As incorporated in the films. However, this suggests instead that the different configuration of Ga atoms on the surface for different polarities leads to the As being incorporated in different preferential lattice positions.

V. CONCLUSIONS

The polarity of the film has a strong influence on the morphology and the optical properties of MBE grown As-doped GaN layers. Strong blue emission from As-doped GaN was observed only in the case of N-polarity (000-1) layers grown by MBE. The possible explanation is that the polarity of the growth influences the location of the As in the GaN lattice. The concentration of Ga dangling bonds is highest for N-polarity of a GaN surface because there are 3 dangling bonds at the surface for each Ga atom for the case of N-polarity (000-1) GaN. The concentration of Ga dangling bonds on the surface is crucial for achieving strong blue emission and the polarity of the GaN growth strongly influences the concentration of Ga dangling bonds.

REFERENCES

[1] G. Martínez-Criado, A. Cros, A. Cantarero, C. R. Miskys, O. Ambacher, R. Dimitrov and M. Stutzmann, "Photoluminescence of Ga-face AlGaN/GaN single heterostructures," *Materials Science and Engineering B*, Vol. 82, Issues 1-3, pp.200-202, May 2001.

[2] N. Grandjean, J. Massies and M. Leroux, "Self-limitation of AlGaN/GaN quantum well energy by built-in polarization field," *Appl. Phys. Lett.*, Vol. 74, Issue 16, pp.2361-2363, April 1999.

[3] J. S. Im, H. Kollmer, J. Off, A. Sohmer, F. Scholz and A. Hangleiter, "Carrier confinement in GaInN/AlGaN/GaN quantum wells with asymmetric barriers: direction of the piezoelectric field," *Materials Science and Engineering B*, Vol. 59, Issues 1-3, pp.315-318, May 1999.

[4] A. E. Belyaev, C. T. Foxon, S. V. Novikov, O. Makarovsky, L. Eaves, M. J. Kappers and C. J. Humphreys, "Comment on "AlN/GaN double-barrier resonant tunneling diodes grown by rf-plasma-assisted molecular-beam epitaxy", *Appl. Phys. Lett.*, Vol. 83, Issue 17, pp.3626-3627, October 2003.

[5] C. G. Van de Walle, J. Neugebauer, "Arsenic impurities in GaN," *Appl. Phys. Lett.*, Volume 76, Issue 8, pp.1009-1011, February 2000.

[6] S. Tripathy, R. K. Soni, H. Asahi, K. Iwata, R. Kuroiwa, K. Asami and S. Gonda, "Optical properties of GaN layers grown on *C*-, *A*-, *R*-, and *M*-plane sapphire substrates by gas source molecular beam Epitaxy," *J. Appl. Phys*, Vol. 85, Issue 12, pp.8386-8399, June 1999.

[7] C.T. Foxon, S.V. Novikov, L.X. Zhao, K.W. Edmonds, A.D. Giddings, K.Y. Wang, R.P. Campion, C.R. Staddon, M.W. Fay, Y. Han, "Molecular beam epitaxy of p-type cubic GaMnN layers," *Journal of Crystal Growth*, Vol. 278, Issues 1-4, pp.685-689, May 2005.

[8] Y. Han, M.W. Fay, P.D. Brown, S.V. Novikov, K.W. Edmonds, B.L. Gallagher, R.P. Campion, C.R. Staddon and C.T. Foxon, "Structural characterisation of zinc-blende Ga1−xMnxN epilayers grown by MBE as a function of Ga flux," *Journal of Crystal Growth*, Vol. 284, Issues 3-4, pp.324-334, November 2005.

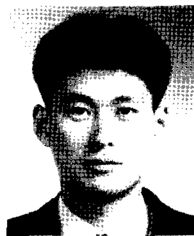
[9] A. Chakraborty, H. Xing, M.Craven, S.Keller, T.Mates, J.Speck, S.DenBaars, U.Mishra, "Nonpolar *a*-plane *p*-type GaN and *p-n* Junction Diodes," *J. Appl. Phys.*, Vol. 96, Issue 8, pp.4494-4499, October 2004.

[10] F.Wu, M. Craven, S. Lim, J. Speck, "Polarity determination of a-plane GaN on *r*-plane sapphire and its effects on lateral overgrowth and heteroepitaxy," *J. Appl. Phys.*, Vol. 94, Issue 2, pp.942-947, July 2003.

[11] J. Bai, T. Wang, H. Li, N. Jiang, S. Sakai, "(0 0 0 1) oriented GaN epilayer grown on r-sapphire by MOCVD," *J. Crystal Growth*, Vol. 231, Issues 1-2, pp.41-47, September 2001.

[12] E.S. Hellman, "The Polarity of GaN: a Critical Review," *MRS Internet J. Nitride Semicond. Res.*, Vol. 3, Article 11, July 1998.

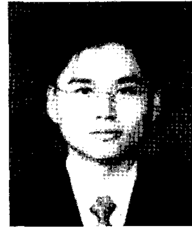
Sang Won Kang received the B.S. and M.S degree in Chemical Engineering from Chung-Ang University in 1996 and 1998 respectively and the Ph.D. degree in Chemical Engineering from University of Florida in 2004. He has been working as a Senior Engineer of Samsung Electro-Mechanics Co., Ltd since 2005. His research interests are mainly in the area of epitaxial growth of nitride semiconductors by metal-organic chemical vapor deposition (MOCVD).



Hyun Wook Shim received the B.S. degree in Physics from Chonbuk National University in 1995 and the M.S. and Ph.D. degrees in Semiconductor Science and Technology from Chonbuk National University in 1997 and 2004, respectively. He is working as an member of research staff of Samsung Electro-Mechnics from 2004.

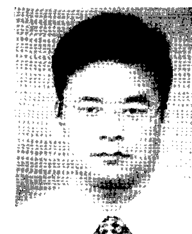
Dong-Yul Lee received the BS degree from the Daegu Haany University and the M.S. and Ph.D. degrees in Materials Science & Engineering from Yeungnam university. Since 2004, he has worked as a Senior Engineer of Samsung Electro-Mechanics Co., Ltd.

Sang-Heon Han received the B.S. in the metallurgical engineering from KyungPook National University in 1999 and the M.S. in the materials science and engineering from GIST(Gwangju Institute of Science and Technology) in 2001, KOREA, respectively. He is currently MOCVD engineer on GaN LED in SEMCO.



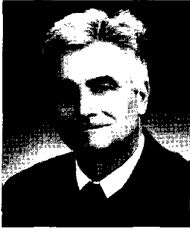
Dong Joon Kim received the M.S. and Ph.D. degrees in Materials Science & Engineering from Gwangju Institute of Science & Technology in 1998 and 2002, respectively. Since 2002, he has worked as a Senior Engineer of Samsung Electro-Mechanics Co., Ltd.

Je Won Kim received the B.S., M.S. and Ph. D. degrees from the Korea University, Korea, in 1994, 1996 and 2000, respectively. He was a pre-doctoral researcher working on the growth and characterization of III-nitride semiconductors at the Walter Schottky Institute in Technical University of München in 1997. He was a commissioned researcher working on the optical and electrical properties of GaN-related materials in the Korea Institute of Science and Technology (KIST) from 1998 to 2000. He is currently a principal researcher at the research and development group in Samsung Electro-Mechanics Co.



Bang Won Oh received the BS degree from the Seoul National University and the M.S. and Ph.D. degrees in Materials Science & Engineering from Korea Advanced Institute of Science & Technology. He joined Samsung Electro-Mechanics in 1995 where he is currently a vice president in LED RnD Group.

Olga Kryliouk received Ph.D., from Moscow State University, Russia in 1986. She joined a faculty of Chemical Engineering Department in University of Florida as a Research Associate Professor in 1999. Her research interests are primarily in the area of electronic materials and processing.



Timothy J. Anderson received Ph.D. degree from University of California-Berkeley in 1979. He is now Associate Dean of Research and Graduate Programs for the College of Engineering. Anderson's research includes the study of advanced electronic and photonic materials processing. He has been recognized for his research accomplishments through numerous awards, including the AIChE George Lappin Award (2003), Union Carbide Lectureship Award, ASEE (2001), AIChE Gary L. Leach Award (1996), and the AIChE Charles M. A. Stine Award (1994). Anderson is associate editor of the Journal of Phase Equilibria, a member of the Editorial Advisory Board of J. SMET Education, consulting editor of the AIChE Journal, as well as editor of the Chemical Engineering Education journal.