

# INDUCTIVELY COUPLED PLASMA ETCHING OF III-NITRIDES IN Cl<sub>2</sub>/Xe, Cl<sub>2</sub>/Ar AND Cl<sub>2</sub>/He

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## **Abstract**

The role of additive noble gases He, Ar and Xe to Cl<sub>2</sub>-based Inductively Coupled Plasmas for etching of GaN, AlN and InN were examined. The etch rates were a strong function of chlorine concentration, rf chuck power and ICP source power. The highest etch rates for InN were obtained with Cl<sub>2</sub>/Xe, while the highest rates for AlN and GaN were obtained with Cl<sub>2</sub>/He. Efficient breaking of the III-nitrogen bond is crucial for attaining high etch rates. The InN etching was dominated by physical sputtering, in contrast to GaN and AlN. In the latter cases, the etch rates were limited by initial breaking of the III-nitrogen bond. Maximum selectivities of ~ 80 for InN to GaN and InN to AlN were obtained.

## **Introduction**

There have been a number of studies of high density plasma etching techniques for patterning of III-nitrides for photonic device applications such as laser diodes and light-emitting diodes (LEDs) [1-12]. Essentially all of the LEDs and a majority of the lasers are ridge wave guide structures in which the mesas are formed by dry etching [13]. Most of the previous etching studies have been focused on obtaining relatively the large etch depths (2-4μm) typical of ridge or facet heights in LEDs or laser diodes, where the final surface morphology on the field is less important. There is increasing interest in the development of GaN-based high power/high temperature electronics for power switching and transmission applications [14-18]. In these devices, the etch depth is much shallower, but smooth morphologies and high selectivities for InN over the other nitrides are required because layers based on InN will probably be used to obtain low ohmic contact resistance.

Shul et al. [1,10] first reported Inductively Coupled Plasma (ICP) etching of GaN, AlN, InN, InAlN and InGaN at low dc biases ( $\leq -100V$ ) with Cl<sub>2</sub>, CH<sub>4</sub>/H<sub>2</sub>, Cl<sub>2</sub>/Ar, Cl<sub>2</sub>/N<sub>2</sub> and Cl<sub>2</sub>/H<sub>2</sub> plasma chemistries. They controlled the etch rates in the range of 500-1500Å/min for electronic device structures, and obtained maximum etch selectivities of ~ 6 at higher ICP source powers (850W) for InN over the other nitrides.

In this paper, the influence of the inert gas species (He, Ar and Xe) in chlorine-based ICP etching of GaN, AlN and InN was studied for various plasma parameters. The results are explained in a systematic way based on calculated ion fluxes at the sheath edge, Bohm velocity and sheath thickness. The ICP discharges are well suited for achieving controllable etch rates (500–1500Å/min) and high selectivities (up to 80) for InN over AlN and GaN, using simple Cl<sub>2</sub>/neutral gas chemistries.

## **Experimental**

The AlN and InN samples were grown by Metal Organic Molecular Beam Epitaxy (MOMBE) on Al<sub>2</sub>O<sub>3</sub> substrates at 800°C and 575°C, respectively in an Intevac Gen II system [19,20]. The GaN was grown at 1040°C on Al<sub>2</sub>O<sub>3</sub> substrates by Metal Organic Chemical Vapor Deposition (MOCVD). Total layer thicknesses were ~ 1µm for the AlN and InN, and 2-3µm for the GaN.

The samples were patterned with Apiezon wax and etched in a Plasma-Therm ICP 790 system. The temperature of the back-side cooled chuck was held at 23°C. The rf chuck power was varied between 50 and 350W, and ICP source power between 300 and 1000 W. The process pressure was held constant at 5mTorr, while the total flow rate of Cl<sub>2</sub>-additive gas was 15 standard cubic centimeter per min (sccm). Etch rates were calculated from stylus profilometry measurements of the etched samples after the removal of the mask material. The error of these measurements is approximately ±5%. The selectivity was calculated for InN over AlN and GaN.

## **Results and discussion**

We first examined the effect of discharge composition for the three chemistries. Figure 1 shows the effect of Cl<sub>2</sub> concentration on etch rates of InN, AlN and GaN in Cl<sub>2</sub>/He, Cl<sub>2</sub>/Ar and Cl<sub>2</sub>/Xe discharges at 5mTorr, 750W source power and 250W rf chuck power. It is seen that the effects of noble gas additives are strongly dependent on the particular III-nitride material: the highest etch rates for InN were obtained with Cl<sub>2</sub>/Xe (Figure 1, top) and for AlN (center) and GaN (bottom) with Cl<sub>2</sub>/He. It is also seen that etch rates of AlN and GaN were much lower in chlorine-based plasmas compared to InN. The high rates for the latter are similar to the previously reported results observed for InP where efficient ion-assisted desorption of the InCl<sub>x</sub> occurs under ICP conditions [21]. These results indicate that etch mechanism is dependent on the material bond strengths and on the particular plasma chemistry employed, and optimization of the ICP etching process is crucial for obtaining the best results.

The highest etch rates for AlN and GaN at these low bias conditions were obtained with Cl<sub>2</sub>/He discharges. Ion fluxes and Bohm velocities at the sheath edge at 66.7% Cl<sub>2</sub> are, respectively, 1.59x10<sup>16</sup>cm<sup>-2</sup>s<sup>-1</sup> (Cl<sub>2</sub>/Ar), 1.84x10<sup>16</sup>cm<sup>-2</sup>s<sup>-1</sup> (Cl<sub>2</sub>/He) and 1.92x10<sup>16</sup>cm<sup>-2</sup>s<sup>-1</sup> (Cl<sub>2</sub>/Xe), and 1,740m/s (Cl<sub>2</sub>/Xe), 2,350m/s (Cl<sub>2</sub>/Ar) and 2,660m/s (Cl<sub>2</sub>/He). In other words, the Cl<sub>2</sub>/Xe discharges showed the highest ion flux at the sheath edge, while the ions created by Cl<sub>2</sub>/He discharge have the greatest Bohm velocity. It is interesting to see that the ion fluxes and sheath edge velocities are in the same order as we expected based on ionization energy [Ar (15.76eV) > He (13.6eV) > Xe (12.13eV)] [22] and atomic mass. The predicted ion fluxes and Bohm velocities explain why the etch rates with Cl<sub>2</sub>/Ar are the lowest, while the highest are obtained with Cl<sub>2</sub>/He. Ions created in the Cl<sub>2</sub>/He discharge, having the fastest velocity, arrive at the surface with higher velocities, helping activate the nitride surface for the coincident reactive chlorine neutral flux. They also provide the impetus for directional etching. In the ICP system, the sheath layer near the sample position is determined mainly by the capacitively coupled power because the sheath thickness due to the inductively coupled power is much smaller. The values of sheath thickness predicted at 66.7% Cl<sub>2</sub>, 750W ICP and 250W rf powers are 0.62cm in Cl<sub>2</sub>/He, and 0.44cm in Cl<sub>2</sub>/Xe discharges. Although the heavier Xe ions are accelerated within the sheath region, the sheath thickness is not long enough for them to reach the energy carried by the fast-moving ions created by the Cl<sub>2</sub>/He discharge. This partially explains the difference in etch rates between the different chemistries.

The effect of rf chuck power on the etch rates is shown in Figure 2. The etch rates of InN with Cl<sub>2</sub>/Xe and Cl<sub>2</sub>/He discharges increased up to 250 W and decreased at higher power (Figure 2, top), but increased monotonically with Cl<sub>2</sub>/Ar as the rf power increased. The increase in etch

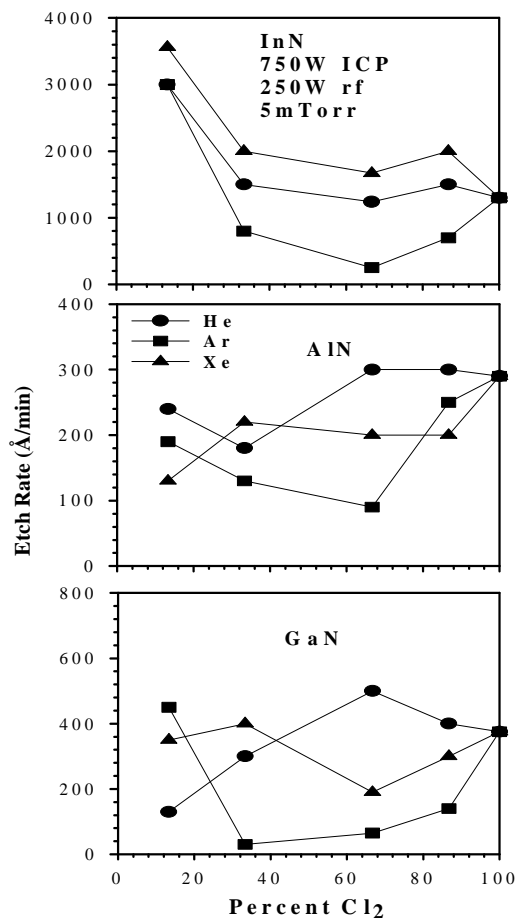


Figure 1. Effect of chlorine concentration on etch rates of InN (top), AlN (center) and GaN (bottom) with  $\text{Cl}_2/\text{He}$ ,  $\text{Cl}_2/\text{Ar}$  and  $\text{Cl}_2/\text{Xe}$  plasma chemistries (750W source power, 250W rf chuck power, 5mTorr).

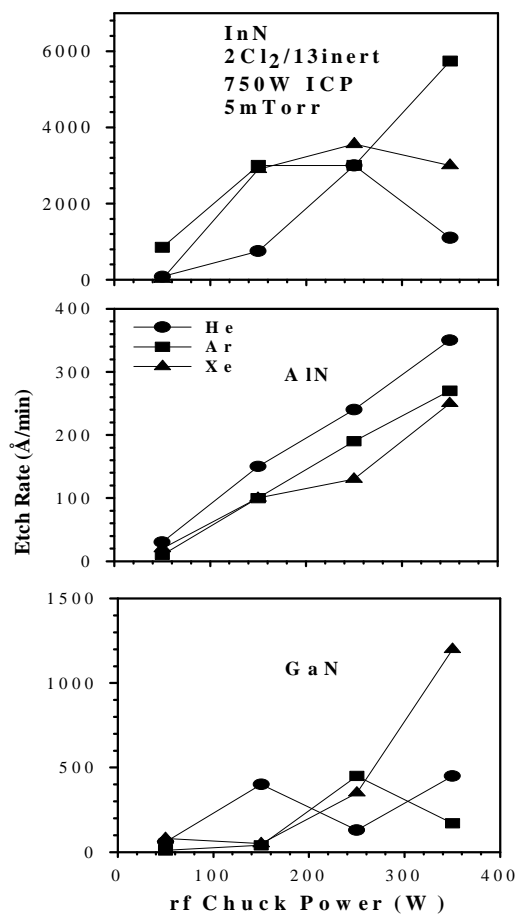


Figure 2. Effect of rf chuck power on etch rates of InN (top), AlN (center) and GaN (bottom) with  $2\text{Cl}_2/13\text{He}$ ,  $2\text{Cl}_2/13\text{Ar}$  and  $2\text{Cl}_2/13\text{Xe}$  plasma chemistries (750W source power, 5mTorr).

rate can be attributed to enhanced sputter desorption of etch products as well as dominant physical sputtering of the InN surface. The etch rates of AlN increased monotonically as the rf power increased with all  $\text{Cl}_2$ -based discharges (Figure 2, center). However, GaN etching in  $\text{Cl}_2/\text{He}$  and  $\text{Cl}_2/\text{Ar}$  showed relatively constant etch rates with some fluctuations, and increased rapidly in the  $\text{Cl}_2/\text{Xe}$  chemistry as the rf power increased (Figure 2, bottom). Again, He and Xe additives resulted in overall better etch rates than Ar.

The monotonic increase in AlN etch is mainly due to the higher bond strength of AlN (11.52eV) compared to InN and GaN, indicating that AlN etch rate is limited by breaking the Al-N bond. In order to initiate etching, breaking the group III-nitrogen bond is crucial, since this must precede the formation of etch products. Bond energies are in the order of InN (7.72eV) < GaN (8.92eV) < AlN (11.52eV) [22]. The etch rate is also related to volatilities of the etch products. In chlorine-based plasmas, the boiling points are  $\text{AlCl}_3$  (183°C) <  $\text{GaCl}_3$  (201°C) <  $\text{InCl}_3$  (600°C) [22]. In addition to the experimental results, from the view points of bond strength and boiling point, two conclusions may be drawn: 1) the etch rates of InN are dominated by physical sputtering, due to the relatively low bond strength, but possibly limited by desorption of etch products due to the lowest volatility of  $\text{InCl}_3$  and 2) lower etch rates of GaN and AlN are limited by initial breaking of the III-nitrogen bond. The dc bias increased monotonically with increasing rf chuck power from 50 to 350W, but the ion flux at the sheath edge increased

slightly. Ion fluxes in Cl<sub>2</sub>/He and Cl<sub>2</sub>/Xe discharges were  $\sim 1.9 \times 10^{16} \text{ cm}^2 \cdot \text{s}^{-1}$  at 750W source power, while that with Cl<sub>2</sub>/Ar was lower,  $\sim 1.6 \times 10^{16} \text{ cm}^2 \cdot \text{s}^{-1}$ .

The effect of the rf power on ion fluxes at the sheath edge, respectively, generated by capacitive and inductively coupled discharges with chlorine-based chemistries was calculated from a simple model (Figure 3). The ion flux generated by the capacitive discharge increases substantially with increasing rf power, while that in the counterpart by the inductively coupled discharge maintains an essentially constant value. The rf power increases the ion bombarding energy, resulting in an increase in etch rate with increasing the chuck power. However, the predicted ion flux (or bulk ion density) showed that the contribution of the capacitive discharge to total ion flux in the ICP etching process is less than 2%, indicating that the main role of the chuck power is to increase the ion bombarding energy.

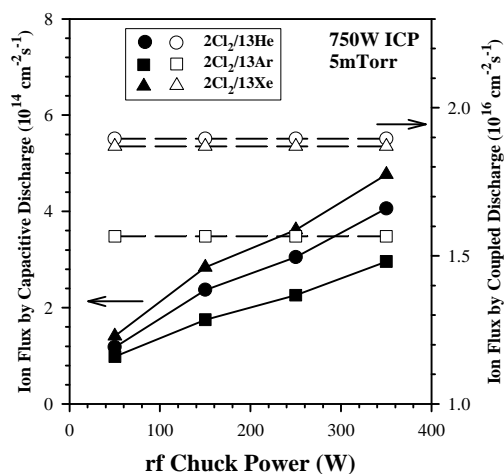


Figure 3. Effect of rf chuck power on the ion fluxes generated by capacitive discharge and inductively coupled discharge with 2Cl<sub>2</sub>/13He, 2Cl<sub>2</sub>/13Ar and 2Cl<sub>2</sub>/13Xe plasma chemistries (750W source power, 5mTorr).

The effect of ICP source power on etch rate is shown in Figure 4. The influence of additive noble gases was dependent on III-nitride materials: the best etch rate for InN was obtained with Cl<sub>2</sub>/Xe (Figure 4, top), while the overall highest rates for the other materials were achieved with Cl<sub>2</sub>/He. InN showed higher etch rates again than AlN and GaN. The etch rates of InN with Cl<sub>2</sub>/He and Cl<sub>2</sub>/Xe discharges increased up to 750W ICP power, and decreased at > 750W. However, the Cl<sub>2</sub>/Ar discharge showed the highest etch rate of InN at 1000 W. AlN etch rate increased slightly with the source power, but resulted in low etch rates. GaN etch rates with Cl<sub>2</sub>/He and Cl<sub>2</sub>/Ar chemistries showed maxima as the source power increased, but relatively constant etch rates with Cl<sub>2</sub>/Xe. The increase in etch rate with increasing source power is due to the higher concentration of reactive species in the plasma, suggesting a reactant-limited regime, and to higher ion flux to the substrate surface. Increased numbers of ions also make the surface more active with respect to the reactive neutrals. The decrease in etch rate with further increase of the ICP power is attributed either to lower ion energies or ion-assisted desorption of the reactive species at the substrate surface prior to etch reactions. The dc bias of the sample chuck was decreased as the ICP power increased mainly due to the increased ion density.

In order to reduce the currently high contact resistance in GaN-based heterostructure field transistors [23], and eventually heterojunction bipolar transistors, it is expected that InN-based contact layers will be necessary [24-26], in analogy to InGaAs on GaAs. In such a case, the ability to selectively etch InN relative to the other nitrides will be crucial. Figures 5 shows some selectivity data as functions of rf power in chlorine-noble discharges. As the rf power increased, the Cl<sub>2</sub>/Ar discharge showed overall the best selectivity of InN over GaN, but the Cl<sub>2</sub>/He chemistry yielded the lowest selectivities for InN over AlN as well as over GaN. The selectivity data obtained in this work showed overall higher selectivity characteristics for InN over GaN and AlN in Cl<sub>2</sub>/He, Cl<sub>2</sub>/Ar and Cl<sub>2</sub>/Xe than that previously reported [1,12].

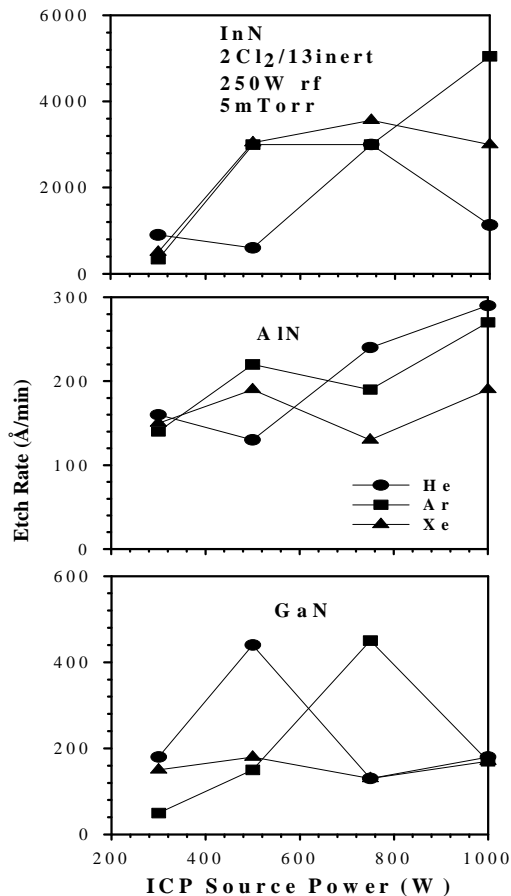


Figure 4. Effect of ICP source power on etch rates of InN (top), AlN (center) and GaN (bottom) with  $2\text{Cl}_2/13\text{He}$ ,  $2\text{Cl}_2/13\text{Ar}$  and  $2\text{Cl}_2/13\text{Xe}$  plasma chemistries (250W rf chuck power, 5mTorr).

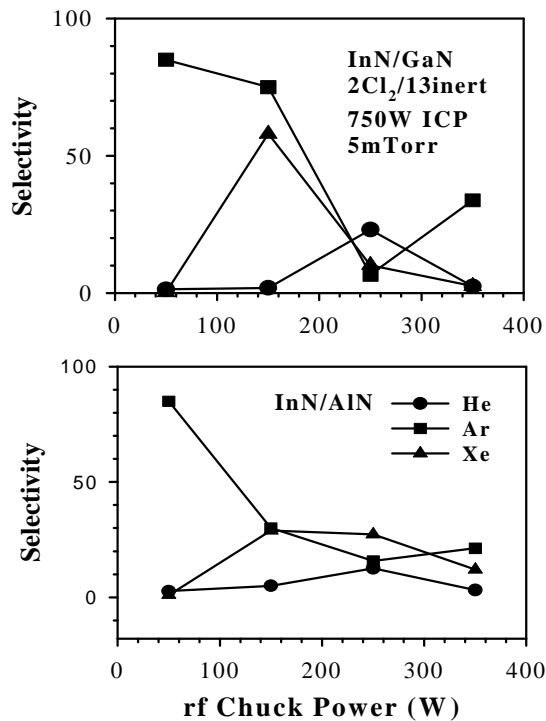


Figure 5. Effect of rf chuck power on the selectivity for InN over GaN and AlN (750W source power, 5mTorr,  $2\text{Cl}_2/13$  noble gas).

## Summary and conclusions

The effect of the noble gas additive to  $\text{Cl}_2$  ICP discharges was examined for etching of GaN, AlN and InN. The etch rates were greatly affected by chlorine concentration, rf chuck power and ICP source power. The influence of the additive gases was much dependent on the particular III-nitride material, with InN showing higher etch rates than the other nitrides. Efficient breaking of the III-nitrogen bond is crucial for achieving high etch rates. The InN etching was dominated by physical sputtering because of the low volatility of  $\text{InCl}_3$ , while GaN and AlN etching was limited by initial breaking of the III-nitrogen bond. The contribution of the capacitive discharge to total ion flux in the ICP etching process is less than 2%, indicating that the main role of the chuck power is to increase the ion bombarding energy. The etch rates increased with increasing ICP source power due mainly to increased ion flux. Selectivities up to  $\sim 80$  for InN over GaN and AlN were achieved.

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## **References**

1. R. J. Shul, G. B. McClellan, S. A. Casalnuova, D. J. Rieger, S. J. Pearton, C. Constantine, C. Barrat, R. F. Karliceck, Jr., C. Tran, and M. Schurman, *Appl. Phys. Lett.*, **69** 1119 (1996).
2. R. J. Shul, in *GaN and Related Materials*, ed. S. J. Pearton (Gordon and Breach, N. Y., 1997).
3. H. P. Gillis, D. A. Choutov, and K. P. Martin, *JOM*, **48** 50 (1996).
4. I. Adesida, A. Mahajan, E. Andideh, M. A. Khan, D. T. Olsen, and J. N. Kuznia, *Appl. Phys. Lett.*, **63** 2777 (1993).
5. M. E. Lin, Z. F. Fan, Z. Ma, L. H. Allen, and H. Morkoc, *Appl. Phys. Lett.*, **64** 887 (1994).
6. H. Lee, D. B. Oberman, and J. S. Harris, Jr., *Appl. Phys. Lett.*, **67** 1754 (1995).
7. W. Pletschen, R. Niegurch, and K. H. Bachem, *Proc. Symp. Wide Bandgap Semiconductors and Devices*, **Vol. 95-21** (Electrochemical Society, Pennington, N. J., 1995), p.241.
8. S. J. Pearton, C. R. Abernathy, and F. Ren, *Appl. Phys. Lett.*, **64** 2294 (1994).
9. L. Zhang, J. Ramer, J. Brown, K. Zhang, L.F. Lester, and S. D. Hersee, *Appl. Phys. Lett.*, **68** 367 (1996).
10. R. J. Shul, R. D. Briggs, S. J. Pearton, C. B. Vartuli, C. R. Abernathy, J. W. Lee, C. Constantine, and C. Barratt, *Mat. Res. Soc. Symp. Proc.*, **449** 969 (1997).
11. H. Cho, C. B. Vartuli, S. M. Donovan, C. R. Abernathy, S. J. Pearton, R. J. Shul, and C. Constantine, *J. Vac. Sci. Technol. A* **16** 1631 (1998).
12. H. Cho, C. B. Vartuli, S. M. Donovan, K. D. Mackenzie, C. R. Abernathy, S. J. Pearton, R. J. Shul, and C. Constantine, *J. Electron. Mat.*, **27** 166 (1998).
13. S. Nakamura, in *GaN and Related Materials*, ed. S. J. Pearton (Gordon and Breach, N. Y. 1997).
14. O. Aktas, Z. Fan, S. N. Mohammad, A. Botcharev, and H. Morkoc, *Appl. Phys. Lett.*, **69** 25 (1996).
15. M. A. Khan, J. N. Kuznia, M. S. Shur, C. Eppens, J. Burm, and W. Schaff, *Appl. Phys. Lett.*, **66** 1083 (1995).
16. Y. F. Wu, B. P. Keller, S. Keller, D. Kapolnek, S. D. Den Baars, and U. K. Mishra, *IEEE Electron. Dev. Lett.*, **17** 455 (1996).
17. M. A. Khan, Q. Chen, M. S. Shur, B. T. McDermott, J. A. Higgins, J. Burm, W. Schaff, and L. F. Eastman, *Electron. Lett.*, **32** 357 (1996).
18. Y. T. Wu, S. Keller, P. Kozodoy, B. P. Keller, P. Parikh, D. Kapolnek, S. P. Denbaars, and V. K. Mishra, *IEEE Electron. Dev. Lett.*, **18** 290 (1997).
19. C. R. Abernathy, *J. Vac. Sci. Technol. A* **11** 869 (1993).
20. C. R. Abernathy, *Mat. Sci. Eng. Rep.*, **R14** 203 (1995).
21. J. W. Lee, J. Hong, and S. J. Pearton, *Appl. Phys. Lett.*, **68** 847 (1996).
22. *CRC Handbook of Chemistry and Physics*, 70<sup>th</sup> Ed., eds. R. C. Weast, D. R. Lide, M. J. Astle, and W. H. Beyer (CRC Press Inc., Boca Raron, FL, 1989).
23. J. Burm, K. Chu, W. J. Schaff, L. F. Eastman, M. A. Khan, Q. Chen, J. W. Yang, and M. S. Shur, *IEEE Electron. Dev. Lett.*, **18** 141 (1997).
24. S. M. Donovan, K. D. MacKenzie, C. R. Abernathy, S. J. Pearton, F. Ren, K. Jones, and M. Cole, *Appl. Phys. Lett.*, **70** 2592 (1997).
25. F. Ren, C. R. Abernathy, S. J. Pearton, and P. W. Wisk, *Appl. Phys. Lett.*, **64** 1508 (1994).
26. F. Ren, R. J. Shul, C. R. Abernathy, S. N. G. Chu, J. R. Lothian, and S. J. Pearton, *Appl. Phys. Lett.*, **66** 1503 (1995).