



Rare-earth chloride seeded growth of GaN nano- and micro-crystals

M.A. Mastro^a, J.A. Freitas Jr.^a, R.T. Holm^a, C.R. Eddy Jr.^a, J. Caldwell^a, K. Liu^a,
O. Glembocki^a, R.L. Henry^a, J. Kim^{b,*}

^a U.S. Naval Research Laboratory, Electronics Science and Technology Division, 4555 Overlook Ave., SW, Washington, DC 20375, United States

^b Department of Chemical and Biological Engineering, Korea University, Anam-Dong 5-1, Seungbuk-Gu, Seoul, South Korea

Received 4 September 2006; accepted 16 January 2007

Available online 30 January 2007

Abstract

A novel rare-earth chloride seed was employed as a catalyst for growth of GaN nano- and micro-crystals on *c*-, *a*- and *r*-plane sapphire. The ErCl₃ seed on the substrate surface enhanced the growth rate and density of the GaN crystals. Distinctive green photoluminescence was measured, confirming that Er³⁺ ions were active in the GaN matrix. This technique can be adapted to selectively grow GaN crystals with emission tailored to the particular optical transitions of the rare-earth seed.

© 2007 Elsevier B.V. All rights reserved.

PACS : 72.80.Ey; 78.55.Cr

Keywords: Gallium nitride; Rare-earth metal

1. Introduction

Nano-scale optoelectronics in the future will serve as the building blocks for a number of advanced optical and mixed optical/electronic circuits [1–6]. The III-nitride material system has proven to be well suited for the production of large-scale light emitting diodes (LEDs), detectors and lasers [7]. Understandably, the fabrication and integration of efficient optoelectronic devices at the nano-scale is more complex.

One major challenge to all nano-scale devices is the ability to pre-determine the placement of the device [1–4]. Several reports have shown that metal (typically Ga, Ni, Fe, or Au) seeded vapor–liquid–solid (VLS) growth can define the placement and, to a lesser degree, the orientation of the GaN nano-structure as well as improve the quality of the nano-structure relative to a continuous film [3–6]. A second limitation to the practical introduction of nano-scale structures is the ability to fabricate stand-alone functional devices that can be contacted and, thus, integrated into a large-scale circuit. The traditional III-nitride optoelectronics, based on a planar quantum well structure surrounded by a p–n junction with

metal contacts, are difficult to integrate as a nano-wire or rod geometry [4,5] particularly into Si microelectronics [8–10]. A simpler design is to base the active material on a rare-earth doped GaN nano-structure [11].

In addition to the optoelectronic motivation presented, the results of this work also open a novel chloride-seeded fabrication technique for nano- or micro-scale, spintronic devices based on diluted magnetic semiconductor (DMS) in which the crystal exhibits long-range ferromagnetic order when heavily doped with, for example, a rare-earth ion such as Gd [12]. The reduced growth temperature of the catalyst-assisted deposition process presented in this paper could theoretically permit the high level of rare-earth ion incorporation that is necessary to reach a curie temperature higher than room temperature [13]. Additionally, the wide bandgap of sapphire is advantageous for the formation of a DMS on insulator structure.

This paper presents a novel route via an erbium trichloride (ErCl₃) seed for catalyst-assisted growth of GaN nano-structures. A chloride compound is used to lower the melting point of the rare-earth seed below the GaN growth temperature and, thus, allow a catalyst enhanced growth mechanism that also improves the solubility of the rare-earth ion into the GaN matrix. The incorporation of rare-earth elements into a semiconductor matrix allows tunable optical transitions based on selection of the appropriate rare-earth dopants. In GaN, this

* Corresponding author. Tel.: +82 2 3290 3291; fax: +82 2 926 6102.

E-mail address: hyunhyun7@korea.ac.kr (J. Kim).

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE SEP 2006		2. REPORT TYPE		3. DATES COVERED 00-00-2006 to 00-00-2006	
4. TITLE AND SUBTITLE Rare-earth chloride seeded growth of GaN nano- and micro-crystals				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory, 4555 Overlook Avenue SW, Washington, DC, 20375				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT A novel rare-earth chloride seed was employed as a catalyst for growth of GaN nano- and micro-crystals on c-, a- and r-plane sapphire. The ErCl₃ seed on the substrate surface enhanced the growth rate and density of the GaN crystals. Distinctive green photoluminescence was measured confirming that Er³⁺ ions were active in the GaN matrix. This technique can be adapted to selectively grow GaN crystals with emission tailored to the particular optical transitions of the rare-earth seed.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 5	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

is particularly interesting for an Eu^{3+} ion with an emission peak in the red as well as an Er^{3+} ion with transitions in the green and an infrared transition at approximately 1550 nm, which is the dominant wavelength for fiber optic communications.

2. Experimental

In this study, GaN crystals were grown via an ErCl_3 seed on *c*-, *a*- and *r*-plane sapphire substrates. The ErCl_3 was dissolved into deionized water, then either dripped or spun onto the substrate. The substrate was heated to approximately 60 °C to drive off excess water then loaded into a modified vertical impinging flow, metal organic chemical vapor deposition (MOCVD) reactor. A 50-Torr, H_2 atmosphere was used during the ramp to growth temperature. Trimethylgallium was flowed for 2 s prior to the onset of NH_3 flow to prevent nitridation of the Er seeds. A series of samples was produced for a growth duration of 1, 5, 10, 20, and 30 min. Results are presented for a growth temperature of 900 °C although this technique was demonstrated from 700 to 1050 °C.

Structural characterization was performed with a Panalytical X'pert X-ray diffraction (XRD) system and a LEO FE Scanning Electron Microscope (SEM). The XRD characterization data can be considered as information from an ensemble of crystals within the approximately millimeter-diameter X-ray beam. The luminescence was excited at room temperature with the 325-nm line of a He–Cd laser. The uncorrected photoluminescence (PL) spectra were acquired with a small fiber optical spectrometer, which is fitted with an UV-extended linear CCD array and a grating blazed at 350 nm, coupled to a near-UV transmitting optical microscope. The real-color red/green/blue (RGB) and single-color (R, G, and B) optical images were obtained with a

near-UV CCD camera fitted with a wheel filters attached to one of the microscope ports.

3. Results

Bright field Normarski microscopy in Fig. 1a–c and electron micrographs in Fig. 1d–f reveal a high concentration of approximately 5- μm in length GaN crystals after 10 min of deposition on *r*-, *c*- and *a*-plane sapphire. X-ray diffraction showed the growth direction to be *a*-plane GaN on *r*-plane sapphire, mixed *m*- and *c*-plane GaN on *a*-plane sapphire, and *c*-plane GaN on *c*-plane sapphire. The elongated *a*- and *m*-plane GaN crystals showed a long-range ordering in contrast to the lack of symmetry in the arrangement of the *c*-plane GaN crystals (Figs. 1 and 2). The size of the GaN crystals varied with growth time from tens of nanometers for a 1 min growth to tens or microns for a 30 min growth. The GaN crystals did maintain approximately the same geometric proportions for length:width:height independent of growth time.

Optical analysis as seen in Figs. 1 and 2 displayed low-density regions of uniformly spaced crystals as well as high-density regions in the vicinity of a concentrated ErCl_3 seed. Two such high-density cluster regions are present in the upper-left and center of Fig. 2c and d. The crystal cluster in the center of Fig. 2c and d is obscured by the resolidified rare-earth seed that is suspended on top of the GaN crystals. Also, a ring of negligible deposition was occasionally observed in the vicinity of the resolidified rare-earth seed (Fig. 1a).

Luminescence images and spectrum of the GaN crystals are displayed in Figs. 3–5. The RGB image of a region containing individual crystals and cluster of crystals, represented in Fig. 3a, displays visibly the bright green-yellow emission

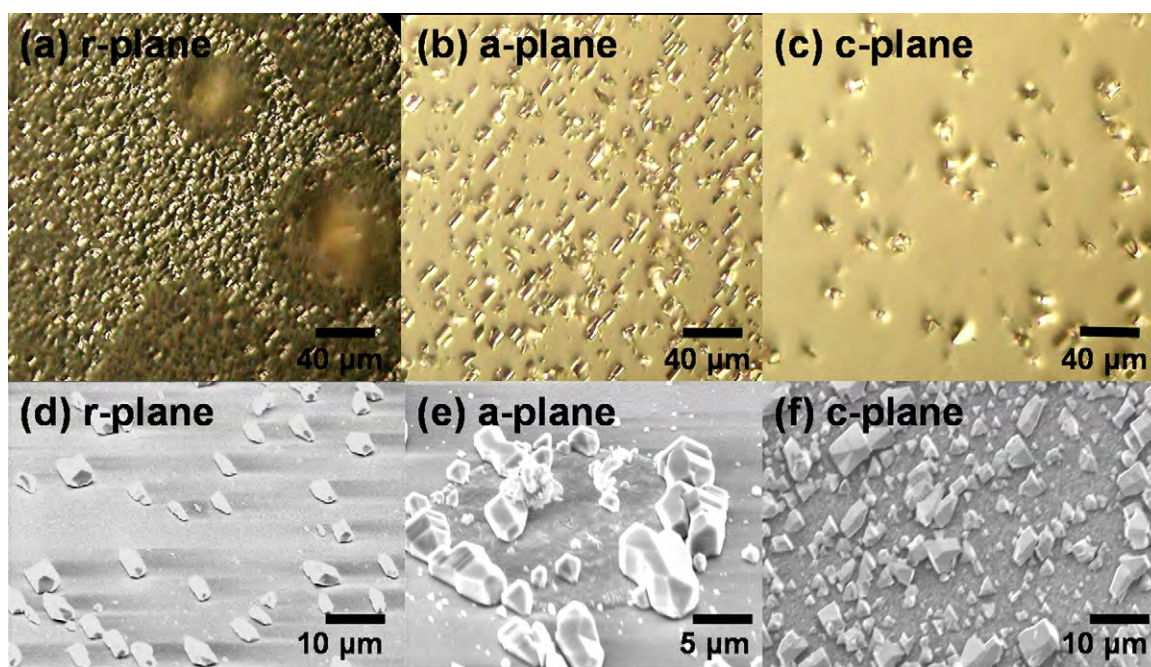


Fig. 1. Normarski micrograph (a–c) and electron microscopy (d–f) of (a and d) *a*-plane GaN crystals on *r*-plane sapphire, (b and e) mixed *m*- and *c*-plane GaN crystals on *a*-plane sapphire, and (c and f) *c*-plane GaN crystal with no long range ordering on *c*-plane sapphire. The two large objects in (a) are resolidified rare-earth seed on top of a cluster of GaN crystals.

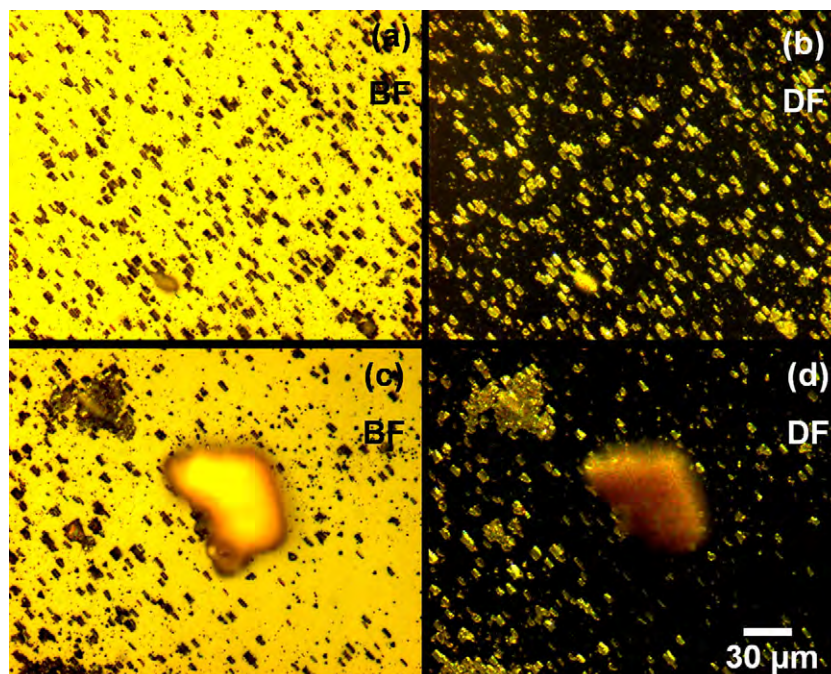


Fig. 2. (a and c) Bright field and (b and d) dark field optical micrograph of GaN crystals. (a and b) Distinct GaN crystals are observable in a region of the substrate with a light application of seed. (c and d) Excessive concentration of the seed results in clustered growth of GaN crystals. The large object in the center of the figure is a resolidified seed located on top of a high-density crystal cluster.

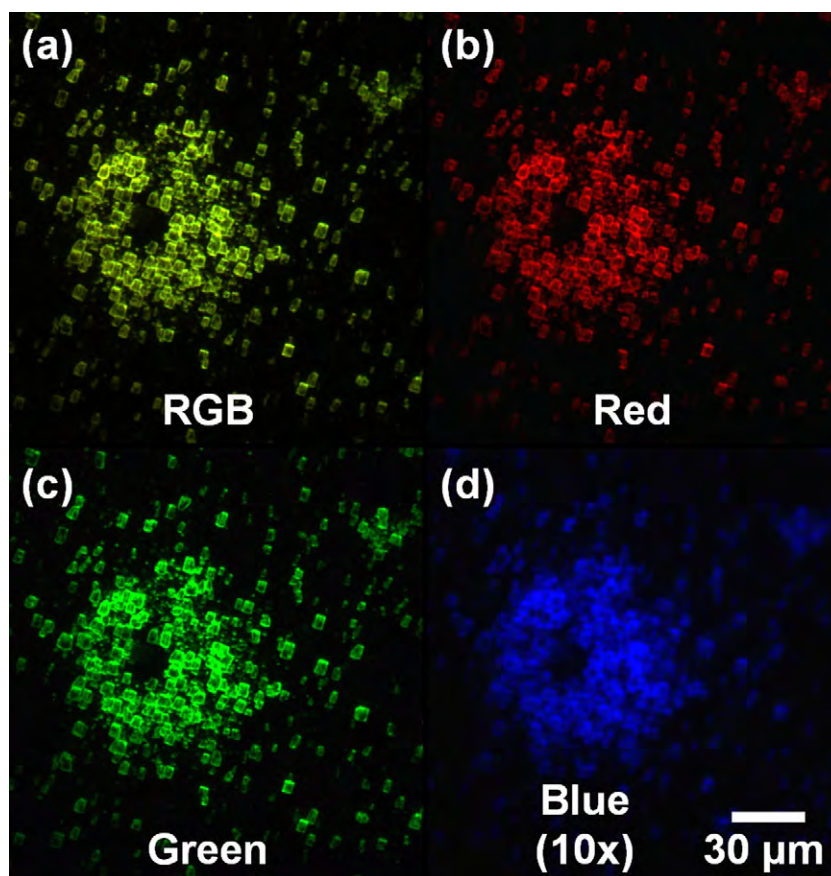


Fig. 3. Luminescence micrograph of a cluster of GaN crystals illuminated with 325 nm HeCd laser line and acquired with a CCD fitted with a wheel filter. (a) Real-color (RGB), (b) red filter, (c) green filter, and (d) blue filter, with 10 times longer integration time than the R and G pictures.

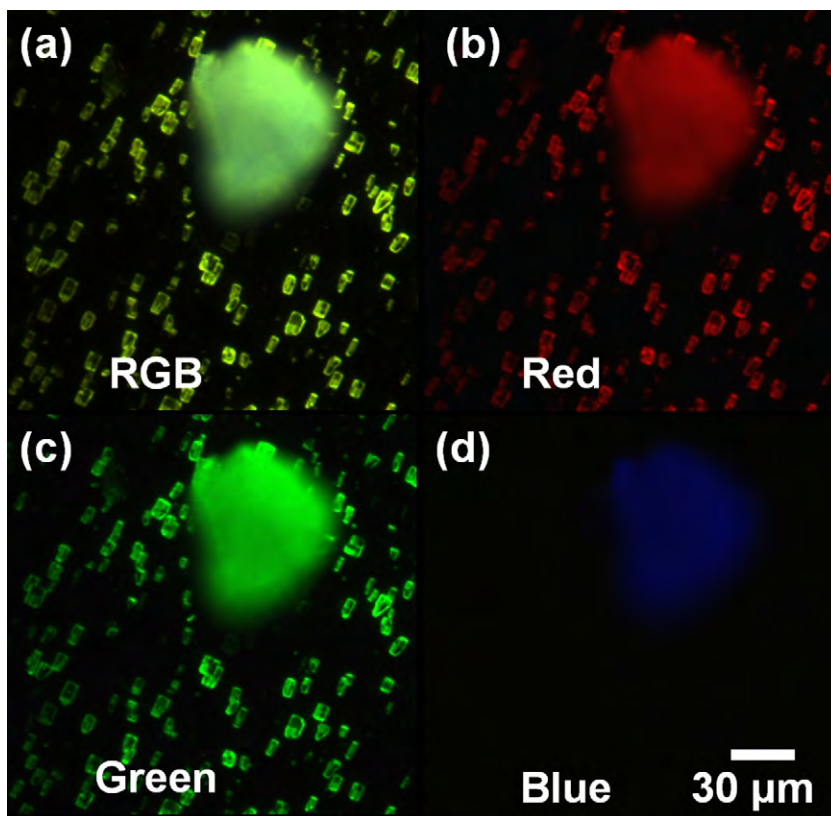


Fig. 4. Luminescence micrograph of GaN crystals and a resolidified seed illuminated with 325 nm HeCd laser line and acquired with a CCD fitted with a wheel filter. (a) Real-color (RGB), (b) red filter, (c) green filter, and (d) blue filter ($1\times$). A dense cluster of GaN crystals exists underneath the seed.

typical for these Er^{3+} doped crystals. The individual red, green, and blue color pictures, represented in Fig. 3b–d, demonstrate that green is the dominant component of the crystal emission. In general, all the crystal clusters and individual crystals were optically active.

Fig. 4 shows the remains of a rare-earth seed that resolidified upon cooling from growth temperature. The location of the cluster of GaN crystals underneath this resolidified rare-earth

seed was observed by varying the focus depth in the microscope.

Fig. 5 depicts the uncorrected PL spectrum of the sample region represented in Fig. 3. A broad emission band extending from 450 to 750 nm with a peak near 560 nm dominates the emission spectra. Also observed is a weak emission band around 400 nm. To verify the nature of the recombination processes we measured the PL spectra of a thin ($\leq 3\ \mu\text{m}$) MOCVD GaN film on sapphire and of a thick ($\geq 200\ \mu\text{m}$) hydride vapor phase epitaxy (HVPE) freestanding GaN film (not shown). We observed that both films have similar spectra, and which are dominated by a relatively intense emission band extending from 400 to 650 nm with peak at 525 nm. The spectral intensity distribution of this band is quite different from the spectra observed from the GaN:Er crystallites. Presently, we cannot rule out possible contribution of the 525 nm undoped GaN emission band to the GaN:Er crystallites spectra. However, we can clearly distinguish the primary Er^{3+} green transitions at $\sim 539\ \text{nm}$ ($^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$), the yellow transition at $\sim 560\ \text{nm}$ ($^2\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$), and the red transition at 625 nm ($^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$). In addition, we observe a weak violet Er^{3+} transitions at $\sim 409\ \text{nm}$ ($^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$), which may overlap with a weaker GaN bandedge emission.

4. Discussion

Heteroepitaxial growth of GaN nanostructures is critically dependent on a number of parameters, including the presence of

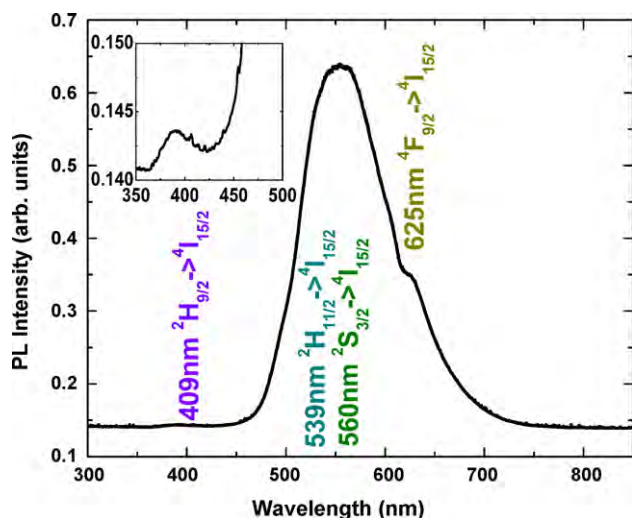


Fig. 5. PL spectrum of GaN:Er crystal. Characteristic Er^{3+} transitions are labeled for reference.

a surfactant or etchant, interfacial mismatch strain with a lattice-mismatched substrate and the underlying bonding of the substrate.

During VLS growth, a metallic or, in this case, rare-earth catalyst enhances the growth via a supersaturation in the seed which leads to precipitation of the semiconductor crystal [14,15]. It is known that once a single grain crystal forms on the surface of a small-volume seed, this orientation is maintained and the growth rate is enhanced by the surfactant effect of the seed present at the growth surface [17]. This is clearly seen in this work by the growth of distinct GaN crystals in region with low-levels of dispersed seed. In contrast, this enhanced growth can become unrestrained for excessively large seed particles that can accommodate multiple nucleation sites [16]. This was seen in this study by the accumulation (clustering) of GaN crystal in regions with a higher density of seed.

Figs. 2 and 4 of the rare-earth seed on top of the GaN crystal clusters is telling as this is a snap shot of an uncompleted catalysis-enhanced reaction. The presence of the metallic seed at the end of a semiconductor nano-wire is often cited as proof of the VLS mechanism [14,15]. In this work it is also desired to similarly enhance the GaN growth by forming a Ga–Er–N liquid alloy wherein the GaN diffuses through this liquid to the growth front of the crystal. In contrast to traditional VLS growth, here it is desired to intentionally dissolve this rare-earth seed into the semiconductor matrix. This solubility of Er into the GaN host via a rare-earth chloride seed is confirmed by the presence of Er^{3+} luminescent transitions in Fig. 5.

In this study, it is demonstrated that the choice of substrate influences the growth mechanism. The standard for GaN fabrication is in the *c*-direction [0 0 0 1] on *c*-plane (0 0 0 1) sapphire. *a*-Plane (1 1 $\bar{2}$ 0) GaN can be deposited readily by employing *r*-plane (1 $\bar{1}$ 0 2) sapphire [18]. Epitaxy on *a*-plane (1 1 $\bar{2}$ 0) sapphire can yield either *c*- or *m*-plane (1 $\bar{1}$ 0 0) GaN by adjusting the conditions of growth [19,20]. This corresponds well with the results in this study that showed crystals of *a*-plane, *c*-plane, and mixed *m*- and *c*-plane GaN on *r*-plane, *c*-plane, and *a*-plane sapphire, respectively. Qualitatively, there was an increase in the ratio of aligned *m*-plane (or *a*-plane) crystals to random *c*-plane crystals in areas of the *a*-plane (or *r*-plane) sapphire with a high density of seed. Evidently, the presence of the catalyst alters the epitaxial relationship of GaN with the substrate.

One additional influence on the growth is the Cl atom in the seed, which will react with free Ga to form a GaCl reactant similar to the reaction chemistry in HVPE. Conversely, an excess accumulation of Cl will act as an etchant that locally suppresses nucleation [21,22].

5. Conclusion

A novel rare-earth chloride seeded growth process was developed for the fabrication of optically active GaN nano-

crystals. Additionally, the horizontal geometry of these rare-earth doped nano-crystals is intriguing for use as in-plane light emitting devices as well as DMS transistors.

Acknowledgements

Research at the Naval Research Lab is supported by Office of Naval Research and ONR-Global (N00014-06-1-4046); support for M.A.M. was partially provided by the American Society for Engineering Education; support for J.K. was partially provided by Brain Korea 21 program in 2006.

References

- [1] M. Law, J. Goldberger, P. Yang, *Annu. Rev. Mater. Sci.* 34 (2004) 83.
- [2] H. Choi, J. Johnson, R. He, S. Lee, F. Kim, P. Pauzauskie, J. Goldberger, R. Saykally, *P. Yang, J. Phys. Chem. B* 107 (2003) 8721.
- [3] E. Stach, P. Pauzauskie, T. Kuykendall, J. Goldberger, P. Yang, *Nano Lett.* 3 (2003) 867.
- [4] Y. Xia, P. Yang, Y. Sun, Y. Wu, B. Mayers, B. Gates, Y. Yin, F. Kim, H. Yan, *Adv. Mater.* 15 (2003) 353.
- [5] T. Kuykendall, P. Pauzauskie, S.K. Lee, Y. Zhang, P. Yang, *Nano. Lett.* 3 (2003) 1063.
- [6] J.H. Song, F. Kim, D. Kim, P. Yang, *Chem. Euro. J.* 11 (2005) 910.
- [7] S. Nakamura, G. Fasol, S.J. Pearton, *The Blue Laser Diode: The Complete Story*, Springer, Berlin, 2000.
- [8] M.A. Mastro, R.T. Holm, N.D. Bassim, C.R. Eddy Jr., R.L. Henry, M.E. Twigg, A. Rosenberg, *Jpn. J. Appl. Phys.* 45-31 (2006) L814.
- [9] M.A. Mastro, R.T. Holm, N.D. Bassim, C.R. Eddy Jr., D.K. Gaskill, R.L. Henry, M.E. Twigg, *Appl. Phys. Lett.* 87 (2005) 241103.
- [10] M.A. Mastro, R.T. Holm, N.D. Bassim, D.K. Gaskill, J.C. Culbertson, M. Fatemi, C.R. Eddy Jr., R.L. Henry, M.E. Twigg, *J. Vac. Sci. Technol. A* 24 (2006) 1631.
- [11] A.J. Steckl, J. Heikenfeld, D.S. Lee, M. Garter, *Mater. Sci. Eng. B* 81 (2001) 97.
- [12] M. Hashimoto, S. Emura, R. Asano, H. Tanaka, N. Teraguchi, A. Suzuki, Y. Nanishi, T. Homma, N. Umesaki, H. Asahi, *Phys. Status Solidi (c)* 0–7 (2003) 2650.
- [13] H. Choi, H. Seong, J. Chang, Y. Park, J. Kim, R. He, T. Kuykendall, P. Yang, *Adv. Mater.* 17 (2005) 1351.
- [14] T.J. Trentler, K.M. Hickman, S.C. Geol, A.M. Viano, P.C. Gibbons, W.E. Buhro, *Science* 270 (1995) 1791.
- [15] J.D. Holmes, K.P. Johnston, R.C. Doty, B.A. Korgel, *Science* 287 (2000) 1471.
- [16] S.H. Kan, A. Aharoni, T. Mokari, U. Banin, *Faraday Discuss.* 125 (2004) 23.
- [17] Y. Wu, P. Yang, *J. Am. Chem. Soc.* 123 (2001) 3165.
- [18] C.R. Eddy Jr., R.T. Holm, R.L. Henry, J.C. Culbertson, M.E. Twigg, *J. Electron. Mater.* 34 (9) (2005) 1187.
- [19] D. Doppalapudi, E. Iliopoulos, S.N. Basu, T.D. Moustakas, *J. Appl. Phys.* 85 (1999) 3582.
- [20] T. Kato, H. Ohsato, T. Okuda, P. Kung, A. Saxler, C. Sun, M. Razeghi, *J. Cryst. Growth* 173 (1997) 244.
- [21] M.A. Mastro, D.V. Tsvetkov, A.I. Pechnikov, V.A. Soukhoveev, G.H. Gainer, A. Usikov, V. Dmitriev, B. Luo, F. Ren, K.H. Baik, S.J. Pearton, *Mater. Res. Soc. Symp. Proc.* 764 (2003) C2.2.
- [22] M.A. Mastro, D.V. Tsvetkov, V. Soukhoveev, A. Usikov, V. Dmitriev, B. Luo, F. Ren, K.H. Baik, S.J. Pearton, *Solid State Electron.* 48 (2004) 179.