CHAPTER 3

GALLIUM NITRIDE MATERIALS TECHNOLOGY

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EVOLUTION OF GaN TECHNOLOGY

Recently, Group III nitride-based semiconductors have emerged as the leading material for the production of blue LEDs, blue laser diodes, and high-power, high-temperature electronics. The achievement of high brightness blue InGaN LEDs has basically caused a revolution in LED technology and opened up enormous new, previously inaccessible markets. The use of InGaN/GaN double heterostructures in LEDs in 1994 by Nakamura et al. (1994) and the achievement of *p*-doping in GaN by Akasaki (Amano et al. 1989) are widely credited with re-igniting the III-V nitride system. The historical evolution of GaN materials and device technology in Japan in the early 1990s is regarded as one of the key developments in solid-state devices today. These remarkable advancements in GaN-based LED materials have depended on several key breakthroughs in materials synthesis and fabrication. The lack of *p-n* junctions in Group III nitrides and their poor crystal quality slowed research for many decades. The recent realization of blue lasers has taken over 20 years from the time the first optical pumped stimulated emission was observed in GaN crystals (Dingle et al. 1994) and the first LEDs (Pankove et al. 1971) were fabricated. The purpose of this chapter is to review the status of GaN materials technology in Japan.

MATERIALS PROPERTIES

Energy Band Structure/Lattice Constants

The bandgap in the (Al,Ga,In) N-based materials system ranges from 1.9 eV (InN) to 3.4 eV (GaN) to 6.2 eV (AlN). The band structure is currently thought to be a direct bandgap across the entire alloy range. Therefore, as illustrated in Figure 3.1, almost the entire visible range of wavelengths is spanned in the Group III nitride alloy system. This direct bandgap is especially fortuitous as it allows for high quantum efficiency light emitters to be fabricated in this system.

GaN Physical Properties

Group III nitrides possess several remarkable physical properties that make them particularly attractive for reliable solid state device applications. The wide bandgap materials possess low dielectric constants with high thermal conductivity pathways. Group III nitrides exhibit fairly high bond strengths and very high melting temperatures. The large bond strengths could possibly inhibit dislocation motion and improve reliability in comparison to other II-VI and III-V materials. In addition, the nitrides are resistant to chemical etching and should allow GaN-based devices to be operated in harsh environments. These properties may lead to devices with superior reliability.

Optoelectronic Materials

Because of the large commercial need for GaN blue LEDs and lasers in displays, illumination, and optical storage, over 40 companies in Japan are working on the optoelectronic applications of GaN. Numerous companies in Japan are working to commercialize blue and green GaN LEDs. Currently, Nichia and Toyoda Gosei are the main blue and green GaN LED suppliers in Japan. If they are successful, LED lighting technology will have greatly improved energy savings and environmental conditions. The sources will be compact and highly reliable (>10 years) and could result in enormous cost savings compared to conventional light sources. The Japanese Ministry of International Trade and Industry estimates that energy savings will be on the order of 10 million kiloliters of petroleum a year for Japan alone. The use of GaN-based LEDs may also result in large scale reduction of greenhouse gases, such as carbon dioxide, and minimize the risk of global warming. In addition, the GaN LED chip is much less toxic than arsenide-based LEDs and mercury-containing fluorescent lamps. For these reasons alone, the Japanese government has initiated a $50 million program over 5 years to fund Japanese based corporations and universities to develop a LED light bulb.

LED Materials

Advances in GaN-based LEDs have opened many new markets for LEDs. Now one can use 3 LEDs to tune to any color in the visible range or use a single blue LED in combination with phosphors to make “white” LEDs. The concept is particularly attractive because the solid state nature of semiconductor devices produces very high reliability. The average life span of an LED is on the order of tens of years (Craford 1997).

Full-color and white LEDs are now appearing in numerous applications ranging from outdoor TVs, traffic signals, scanners, flashlights, and automotive back-lighting. Another potentially large application of GaN is in fabricating blue laser diodes (LDs) for extremely high density optical storage systems. Because the storage density of optical compact discs (CDs) and digital video discs (DVDs) is inversely proportional to the square of the laser wavelength, a 4-8 fold increase in capacity could be realized with short wavelength laser diodes. Future research is needed to commercialize GaN for optical storage, energy efficient lighting, communications, printing, projection TV, and even surgery. As GaN manufacturing volumes increase and costs decrease, one can expect to see GaN LEDs and LDs in ever-increasing applications wherever economical and reliable illumination is needed.

Two types of blue LEDs are commercially available: laterally contacted devices with single quantum well (SQW) InGaN active regions on sapphire substrates from Nichia Chemical Industries Ltd., Toyoda Gosei, and Hewlett-Packard Optoelectronics, and vertically contacted GaN/AlGaN double heterostructure devices on conducting SiC substrates by Cree Research Inc. and Siemens. The SQW LEDs are extremely efficient. Currently, the best external efficiencies Nichia has achieved for blue and green LEDs are 10% and 12% external quantum efficiencies, respectively (Nakamura et al. 1997). White LEDs are approximately 5% and have a luminous efficacy of 10 lumens/watt, which is becoming competitive with existing incandescent sources. In addition, newly developed InGaN amber LEDs are superior to conventional AlGaInP amber LEDs in terms of temperature performance. The wavelength shift as a function of temperature is much smaller in GaN than in GaAs-based LEDs. Dr. Nakamura has compared InGaN- to AlGaInP-based LEDs at an elevated temperature of 80°C in which the InGaN LED light output is decreased by only 20%, whereas the AlGaInP LED light output is down by 70% (Mukai et al. 1998). This excellent temperature performance for GaN-based LEDs in comparison to conventional GaAs-based LEDs also appears when compared to GaP green and AlGaAs red LEDs. The InGaN yellow LEDs are not as bright as transparent substrate AlGaInP LEDs, but the InGaN LEDs’ performance rivals absorbing substrate AlGaInP LEDs. At 20 mA, the new yellow LED is 4 Candela and has an external efficiency of 3.3% at 594 nm (Dingle et al. 1994). With such achievements, nitride LEDs rank among the highest efficiency LEDs on the market as shown in Figure 3.1.

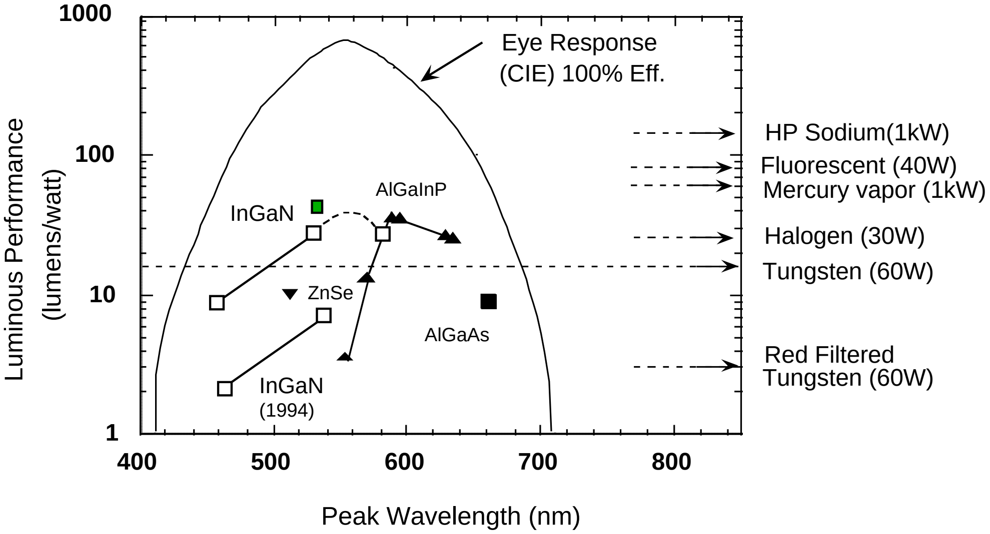

Fig. 3.1. InGaN-based LEDs extend the range of LEDs into blue and achieve efficiencies exceeding tungsten light bulbs (12 lumens/watt).

Cree Research Inc. makes the second type of LED structure grown on SiC substrates. These devices feature a MOCVD-grown GaN-AlGaN *p-n* junction grown on 6H-SiC substrates. SiC has a smaller lattice misfit to GaN and could provide *n*-doped substrates. The vertical conduction pathway also allows for a drop in replacement parts, similar to the other GaP- and GaAs-based structures that have the same vertical geometry. The high thermal conductivity of SiC substrates might also benefit the high-temperature, high-output power applications of GaN LEDs. GaN/SiC output power is lower than that available on sapphire and is commercially available with 1.0 mW and an external quantum efficiency of 2.0% (Cree Research Inc. 1995).

Blue Laser Materials

Several groups in Japan and in the United States have recently reported obtaining laser diodes in the GaN materials system, as shown in Table 3.1. Of these groups, only Nichia has obtained long-life continuous wave (CW) emission. Its laser diode was market released in January 1999. Nichia was the first company in the world to successfully achieve a blue laser diode in a GaN materials system. Initially, the GaN laser lasted only a few seconds, but reliability has improved dramatically to a state at which Dr. Nakamura has achieved CW operation up to 10,000 hours at room temperature. Elevated temperature testing at 50°C has projected the actual lifetime as being in excess of 20,000 hours at 2 mW.

Table 3.1

Groups Demonstrating Lasing in GaN Diodes

Japan	U.S.
Nichia (commercial Jan. 1999)	Cree Research
Toshiba	University of California, Santa Barbara
Fujitsu	Xerox
Sony	Hewlett-Packard/Meijo Univ.
Pioneer	SDL
Meijo Univ.	
Meijo Univ./Hewlett-Packard	
Panasonic	

Dr. Nakamura believes that a blue laser diode product will be available soon from Nichia. Nichia is developing this laser for use in the largest market first, that being the next generation of high density DVD optical storage systems. The reduction in the spot size that can be achieved with blue GaN lasers is estimated to yield a storage capacity of 12 GB per 5.25 in diameter discs, enough for recording a full-length motion picture in high resolution mode. Table 3.2 shows increases in storage capacity for various laser wavelengths.

Table 3.2

Increase in Storage Capacity for Various Laser Wavelengths

Laser Wavelength	Spot Reduction	Optics Improve	Storage Capacity	#CDs
860 nm	1		650 Mb	1
650 nm	1.75	4.1	4.7 Gb	7
400 nm	4.6	4.1	12.4 Gb	19
400 nm (dual sided-dual level)			44.9 Gb	69

NITRIDE MATERIALS GROWTH ISSUES

MOCVD Growth

MOCVD is a non-equilibrium growth technique that relies on vapor transport of the precursors and subsequent reactions of Group III alkyls and Group V hydrides in a heated zone. The MOCVD technique originated from the early research of Manasevit (1968) who demonstrated that triethylgallium (TEGa) and arsine deposited single crystal GaAs pyrolytically in an open tube, cold-wall reactor. The basic MOCVD reaction describing the GaN deposition process is:

$$Ga(CH_3)_3(v) + NH_3(v) \rightarrow GaN(s) + 3CH_4(v) \qquad (1)$$

However, the details of the reaction are not well known, and the intermediate reactions are thought to be complex. Further work is needed to understand the fundamentals of this crystal growth process.

Various researchers employ both atmospheric-pressure and low-pressure MOCVD reactors in the growth of GaN. The majority of research groups in Japan utilize atmospheric pressure reactors because of the high partial pressures of ammonia. Nakamura and his colleagues achieved the breakthrough in bright blue LEDs using a modified MOCVD system (Nakamura et al. 1994a). Nichia Chemistries Inc. has employed a novel two-flow approach that yields excellent film quality. As shown in Figure 3.2, sources are supplied in this reactor from a horizontal inlet and from a vertical subflow rather than driving the reactants to the growing film surface.

MOCVD reactor designs for GaN growth must overcome problems presented by high growth temperatures, prereactions, and flow and film non-uniformity. Typically in GaN growth, very high temperatures are required because of the high bond-strength of the N-H bond in ammonia precursors. Compounding this fact is the thermodynamic tendency of ammonia to prereact with Group III metalorganic compounds to form non-volatile adducts. These factors contribute to the difficulties currently facing researchers in the design and scale-up of III-V nitride deposition systems. Much research activity is needed in the scale-up and understanding of the mechanism of gallium nitride growth by MOCVD.

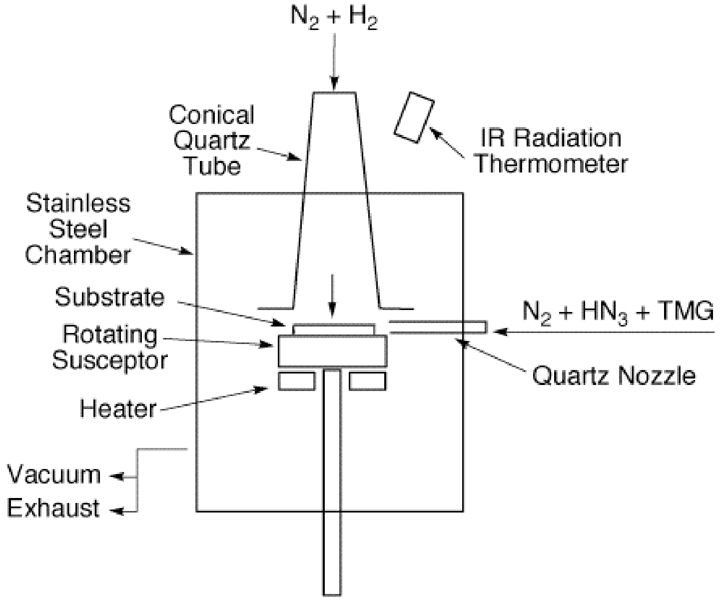

Fig. 3.2. Two-flow atmospheric pressure MOCVD approach at Nichia (after Nakamura et al. 1994).

Molecular Beam Epitaxy (MBE)

Several researchers in Japan have begun developing MBE for growth of III-V nitrides. Several approaches have been investigated for supplying an atomic source of nitrogen. RF plasma and electron cyclotron resonance (ECR) microwave plasma sources are the two most successful techniques discovered so far (Lei et al. 1991; Strite et al. 1991; Paisley et al. 1989). In these RF plasma MBE systems, the plasma source is used to crack molecular nitrogen. These plasma sources use cylindrical cavity geometry to efficiently pump microwave energy into the nitrogen discharge area. The plasma stream is a complex mixture of atomic, molecular, and ionic N radicals. When using ECR sources, a tradeoff between growth rate and ion damage occurs (Lei et al. 1991). Under normal ECR use, the flux of the low energy reactive N species is so low that only low growth rates of 500 Å/hr can be achieved. At higher microwave powers, higher growth rates can be achieved, but ion damage leading to deep levels and semi-insulating electrical properties occurs. A major advantage of MBE for nitride growth is the low growth temperature that can be achieved because of the atomic nitrogen source. This is in contrast to MOCVD, which must employ high growth temperatures (>1000°C) to crack the ammonia molecules. The lower growth temperatures should result in lower thermal stress upon cooling, less diffusion, and reduced alloy segregation. This lower growth temperature is especially important in the AlGaN alloys that have a large mismatch in their thermal expansion coefficients.

Electronic Materials and Epitaxial Lateral Overgrowth

Research on the electronic device applications of GaN is progressing more slowly in Japan than in the United States because there is less commercial need for such high power electronic devices. As of 1998, 6 groups in Japan were actively working on GaN electronic devices: Sony, NEC, Furukawa Electric, Meijo University, Electrotechnical Laboratories, and Kyoto University. However, many other groups the panel visited stated unofficially that they would begin efforts in the near future as soon as the materials properties improved. At most, group mobilities for bulk GaN have exceeded 600 cm^2/V-sec, and AlGaN/GaN 2-dimensional gas mobilities exceeding 900 cm^2/V-sec have been obtained at the Sony Research Center. Sony, NEC, Furukawa, and Meijo University all demonstrated working high electron mobility transistors (HEMTs). At the time of the panel's visit, no RF power results had been reported in Japan. One strength that the panel saw was the dedication of several groups to basic materials research. Of particular note was the epitaxial lateral overall (ELO) growth method being developed at both Nichia and NEC for defect reduction in GaN on sapphire substrates. Lateral epitaxial overgrowth (LEO) is an attractive method for producing GaN films with a low density of extended defects, which is beneficial both to studies of the fundamental properties of the GaInAlN materials system and to GaN-based device technology. The basic concept is to reduce defect propagation in masked regions of the substrate where the laterally overgrowing GaN is defect free. This is illustrated in the transmission electron micrograph in Figure 3.3. Recent studies in Japan and in the United States have confirmed that the density of threading dislocations (TDs) is reduced by 3-4 orders of magnitude in LEO material grown on 6H-SiC substrates (Zheleva et al. 1997) and Al_2O_3 (Sakai et al. 1997; Marchand et al. 1998; Marchand et al. 1998). The mechanisms of threading dislocations evolution during LEO have also been investigated (Nam et al. 1997; Sakai et al. 1998). Studies of the optical properties of LEO GaN (Chichibu et al. 1989; Freitas et al. 1998) and InGaN quantum wells (Rosner et al. n.d.) have revealed that TDs act as non-radiative recombination centers. However, the minority carrier diffusion length (<200 nm) is smaller than the average distance between TDs so that the emission mechanisms of the carriers that do recombine radiatively appear to be unaffected by moderate TD densities (~10^6-10^9 cm^{-2}). On the other hand, reducing the TD density has been shown to reduce the reverse leakage current by ~3 orders of magnitude in GaN *p-n* junctions (Kozodoy et al. 1998), in InGaN single (Mukai et al. 1998) and multiple (Sasaoka et al. 1998) quantum well light emitting diodes, and in GaN/AlGaN heterojunction field-effect transistors (Vetury et al. 1998) fabricated on LEO GaN. More recently, ultraviolet p-i-n photodetectors fabricated on LEO AlGaN have exhibited a similar reduction of the reverse leakage current by up to 6 orders of magnitude (Parish et al. 1998). The use of LEO GaN has also resulted in marked improvements in the lifetime of InGaN/GaN laser diodes (Nakamura et al. 1998).

At Nichia, a key development in obtaining reliable CW laser performance was defect reduction by using an epitaxial lateral overgrowth GaN (ELOG) substrate. In this technique, a silicon dioxide mask is used to block dislocation propagation, and a "defect free" film is achieved in the laterally overgrown region. After 100 microns of growth, a fully coalesced GaN thin film is achieved, and a proprietary process removes the sapphire substrate. The ELO process is shown schematically below (Fig. 3.3). Laser diodes with InGaN/GaN multiple quantum well (MQW) active regions are then grown on top of this virtual bulk GaN substrate. The active regions are then defect free and can survive under high current operation (3 kA/cm^2).

At NEC, Dr. Usui has achieved remarkable success in pioneering defect reduction in GaN with the lateral epitaxial overgrowth (LEO) method. Dr. Usui calls this NEC process "facet initiated epitaxial lateral overgrowth" (FIELO). In this technique, defects are reduced by having the growing facet steer the edge defect parallel to the surface so that they cannot propagate on the surface. The defect density is reduced from 1E+9/cm^2 to less than 1E+7/cm^2. Dr. Usui has even made "bulk-like" GaN substrates by lifting thick GaN epitaxial films from the sapphire substrate using a proprietary technique. These bulk-like GaN films are 100 to 200 microns thick and 1 cm by 1 cm wide. These low defect films can be used to make conventional type edge-emitting lasers. Dr. Usui has developed a hydride vapor phase epitaxy (HVPE) method for depositing the thick LEO films on sapphire substrates. The films are grown at 1000ºC and are 100 to 200 microns thick after a few hours. The best X-ray line width is 150 arcseconds, and mobilities of 863 cm^2/V-sec and 2780 cm^2/V-sec have been obtained at 300K and 77K, respectively.

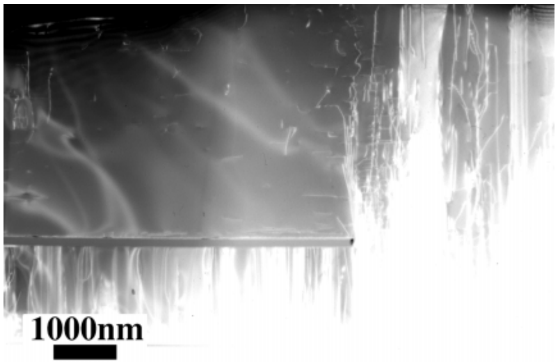

Fig. 3.3. Cross-sectional TEM of LEO GaN displaying large reduction of threading dislocation in lateral overgrown GaN region.

CONCLUSIONS

Group III nitride semiconductors have emerged as the leading material for fabricating high reliability short wavelength emitters and emerging high power electronic devices. MOCVD and MBE are the leading growth technologies for depositing these high quality GaN/InGaN heterostructure-based devices. Several research groups have demonstrated well-controlled doping, low background carrier concentrations, and high mobilities exceeding 600 cm^2/V-sec. Optimization of the MOCVD growth of InGaN/GaN-based quantum structures has enabled high efficiency blue LEDs and laser diodes to be achieved. GaN-based blue and green LEDs with external quantum efficiencies of 10% and 5 mW output power at 20 mA have recently been demonstrated. These are bright enough for full-color outdoor displays. Epitaxial lateral overgrowth (ELO) is being developed in Japan as an alternative GaN substrate. Commercial laser diodes from Nichia are already fabricated on ELO substrates.

REFERENCES

Amano, H., M. Kitoh, K. Hiramatsu, and I. Akasaki. 1990. *Gallium Arsenide and Related Compounds*. Ed. T. Ikoma, H. Watanabe, H. Bristol. UKIOP. pp. 725-30.

Chichibu, S., H. Marchand, S. Keller, P. Fini, J. P. Ibbetson, M. Minsky, S. Fleischer, J. S. Speck, J. Bowers, E. Hu, U.K. Mishra, S. P. DenBaars, T. Deguchi, T. Sota, and S. Nakamura. 1998. 2nd Int. Conf. on Blue Laser and Light Emitting Diodes, Chiba, Japan, Sept. 29 – Oct. 2.

Chichibu, S. et al. *Appl. Phys. Lett.* (in press).

Craford, M.G. 1977. *IEEE Trans. Electron Devices.* ED-24:935.

Cree Research Inc. 1995. Product specification sheet, Super Blue LED. C430-DH85.

Dingle, D., K.L. Shaklee, R.F. Leheny, and R.B. Zetterstrom. 1994. *Appl. Phys. Lett.* 64:1377.

Freitas, J. A., Jr., O. H. Nam, R. F. Davis, G. V. Saparin, and S. K. Obyden. 1998. *Appl. Phys. Lett.* 72:2990

Kozodoy, P., J. P. Ibbetson, H. Marchand, P. T. Fini, S. Keller, S. P. DenBaars, J. S. Speck, U. K. Mishra. 1998. *Appl. Phys. Lett.* 73:975.

Lei, T., M. Fanciulli, R. J. Molnar, T. D. Moustakas, R. J. Graham, and J. D. Scanlon. 1991. *Appl. Physics Lett.* 59:94.

Li, X., S. G. Bishop, and J. J Coleman. 1998. *Appl. Phys. Lett*. 73:1179.

Manasevit, H. M. 1968. *Appl. Phys. Lett*. 12:156.

Marchand, H., J. P. Ibbetson, P. T. Fini, P. Kozodoy, S. Keller, J. S. Speck, S. P. DenBaars, and U. K. Mishra. 1998. MRS Internet *J. Nitride Semicond. Res.* 3:3.

Marchand, H., X. H. Wu, J. P. Ibbetson, P. T. Fini, P. Kozodoy, S. Keller, J. S. Speck, S. P. DenBaars, and U. K. Mishra. 1998. *Appl. Phys. Lett.* 73:747.

Mukai, S., H. Narimatsu, and S. Nakamura. 1998. Amber InGaN-based LEDs operable at high ambient temperatures. *Jap. J. Appl. Physics.* p. L479.

Mukai, T., K. Takekawa, S. Nakamura. 1998. *Jap. J. Appl. Phys.* 37:L839.

Nakamura, S., and G. Fasol. 1997. *The Blue Laser Diode*. Heidelberg, Germany: Springer-Verlag.

Nakamura, S., T. Mukai, and M. Senoh. 1994. *Appl. Phys. Lett.* 64:1687-1689.

Nakamura, S., M. Senoh, S. Nagahama, N. Isawa, T. Yamada, T. Matsushita, H. Kiyoku, Y. Sugimoto, T. Kozaki, H. Umemoto, M. Sano, and M. Chocho. 1998. *Appl. Phys. Lett.* 72:211.

Nam, O. H., M. D. Bremser, T. S. Zheleva, and R. F. Davis. 1997. *Appl. Phys. Lett.* 71:2638.

Paisley, M. J., Z. Sitar, J. B. Posthill, and R. F. Davis. 1989. *J. Vac. Sci. Technol*. A7:701.

Pankove, J. I., E. A. Miller, and J. E. Berkeyheiser. 1971. *RCA Rev*. 32:383.

Parish, G., S. Keller, P. Kozodoy, J. P. Ibbetson, H. Marchand, P. T. Fini, S. B. Fleischer, S. P. DenBaars, U. K. Mishra, and E. J. Tarsa. 1998. Presented at the Conference on Optoelectronic and Microelectronic Materials and Devices. Perth, Australia, December 14-16.

Rosner, S. J., G. Girolami. H. Marchand, P. T. Fini, J. P. Ibbetson, L. Zhao, S. Keller, U. K. Mishra, S. P. DenBaars, J. S. Speck. n.d. *Appl. Phys. Lett.* in press.

Sakai, A., H. Sunakawa, and A. Usui. 1997. *Appl. Phys. Lett.* 71: 2259.

Sakai, A., H. Sunakawa, and A. Usui. 1998. *Appl. Phys. Lett.* 73: 481

Sasaoka, C., H. Sumakawa, A. Kimura, M. Nido, A. Usui, and A. Sakai. 1998. *J. Cryst. Growth.* 189:61.

Strite, S., J. Ruan, Z. Li, N. Manning, A. Salavador, H. Chen, D. J. Smith, W. J. Choyke, and H. Morkoc. 1991. *J. Vac. Sci. Technol.* B9:1924.

Usui, A., H. Sunakawa, N. Kurado, A. Kimura, A. Sakai, and A. A. Yamaguchi. 1998. Presented at the 2nd Int. Conf. on Blue Laser and Light Emitting Diodes, Chiba, Japan, Sept. 29 – Oct. 2.

Vetury, R., H. Marchand, J. P. Ibbetson, P. T. Fini, S. Keller, J. S. Speck, S. P. Denbaars, and U. K. Mishra. 1998. Presented at the 25th Int. Symp. on Compound Semicond., Nara, Japan, Oct 12-16.

Zheleva, T. S., O. H. Nam, M. D. Bremser, and R. F. Davis. 1997. *Appl. Phys. Lett.* 71:2472.