

Growth of GaN on lithium gallate substrates for development of a GaN thin compliant substrate

William A. Doolittle,^{a)} Tom Kropewnicki, C. Carter-Coman, S. Stock, Paul Kohl, Nan Marie Jokerst, Robert A. Metzger, Sangbeom Kang, Kyeong Kyun Lee, Gary May, and April S. Brown

Georgia Institute of Technology, School of Electrical and Computer Engineering, Atlanta, Georgia 30332-0250

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Since we have found that an entire substrate can be chemically removed in less than 5 min and since GaN is impervious to chemical etching, the GaN on lithium gallate (LGO) system is an excellent template (due to near infinite etch selectivity) for developing a thin film/compliant GaN substrate. Here we report on our efforts to grow GaN on LGO, including improvement of the atomic surface morphology using pregrowth pretreatments. We also report the first transferred thin film GaN substrate grown on LGO, transferred off of LGO and mounted on GaAs. With this approach, (InAl)GaN alloys can be grown on thin GaN films, implementing a "compliant" substrate for the nitride alloy system. In addition, the flexibility of bonding to low cost Si, metal or standard ceramic IC packages is an attractive alternative to SiC and hydride vapor phase epitaxy GaN substrates for optimizing cost versus thermal conductivity concerns. We have demonstrated high quality growth of GaN on LGO. X-ray rocking curves of 145 arcsec are shown on a 0.28 μm thick films. For the first time, we present data on the out-of-plane crystalline quality of GaN/LGO material. Likewise, we show two orders of magnitude improvement in residual doping concentration and factors of 4 improvement in electron mobility. We show substantial vendor to vendor and intravendor LGO material quality variations. We have quantified the desorption of Ga and Li from the surface of LGO at typical growth temperatures using *in situ* desorption mass spectroscopy and x-ray photoelectron spectroscopy. © 1998 American Vacuum Society. [S0734-211X(98)06803-6]

I. INTRODUCTION

The growth and applications of GaN has been severely limited by the unavailability of an acceptable substrate material. Typically GaN is grown on substrates such as GaAs, sapphire, or SiC with large lattice mismatches. This has led to an extremely high defect density due to the growth mechanism being three dimensional.¹

Nearly lattice-matched substrates exist for GaN growth. One such substrate, lithium gallate (LGO), LiGaO_2 , has been studied for piezoelectric applications since 1965.² As a well-studied material, much information about its crystal properties including compliance, stiffness, and piezoelectric tensors,³ coefficients of thermal expansion,^{4,5} infrared vibration and bond strengths,⁶ heat capacity, entropy, and enthalpy,⁷ thermal stability,⁸ wet and reactive ion etching (RIE) etch rates⁹ are known. Marezio² first determined its crystal structure as orthorhombic. However, the crystal contains hexagonal symmetry (only slightly distorted from the wurtzite structure) with a lattice match to GaN of 0.19%.^{10,11} These features, influenced Nicholls *et al.*¹⁰ to first attempt molecular beam epitaxy (MBE) growth of GaN on LGO. Since then, several researchers have grown on LGO using MBE¹⁰⁻¹⁴ and with metalorganic chemical vapor deposition (MOCVD).^{15,16} The various structural (x-ray FWHM only), electrical and optical properties resulting are summarized in

Table I. Generally, the x-ray FWHM of films has been unmatched for comparable thickness films on other substrates. Likewise, the optical properties of the material have been superior. Both the excellent x-ray FWHM and optical properties are most likely a result of the excellent lattice match. However, the limited data reported for electrical properties have been worse than possible on other substrates. In particular, high residual doping and low mobility have been a problem.¹⁶

Since we have found that an entire LGO substrate can be chemically removed in less than 5 min and since GaN is impervious to most chemical etching, the GaN on LGO system is an excellent template (due to near infinite etch selectivity) for developing a thin film/compliant GaN substrate. Here we report on our efforts to grow GaN on LGO, including improvement of the atomic surface morphology using pregrowth pretreatments, and detailed crystal quality (x-ray diffraction) assessment including the first out-of-plane x-ray rocking curves. We also report the first transferred thin film GaN substrate grown on LGO, transferred off of LGO and mounted on GaAs. With this approach, (InAl)GaN alloys can be grown on thin GaN films, implementing a "compliant" substrate for the nitride alloy system. In addition, the flexibility of bonding to low cost Si, metal or standard ceramic IC packages is an attractive alternative to SiC and hydride vapor phase epitaxy (HVPE) GaN substrates for optimizing cost versus thermal conductivity concerns.

^{a)}Electronic mail: alan.doolittle@ece.gatech.edu

TABLE I. Comparison of nitride growths on LiGaO₂.

Reference	Growth conditions	Thickness	X-ray FWHM (arcsec)	Room temp. photoluminescence	Mobility	Residual doping
10, 11	rf plasma MBE at 800 °C	1.5–3.25 μm	103 (0002) on 1.5 μm	Extremely strong band edge ~107 meV FWHM, almost no yellow, (MQW of AlGaIn/GaN)	Not reported	Not reported
14	rf plasma MBE at 700 °C	0.4 μm	~260 (0002)	Not reported	Not reported	Not reported
15	MOCVD at greater than 850 °C	<1.0 μm	Estimated from plot as a few hundred (0002)	Not reported	Not reported	Not reported
12, 13	rf plasma MBE at 630 °C	Not reported	Not reported	Strong band-edge, some yellow	Not reported	Not reported
16	MOCVD, 600–1000	Not reported	300 (0002) for 900 °C	Strong band-edge ~180 meV FWHM, almost no yellow	10 cm ² /V s	~1 × 10 ²⁰ cm ⁻³
This work	rf plasma MBE from 600 to 900 °C	0.3–0.8 μm	204 (0002) 145 (0004) 245 (1015)	Not reported	43 cm ² /V s	1.3 × 10 ¹⁸ cm ⁻³

II. COMPLIANT SUBSTRATE APPROACH

The main purpose of a compliant substrate is to allow the substrate to “compress” or “expand” to conform to the lattice constant of the overgrown layer. Georgia Tech has previously successfully demonstrated such substrates, using both an epitaxial liftoff and bonded substrate removal process for the GaAs material system.¹⁷ The process is outlined in Fig. 1. In both processes, a film is grown below the critical thickness on a standard substrate. This means that high quality *thin* films are needed. Because of the large strains in other conventional substrates, these thin, high quality films are not possible without using a lattice-matched substrate like LGO. In the liftoff process, wax is applied to the growth surface, and the substrate is removed (chemically or chem-mechanically). The film is then placed on a “host” substrate via some bonding material chosen for its elasticity and ad-

hesion at the subsequent growth temperature. Thus, a thin, “stretchable” film on a host substrate is produced. The thin film can then be used for homoepitaxial regrowth to a greater thickness, or used as a compliant substrate for growth of other slightly lattice-mismatched materials.

The bonded substrate removal process (see Fig. 1) varies from the epitaxial liftoff process only slightly. Instead of being waxed, the originally grown film is inverted and bonded directly to the host substrate. The original growth substrate is then removed, resulting in a thin “stretchable” film, useful for subsequent regrowth. The bonded substrate removal process has the advantage of scalability to very large area, but requires an etchant that will attack the original growth substrate, but not the bonding layer.

III. EXPERIMENTAL RESULTS

We have found large variability in substrate quality from vendor to vendor, and even from the same vendor. This difficulty, resulting from the immature crystal growth technology, results in different samples responding differently. One such observation was found in the reflection high-energy electron diffraction (RHEED) response to a high-temperature anneal. Originally, material from vendor A showed poor, extremely spotty RHEED as received (solvent cleaned) as indicated in Fig. 2(a). When the material was exposed to a 1050° anneal, the spots slowly merged into relatively smooth streaks [see Fig. 2(b)] with some variation in width along each streak. After cooling the sample, the RHEED pattern smoothed out even more [see Fig. 2(c)], even showing a weak “2×” pattern. As shown in Fig. 3, a residual gas analyzer mounted in front of the sample showed considerable desorption of Ga and Li from the surface starting at temperatures greater than ~900 °C. This seemed to confirm the suspicions of Johnson *et al.*^{11,12} who suggested that the LGO surface begins to degrade at high temperature. However, they found that the RHEED pattern worsened as opposed to our initial observation of improvement. X-ray photoelectron spectroscopy (XPS) was used to compare an as delivered LGO surface, with a LGO surface that underwent a

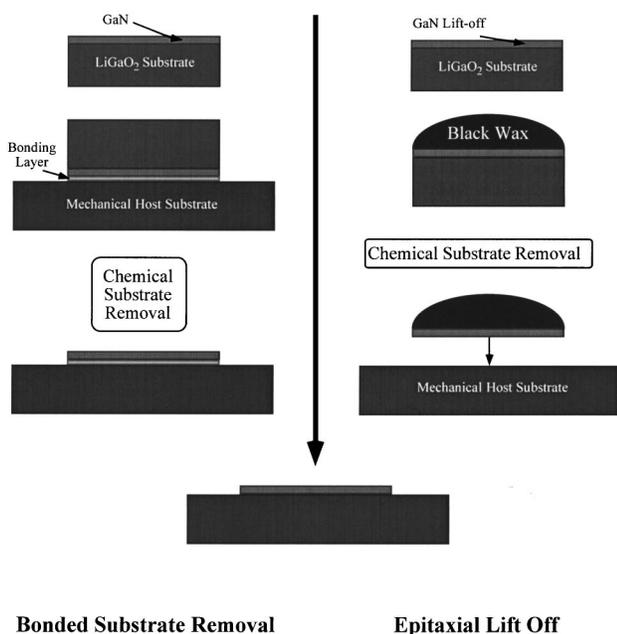


FIG. 1. Bonded substrate removal and epitaxial liftoff processes.

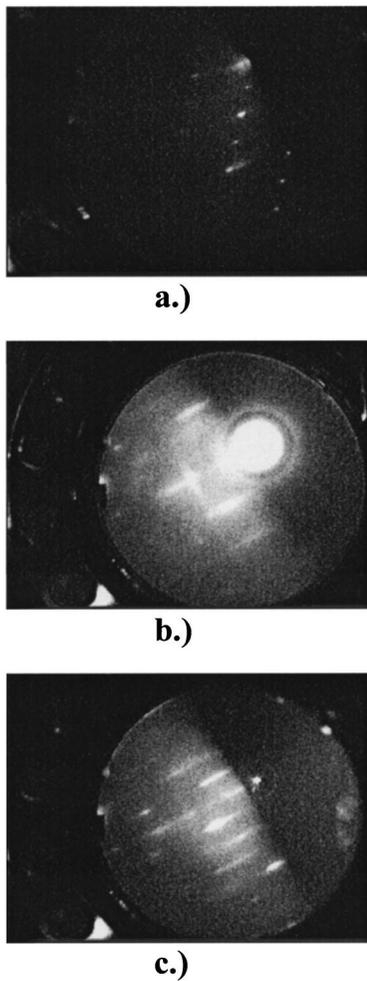


FIG. 2. RHEED images of (a) as received, (b) at 1000 °C and (c) at 600 °C LGO from vendor A.

1050 °C, 20 min vacuum anneal. Figure 4 shows the resulting spectra and atomic percent composition. While the absolute composition determined from XPS is not very accurate, the relative comparison is reliable. Thus, the relative comparison indicates that the surface becomes more lithium rich at the expense of both gallium and oxygen. This supports the supposition of Kryliouk *et al.*¹⁵ who found that GaN films grown at 850° and above had GaN/LGO interfaces observed by transmission electron microscopy (TEM) that were lithium rich. They suggested that a second phase, Li_5GaO_4 , formed at this interface. This suggested surface composition is within the 10% compositional accuracy of our XPS measurements. Understanding this surface phase may provide insight as to further improvements in the growth of GaN on LGO.

Contrary to our first result with material from vendor A, material from vendor B showed smooth but weak RHEED streaks of uniform width as received (see Fig. 5). This pattern degraded in intensity, as described by Johnson *et al.*^{11,12} when the sample temperature was elevated to 900 °C. We have also observed this material nonuniformity between vendors visibly, where vendor A's material has a large number

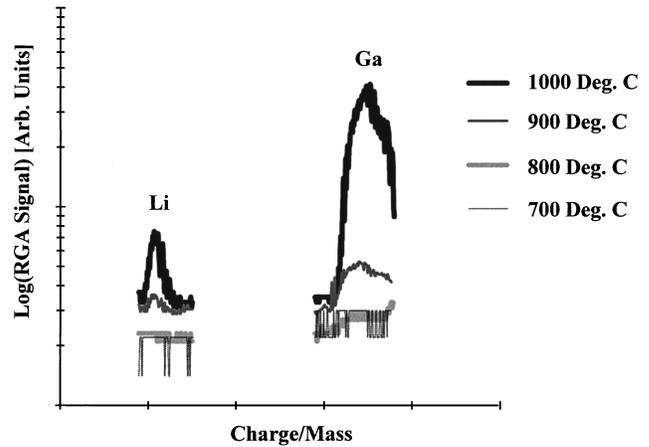


FIG. 3. Lithium and gallium residual gas analyzer signals at four temperatures. Note excessive loss of Ga and Li at 1000 °C and small loss of Ga and Li at 900 °C.

of antiphase or polarity domains.¹⁸ Vendor B's material is void of these antiphase domains. Further nonuniformity is witnessed by comparing x-ray rocking curve full width half maximums of representative material. Our growths have been more successful on vendor B's material. With the recent discovery of a new growth regime allowing single polarity LGO substrates,¹⁴ much of the nonuniformity in materials may soon disappear.

A. Determination and importance of growth face polarity

The problem of GaN films cracking and peeling from the LGO after growth has been well documented.¹⁴⁻¹⁶ Our experience showed that films could only be grown on one side of the material. Films grown on the "wrong" side peeled under vacuum or shortly after exposure to air. Figure 6(a) shows a well adherent GaN film, 0.28 μm thick grown on the side of the material where films do not peel. Note the extremely smooth surface morphology. Figure 6(b) shows a film of approximately the same thickness grown on the side of the material where films do not adhere. Note the cracks in the film are approximately parallel. Recently, Tazoh *et al.*¹⁴ offered confirmation and insight into the problem. They sup-

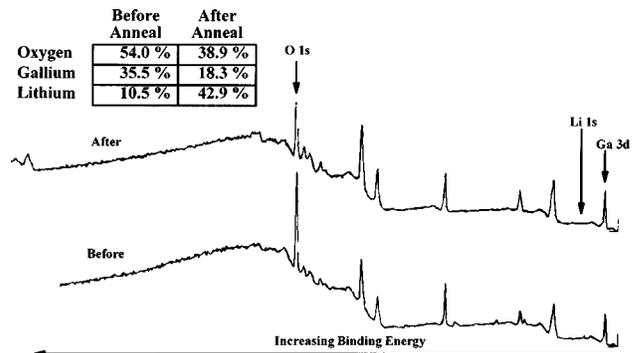


FIG. 4. XPS spectra and at % table for LGO surface before and after 1000 °C anneal. Note the surface becomes Li rich after the anneal.

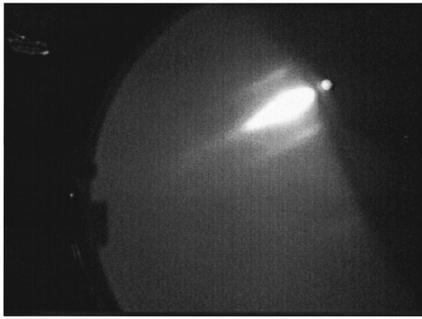


FIG. 5. Faint “2×” reconstruction pattern on as received vendor B LGO.

posed that films grown on the anion (oxygen) face peeled or cracked, while films grown on the cation side were smooth and adherent. The supposition used to determine the surface termination was that the highly acidic etchant used to distinguish the which face was which ($\text{H}_2\text{NO}_3:\text{H}_2\text{O},1:1$) would attack the oxygen terminated face more strongly, due to the presence of two excess electrons on the oxygen surface atoms. Thus, in their solution, the oxygen surface etched faster than the cation surface. We can confirm their conclusion on the surface termination from an opposite approach.

In our search for etches that would etch the LGO but not our materials used for bonding to the host material, we engineered an etchant that is basic ($\text{pH} > 7$) and maximizes the dissolution of GaO_2^- ions from the crystal. The remaining Li^+ ions are then easily dissolved as well. Details of this etchant will be reported elsewhere.¹⁹ Contrary to the approach of Tazoh *et al.*,¹⁴ this approach leads to a faster etch

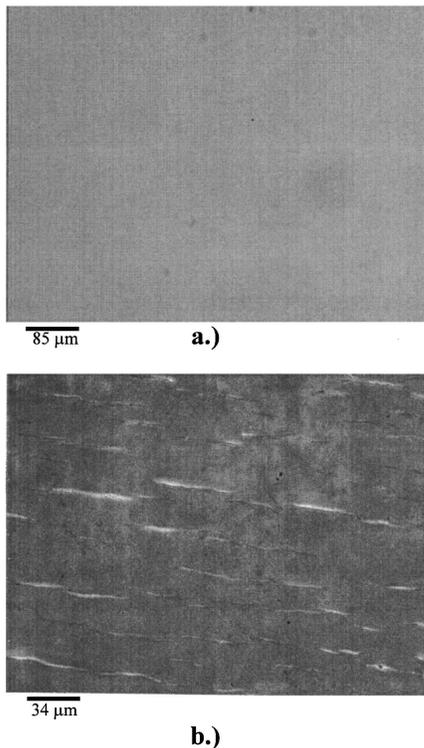


FIG. 6. (a) Adherent and smooth GaN grown on the correct face. (b) Peeling and cracking of GaN grown on incorrect face.

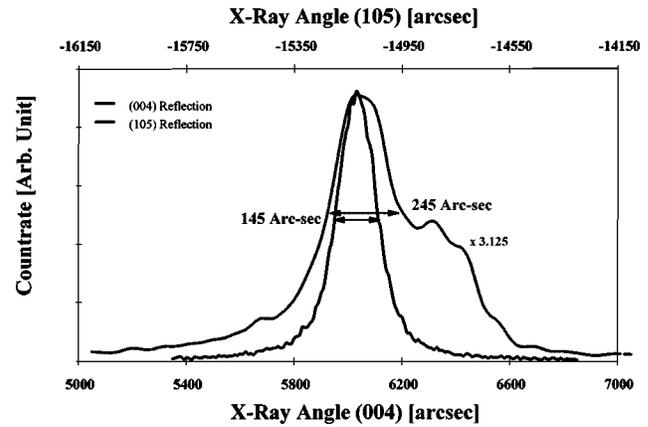


FIG. 7. Double-crystal x-ray rocking curve of $0.28 \mu\text{m}$ thick GaN on LGO showing in plane (004) and out of plane (105) reflections.

rate on the cation side compared to the anion side. We have confirmed that films grown on the side that etches faster in our “basic etchant” (corresponding to the slower etch rate in Tazoh *et al.*’s¹⁴ acidic etchant) adhere.

This etchant also decorates dislocations in a unique manner. The etch pits appear to be hexagons, elongated in one direction. This direction of elongation is constant for all pits in a substrate. This indicates the etch is highly anisotropic and may be used to study crystalline defect orientation in LGO. We have determined etch pit densities of the above-described type of $\sim 400\text{--}600/\text{cm}^2$ on vendor B’s material. Vendor A’s material shows etch pits with slightly asymmetrical elongations that may be a result of defects intersecting the surface at angles. The density on vendor A’s material is $\sim 200\text{--}400/\text{cm}^2$.

B. Results of growths of GaN on LGO

We have grown several GaN on LGO films, varying the growth temperature from 600 to 900° . Films grown on the correct face show smooth morphology and excellent x-ray rocking curves. Figure 6(a) shows the extremely smooth surface of a $0.28 \mu\text{m}$ thick film. This morphology is considerably smoother than comparable thickness films grown on sapphire. The double-crystal x-ray rocking curve for this sample shown in Fig. 7 shows a FWHM of 145 arcsec for the 004 GaN reflection. (Figure 7 includes the $K\alpha 1$ and $K\alpha 2$ contributions which are separated by ~ 26 arcsec.) The LGO 004 substrate peak was found where expected, $\sim 3^\circ$ (2ω) away from the GaN peak further confirming the identity of the GaN peak. Normally films with this good x-ray FWHM require multimicron buffers to be grown. To our knowledge, this is the best x-ray FWHM for films grown this thin on any substrate by any technique. It is worth noting that Johnson *et al.*^{11,12} had 002 FWHM of 103 arcsec for a $1.5 \mu\text{m}$ thick GaN on LGO. This implies that thicker films should have even better crystal quality.

Figure 7 also shows an x-ray rocking curve for the 105 reflection, showing 245 arcsec FWHM. To our knowledge, this is the first report of the “out-of-plane” crystal quality of GaN grown on LGO. Clearly, the excellent crystal quality is not merely a result of columnar growth, which can result in

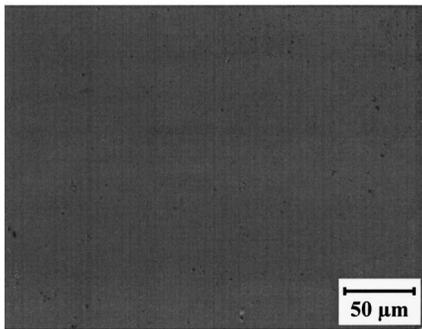


Fig. 8. First reported thin GaN film lifted off of LGO and bonded to GaAs.

low “in-plane” x-ray rocking curves, but is instead a result of the excellent lattice match of LGO to GaN. Since many devices require lateral current flow, excellent out-of-plane crystal quality is preferred.

C. Electrical properties

We have succeeded in reducing the residual electron concentration by two orders of magnitude compared to previously reported MOCVD grown films.¹⁶ To our knowledge, this is the only published report on the electrical parameters of GaN on LGO. We have achieved electron concentrations of $1.3 \times 10^{18} \text{ cm}^{-3}$ and Hall mobilities of $43 \text{ cm}^2/\text{V s}$. This compares to $\sim 1 \times 10^{20} \text{ cm}^{-3}$ and Hall mobilities of $\sim 10 \text{ cm}^2/\text{V s}$ for literature values.¹⁶ No attempt at optimization has yet been performed. While improved from previous efforts, much work is still needed to understand and reduce the impurity contamination we assume to result from the substrates.

D. Demonstration of thin film GaN substrate

Figure 8 shows the first thin GaN $\sim 8000 \text{ \AA}$ GaN film grown on LGO lifted off and bonded to a GaAs wafer. The smooth morphology of this sample indicates substantial promise for this technology. The size of this sample was approximately $1 \times 3 \text{ mm}$. The size was previously limited by the availability of high quality substrates and pinholes and scratch damage on GaN on LGO films. We are currently attempting to scale up to $1 \times 1 \text{ cm}$ material. Since regrowth requires that films be large enough to be held in place with mechanical clips, this size should allow regrowth on such substrates. Additionally, as presented here, our development of smooth, pinhole free, high crystal quality GaN films should expedite the further development of such substrates.

IV. CONCLUSIONS

We have demonstrated high quality growth of GaN on LGO. X-ray rocking curves of 145 arcsec are shown on a

0.28 \mu m thick film. For the first time, we present data on the out-of-plane crystalline quality of GaN/LGO material and demonstrate the first thin GaN grown on LGO and bonded to GaAs. Likewise, we have presented two orders of magnitude improvement in residual doping concentration and factors of 4 improvement in electron mobility. We have shown substantial vendor to vendor and intravendor LGO material quality variations and have quantified the desorption of Ga and Li from the surface of LGO at typical growth temperatures using *in situ* desorption mass spectroscopy and XPS. We have demonstrated that growth of GaN on LGO has some advantages, but much work is still needed to improve substrate and overlayer quality.

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¹T. D. Moustakas, *Mater. Res. Soc. Symp. Proc.* **395**, 111 (1996).

²M. Marezio, *Acta Crystallogr.* **18**, 481 (1965).

³B. A. Auld, *Acoustic Fields and Waves in Solids*, 2nd ed. (Krieger, Malabar, FL, 1990).

⁴H. Neumann, E. Pirl, and G. Kuhn, *J. Mater. Sci. Lett.* **6**, 495 (1987).

⁵S. Nanamatsu, K. Doi, and M. Takahashi, *Jpn. J. Appl. Phys.* **11**, 816 (1972).

⁶H. Neumann, *Cryst. Res. Technol.* **25**, 667 (1990).

⁷H. Neumann, G. Kuhn, H. Neels, E. Nowak, and E. Pirl, *Cryst. Res. Technol.* **22**, 413 (1987).

⁸R. G. Wilson, B. L. H. Chai, S. J. Pearton, C. R. Abernathy, F. Ren, and J. M. Zavada, *Appl. Phys. Lett.* **69**, 3848 (1996).

⁹L. W. Lee, S. J. Pearton, C. R. Abernathy, J. M. Zavada, and B. L. H. Chai, *J. Electrochem. Soc.* **143**, L169 (1996).

¹⁰J. F. H. Nicholls, H. Gallagher, B. Henderson, C. Trager-Cowan, P. G. Middleton, K. P. O'Donnell, T. S. Cheng, C. T. Foxon, and B. H. T. Chai, *Mater. Res. Symp. Proc.* **395**, 535 (1996).

¹¹M. A. L. Johnson, W. C. Hughes, W. H. Rowland, Jr., J. W. Cook, Jr., J. F. Schetzina, M. Leonard, H. S. Kong, J. A. Edmund, and J. Zavada, *J. Cryst. Growth* **175/176**, 72 (1997).

¹²M. A. L. Johnson, Shizuo Fujita, W. H. Rowland, Jr., K. A. Bowers, W. C. Hughes, Y. W. He, N. A. El Masry, J. W. Cook, Jr., J. F. Schetzina, J. Ren, and J. A. Edmund, *Solid-State Electron.* **41**, 213 (1997).

¹³A. V. Andrianov, D. E. Lacklison, J. W. Orton, T. S. Cheng, C. T. Foxon, K. P. O'Donnell, and J. F. H. Nichols, *Semicond. Sci. Technol.* **12**, 59 (1997).

¹⁴Y. Tazoh, T. Ishii, and S. Miyazawa, *Jpn. J. Appl. Phys., Part 2* **36**, L746 (1997).

¹⁵O. M. Kryliouk, T. W. Dann, T. J. Anderson, H. P. Maruska, L. D. Zhu, J. T. Daly, M. Lin, P. Norris, H. T. Chai, D. W. Kisker, J. H. Li, and K. S. Jones, *Mater. Res. Symp. Proc.* **449**, 123 (1997).

¹⁶P. Kung, A. Saxler, X. Zhang, D. Walker, R. Lavado, and M. Razeghi, *Appl. Phys. Lett.* **69**, 2116 (1996).

¹⁷C. Carter-Coman, R. Bicknell-Tassius, A. S. Brown, and N. M. Jokerst, *Appl. Phys. Lett.* **70**, 1754 (1997).

¹⁸T. Ishii, Y. Tazoh, and S. Miyazawa, *Jpn. J. Appl. Phys., Part 2* **36**, L139 (1997).

¹⁹T. Kroppenwicki, W. A. Doolittle, C. Carter-Coman, S. Kang, P. Kohl, and A. S. Brown, *J. Electrochem. Soc. Lett.* (to be published).