GaN ETCHING IN BCl$_3$/Cl$_2$ PLASMAS

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ABSTRACT

GaN etching can be affected by a wide variety of parameters including plasma chemistry and plasma density. Chlorine-based plasmas have been the most widely used plasma chemistries to etch GaN due to the high volatility of the GaCl$_3$ and NCl etch products. The source of Cl and the addition of secondary gases can dramatically influence the etch characteristics primarily due to their effect on the concentration of reactive Cl generated in the plasma. In addition, high-density plasma etch systems have yielded high quality etching of GaN due to plasma densities which are 2 to 4 orders of magnitude higher than reactive ion etch (RIE) plasma systems. The high plasma densities enhance the bond breaking efficiency of the GaN, the formation of volatile etch products, and the sputter desorption of the etch products from the surface. In this study, we report GaN etch results for a high-density inductively coupled plasma (ICP) as a function of BCl$_3$:Cl$_2$ flow ratio, dc-bias, chamber pressure, and ICP source power. GaN etch rates ranging from ~100 Å/min to > 8000 Å/min were obtained with smooth etch morphology and anisotropic profiles.

INTRODUCTION

As III-V nitride device structures become more complicated and design rules shrink, well-controlled etch processes are necessary. To date most of the plasma etch development has been directed toward mesa structures for photonic devices where high-rate, anisotropic, equi-rate etching is required. Recent interest in high power, high temperature electronic devices has added to these etch requirements due to shallower etch depths and smaller critical dimensions than those required for photonic devices. Well-controlled rates, smooth etch morphology, low plasma-induced-damage, and selective etching of one material over another must also be achieved for such devices. Etch requirements are further complicated by the fact that the III-V nitrides etch at much slower rates than conventional III-V compound semiconductors despite similar volatilities of the etch products. Based on the strong bond energies of the III-V nitrides, the rate limiting step of the etch process may be the initial breaking of the group-III-N bonds.[1] GaN has a bond energy of 8.92 eV/atom, InN 7.72 eV/atom, and AlN 11.52 eV/atom as compared to GaAs which has a bond energy of 6.52 eV/atom.[2]

High-density plasma etch systems, including inductively coupled plasmas (ICP), have shown high quality patterning results for group-III nitrides due to plasma densities which are 2 to 4 orders of magnitude higher than reactive ion etch (RIE) systems.[3-12] The high plasma flux improves the efficiency of breaking the group-III-nitrogen bond, the formation of volatile etch products, and the sputter desorption efficiency of etch products from the surface. III-V nitride etch characteristics are also strongly influenced by plasma chemistry.[12] For example, the etch rates for Ga-containing compound semiconductors etched in halogen-based plasmas are often limited by the volatility of the group-III halogen etch product. Therefore, chlorine-based plasmas have been the most widely used plasma chemistry to etch Ga-containing compound semiconductors. For GaN, etch rates are typically fast with anisotropic, smooth etch profiles in Cl$_2$-, BCl$_3$-, SiCl$_4$-, and ICl-based plasmas.[1, 12] The source of Cl and the addition of secondary gases can dramatically influence GaN etch characteristics primarily due to their effect on the concentration of reactive Cl generated in the plasma. The dissociation efficiency and fragmentation pattern of the source gas as well as the recombination rates of reactive Cl formed in the plasma are critical to the etch process.

The combination of BCl$_3$ and Cl$_2$ has been successfully demonstrated for GaAs through-wafer via holes using reactive ion etch (RIE).[13] The addition of BCl$_3$ to Cl$_2$ plasmas often results in highly anisotropic etch profiles due to efficient sputter desorption of etch products by high mass

species formed in the plasma. However, etch rates are often slower due to lower concentrations of reactive Cl. In this study, we report GaN etch results for high-density ICP as a function of BCl_3:Cl_2 flow ratio. Etch characteristics will also be reported as a function of pressure, ICP source power, and dc-bias.

EXPERIMENT

The GaN films etched in this study were grown by metal organic chemical vapor deposition (MOCVD). The ICP reactor was a load-locked Plasma-Therm SLR 770 which used a 2 MHz, 3 turn coil ICP source. All samples were mounted using a thermally conductive paste on an anodized Al carrier that was clamped to the cathode and cooled with He gas. The ion energy or dc-bias was defined by superimposing an rf-bias (13.56 MHz) on the sample. Samples were patterned with AZ-4330 photoresist. Etch rates were calculated from the depth of etched features measured with an Alpha-Step stylus profilometer after the photoresist was removed. Depth measurements were taken at a minimum of 3 positions on samples which were ~1 cm^2. GaN samples were exposed to the plasma for 1 to 3 minutes. Surface morphology, anisotropy, and sidewall undercutting were evaluated with a scanning electron microscope (SEM). The root-mean-square (rms) surface roughness was quantified using a Digital Instruments Dimension 3000 atomic force microscope (AFM) system operating in tapping mode with Si tips. Optical emission spectra (OES) were obtained for most of the plasma conditions reported in this paper. Due to limited optical access immediately above the sample surface, spectra were obtained through a window mounted on the top of the ICP plasma generation region. Consequently, the conclusions drawn from the OES results may be only qualitatively applicable to the conditions at the sample surface, especially at the higher pressures of this study, where mean-free paths were sufficiently short to enable several collisions between the plasma generation region and the sample surface. Even at the lowest pressure (1 mTorr), source-sample separation exceeded the mean-free path. Atomic emission intensities from excited Cl species were normalized by the intensity of the Ar emission at 750.4 nm to correct for variations in excitation efficiency under different plasma conditions.

RESULTS AND DISCUSSIONS

In Figure 1, GaN etch rates and rms roughness are plotted as a function of %Cl_2 in an ICP BCl_3/Cl_2/Ar plasma. The plasma conditions were 40 sccm of BCl_3 + Cl_2, 5 sccm of Ar, 2 mTorr pressure, and -150 V dc bias. GaN etch rates increased (with the exception of 60% Cl_2) up to a maximum of ~ 5840 Å/min at 80% Cl_2 due to increasing concentrations of reactive Cl. This was confirmed using OES where the maximum Cl^0 concentration also occurred at 80% Cl_2. Strong emission from excited neutral Cl^0 atoms was obtained at both 725.7 and 741.4 nm. Only weak emissions from excited Cl$^+$ species were observed, leading to the conclusion that the dominant reactant in these plasmas was the neutral Cl atom rather than the Cl$^+$ ion. Etch rates fell off faster than Cl^0 emission intensity under low %Cl_2 conditions, which may indicate greater Cl loss through recombination with BCl_3-derived species below the plasma source. Slower GaN etch rates observed at 100% Cl_2, were due to lower Cl^0 emission and less efficient sputter desorption of the etch products from the surface. The unusually high etch rate at 50% Cl_2 was not understood and did not correlate to an increase in the Cl^0 emission intensity.

AFM was used to quantify the etched surface morphology as rms roughness for many of the plasma conditions reported in this paper. Rough etch morphology often indicates a non-stoichiometric surface due to preferential removal of either the group-III or group-V species. The rms roughness for the as-grown GaN was 1.02 nm. The surface morphology remained relatively smooth (< 8 nm) throughout this study implying stoichiometric etching of the GaN. The rms roughness obtained as a function of %Cl_2 concentration (Figure 1) was highest at 20% Cl_2 and became smoother as the %Cl_2 and reactive Cl concentration increased.

Lee and co-workers also studied GaN etch rates as a function of Cl concentration in an ICP BCl_3/Cl_2 plasma.[14] Using OES and a Langmuir probe, ion current and Cl radical densities were

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measured. As BCl$_3$ was add to the Cl$_2$ plasma, the ion current density decreased and the Cl radical density decreased except for the addition of 10% BCl$_3$ where the GaN etch rate was fastest.
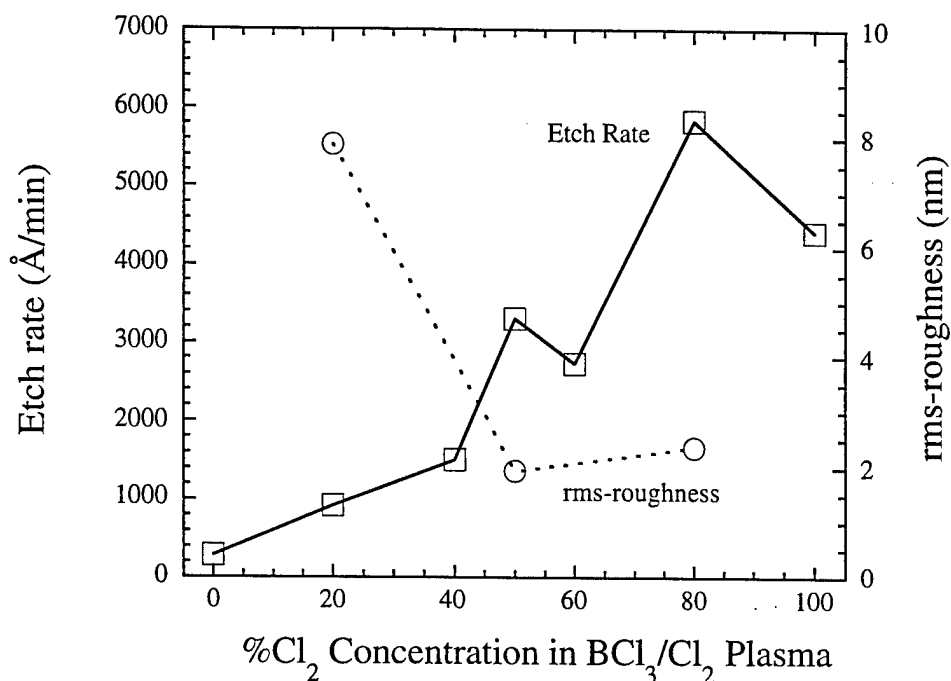

Figure 1. GaN etch rates and rms roughness in an ICP BCl$_3$/Cl$_2$ plasmas as a function of %Cl$_2$. ICP plasma conditions were 40 sccm BCl$_3$/Cl$_2$, 5 sccm Ar, 500 W ICP source power, dc-bias -150 V, and 2 mTorr pressure. The as-grown rms roughness was 1.02 nm.

Plasma conditions often change as a function of pressure, in particular the mean-free path decreases and the collisional frequency increases as the pressure is increased. This results in changes in both ion energy and plasma density which strongly influence etch characteristics. In Figure 2, GaN etch rates and rms roughness are shown as a function of pressure for an ICP-generated BCl$_3$/Cl$_2$ plasma. Plasma conditions were 32 sccm Cl$_2$, 8 sccm BCl$_3$, 5 sccm Ar, 500 W ICP source power, and -150 V dc-bias. Etch rates increased as the pressure was increased from 1 to 2 mTorr suggesting a reactant limited regime at low pressure. As the pressure was increased above 2 mTorr, GaN etch rates decreased due either to lower plasma densities, redeposition, or polymer formation on the substrate surface. Under low pressure etch conditions the etch was anisotropic and smooth, however at 10 mTorr the etch profile was undercut and poorly defined due to a lower mean-free path, higher collisional scattering of the ions, and increased lateral etching of the GaN. For the most part, the rms surface roughness was < 2 nm independent of pressure, similar to the rms roughness for the as-grown GaN. Using OES, Cl^0 emission intensity decreased slower than the GaN etch rates with increasing pressure. This may be due to increased recombination loss of Cl atoms between the plasma region and the sample at higher pressures.

The effect of ion energy and plasma density on etch characteristics are more obvious in high-density plasma etch systems, including ICP, since unlike RIE they can be effectively decoupled. Ion energies influence the physical component of the etch mechanism whereas plasma density can affect both the physical and chemical components. In general, etch rates increase as the ion energy increases due to improved sputter desorption of etch products from the surface as well as more efficient breaking of the group-III-N bonds. However, under high ion bombardment energies etch rates often decrease due to sputter desorption of reactive species from the surface before reaction occurs. This is often referred to as an adsorption limited etch regime. Anisotropy also typically

improves due to the perpendicular path of the ions relative to the substrate surface which improves straight wall profiles.
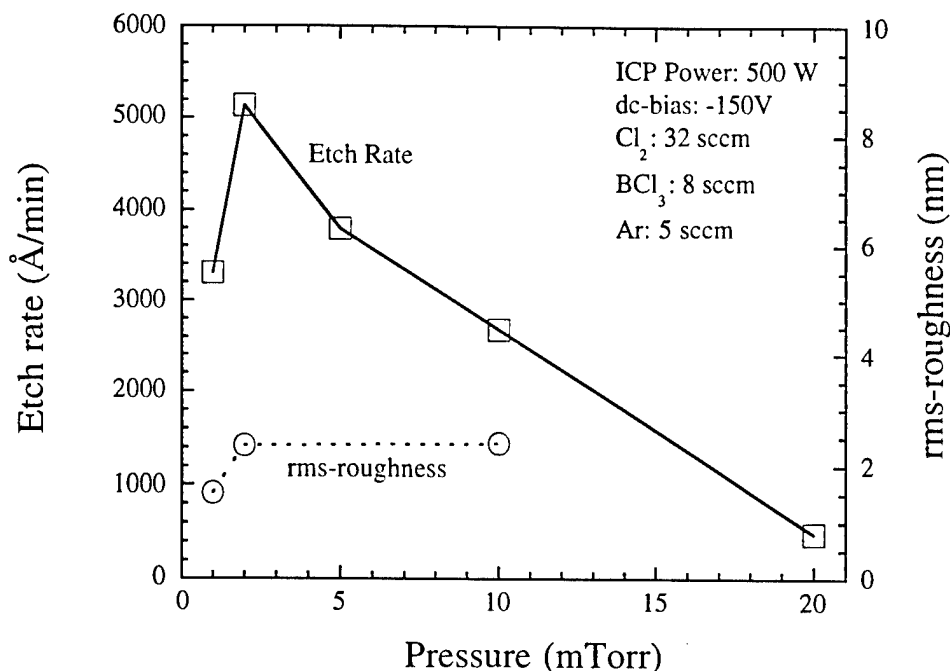

Figure 2. GaN etch rates and rms roughness as a function of pressure in an ICP-generated $BCl_3/Cl_2/Ar$ plasma. Plasma conditions were 32 sccm Cl_2, 8 sccm BCl_3, 5 sccm Ar, 500 W ICP source power, and -150 V dc-bias. The as-grown rms was 1.02 nm.

GaN etch rates and rms roughness are plotted as a function of dc-bias for an ICP-generated BCl_3/Cl_2 discharge in Figure 3. Plasma etch conditions were 2 mTorr pressure, 32 sccm Cl_2, 8 sccm BCl_3, 5 sccm Ar, and 500 W ICP source power. The GaN etch rates increased monotonically as the dc-bias or ion energy increased due to more efficient bond breaking of the GaN and more efficient sputter desorption of the etch products. As the physical component of the etch increased so did the rms roughness up to -300 V dc-bias. This may be due to preferential removal of either the Ga or N species under high ion-bombardment energies. The surface smoothing effect observed at -450 V may be attributed to an angular dependence of the ion bombardment of the surface which resulted in removal of sharp features.[15] As expected, the etch-rate dependence on dc-bias showed little correlation with Cl^0 emission intensity which was somewhat scattered over the conditions studied. In Figure 4, SEM micrographs are shown for a) -50, b) -150, and c) -300 V dc-bias. The etch anisotropy improved as the dc-bias increased from -50 to -150 V dc-bias due to the perpendicular nature of the ion bombardment energies. However, at -300 V dc-bias a tiered etch profile with vertical striations in the sidewall was observed due to erosion of the mask-edge under high ion bombardment energies.

As a function of increasing plasma density or source power, etch rates typically increase due to 1) higher concentrations of reactive species which increase the chemical component of the etch mechanism and/or 2) higher ion flux which increases the bond breaking efficiency and the sputter desorption component of the etch mechanism. However trends have been observed where etch rates stabilize or decrease at high plasma densities due either to saturation of reactive species at the surface or creation of an adsorption limited regime. In Figure 5, GaN etch rates and rms roughness are shown as a function of ICP-source power. ICP etch conditions were 32 sccm Cl_2, 8 sccm BCl_3, 5 sccm Ar, -150 V dc-bias, and 2 mTorr pressure. GaN etch rates increased as the ICP source power was increased, due to higher concentrations of reactive species in the plasma and/or higher ion flux. The rms increased slightly as the ICP source power increased but remained

smooth (<3 nm) under the conditions studied. The etch was anisotropic up to 1000 W ICP power where the feature dimensions and sidewall morphology were poor due to erosion of the resist under high ion flux conditions. From OES, the Ar emission intensity increased linearly with increasing ICP power, indicative of higher plasma electron density. However, there was a relative increase in the 725.7-to-741.4-nm intensity ratio, suggesting that higher ICP source power both increases total electron density and shifts the electron energy distribution toward higher energies. The deviation of etch rate from a linear power dependence may reflect this shift in the electron energy distribution.
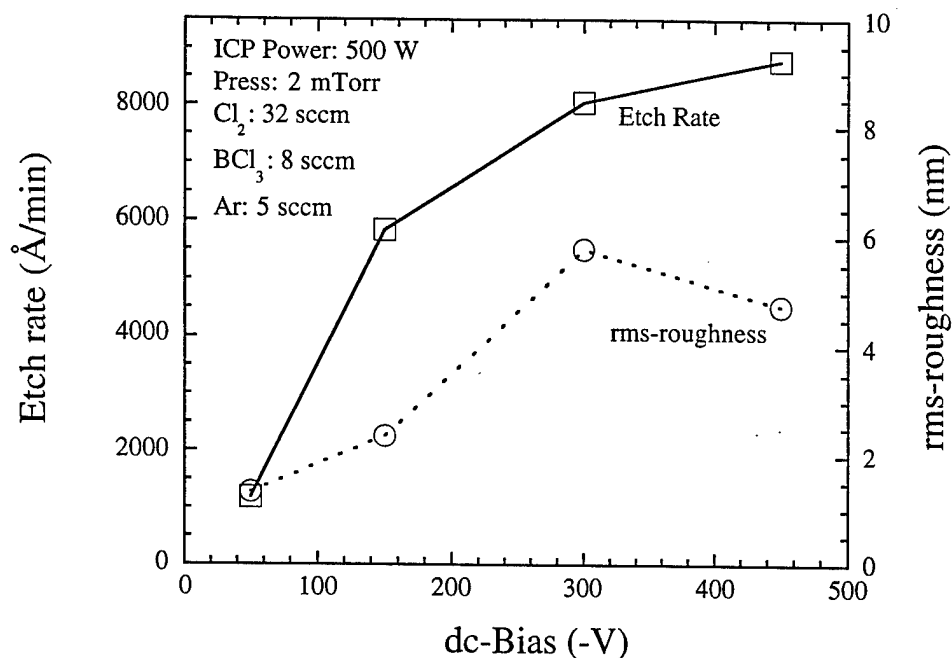

Figure 3. GaN etch rates and rms roughness as a function of dc-bias in an ICP-generated $BCl_3/Cl_2/Ar$ plasma. The plasma conditions were 32 sccm Cl_2, 8 sccm BCl_3, 5 sccm Ar, 500 W ICP source power, and 2 mTorr pressure. The as-grown rms was 1.02 nm.
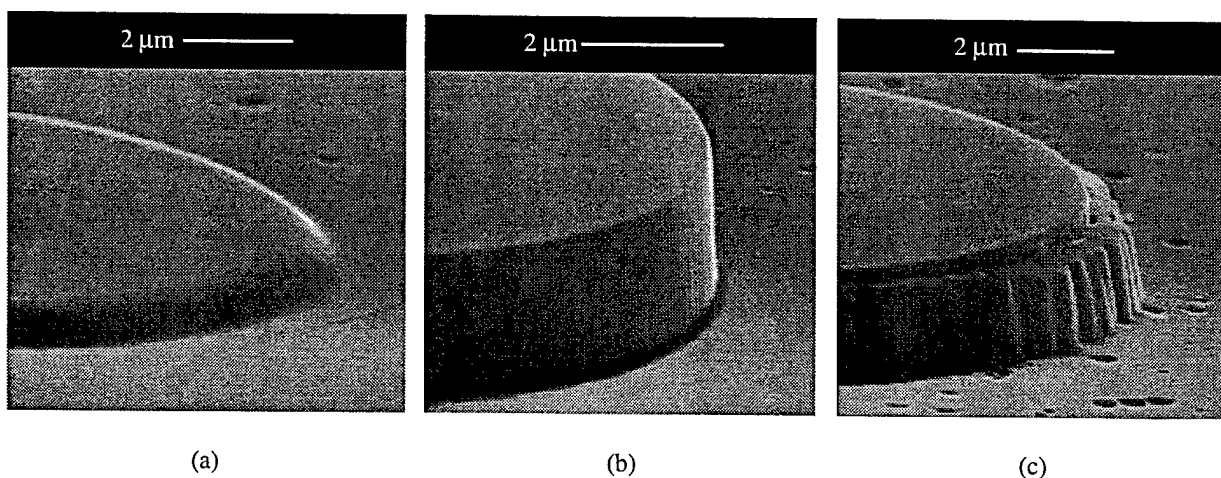

(a)   (b)   (c)

Figure 4. SEM micrographs for GaN etched at a) -50, b) -150, and c) -300 V dc-bias. ICP etch conditions were 32 sccm Cl_2, 8 sccm BCl_3, 5 sccm Ar, 500 W ICP source power, and 2 mTorr pressure.
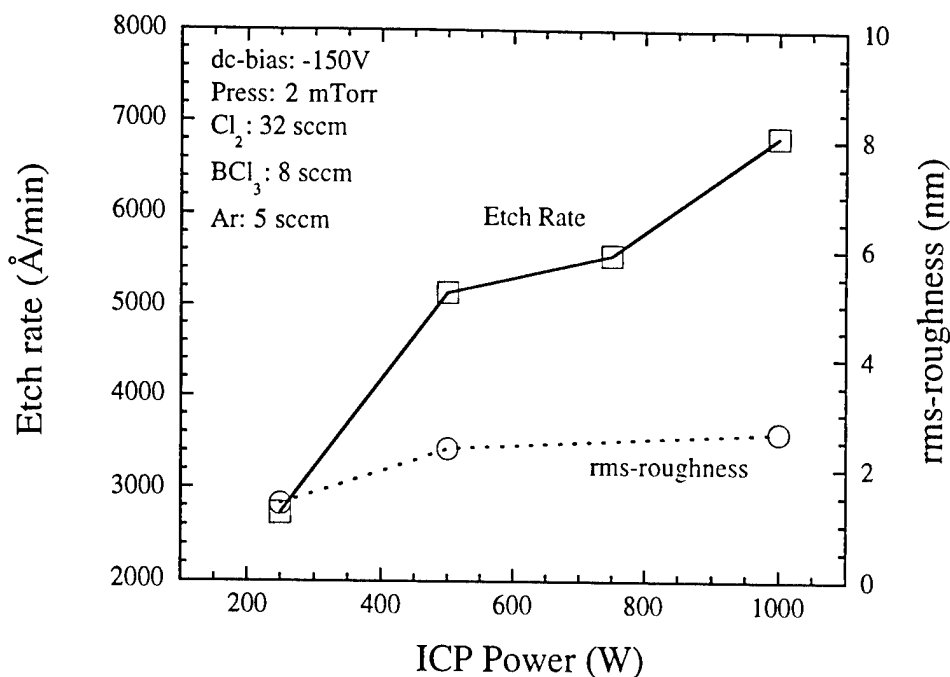
Figure 5. GaN etch rates and rms roughness as a function of ICP source power in an ICP-generated $BCl_3/Cl_2/Ar$ plasma. The plasma conditions were 32 sccm Cl_2, 8 sccm BCl_3, 5 sccm Ar, -150 V dc-bias, and 2 mTorr pressure. The as-grown rms was 1.02 nm.

CONCLUSIONS

In summary, the BCl_3/Cl_2 plasma chemistry appears to provide a very versatile GaN etch process which yielded etch rates ranging from ~ 100 Å/min to > 8000 Å/min. Etch rates increased as the %Cl_2 concentration increased up to 80% Cl_2 due to higher concentrations of reactive Cl. This data was confirmed using OES where the maximum Cl^0 concentration also occurred at 80% Cl_2. GaN etch rates also increased as a function of dc-bias due to improved bond breaking and sputter desorption of the etch products. However, under high dc-bias conditions the etch profile was worse due to breakdown of the mask-edge. These trends show that the chemical and physical components of the GaN etch mechanism. A wide range of plasma conditions were observed which yielded highly anisotropic etch profiles with smooth etch morphologies.

ACKNOWLEDGMENTS

REFERENCES

1. S. J. Pearton and R. J. Shul, in *Gallium Nitride I*, ed. J. I. Pankove and T. D. Moustakas (Academic Press, San Diego, 1998).
2. W. A. Harrison, *Electronic Structure and Properties of Solids*, (Freeman, San Francisco, 1980).
3. M. E. Lin, Z. F. Fan, Z. Ma, L. H. Allen, and H. Morkoc, Appl. Phys. Lett. 64, 887 (1994)
4. R. J. Shul, S. P Kilcoyne, M. Hagerott Crawford, J. E. Parmeter, C. B. Vartuli, C. R. Abernathy, and S. J. Pearton, Appl. Phys. Lett. 66, 1761 (1995).
5. L. Zhang, J. Ramer, J. Brown, K. Zheng, L. F. Lester, and S. D. Hersee, Appl. Phys. Lett. 68, 367 (1996).
6. S. J. Pearton, C. R. Abernathy, and F. Ren, Appl. Phys. Lett. 64, 2294 (1994).
7. H. Lee, D. B. Oberman, and J. S. Harris, Jr., Appl. Phys. Lett. 67, 1754 (1995).
8. C. B. Vartuli, S. J. Pearton, J. W. Lee, J. Hong, J. D. MacKenzie, C. R. Abernathy, and R. J. Shul, Appl. Phys. Lett. 69, 1426 (1996).
9. C. B. Vartuli, J. D. MacKenzie, J. W. Lee, C. R. Abernathy, S. J. Pearton, and R. J. Shul, J. Appl. Phys. 80, 3705 (1996).
10. R. J. Shul, in GaN and Related Materials, ed. S. J. Pearton (Gordon and Breach, NY 1997).
11. R. J. Shul, G. B. McClellan, S. A. Casalnuovo, D. J. Rieger, S. J. Pearton, C. Constantine, C. Barratt, R. F. Karlicek, Jr., C. Tran, and M. Schurman, Appl. Phys. Lett. 69, 1119 (1996).
12. R. J. Shul, R. D. Briggs, J. Han, S. J. Pearton, J. W. Lee, C. B. Vartuli, K. P. Killeen, and M. J. Ludowise, Mat. Res. Soc. Symp. Proc. 468, 355 (1997).
13. L. A. D'Asaro, J. L. DiLorenzo, and H. Fukui, IEEE Trans, Electron Devices ED-25, 5218 (1981).
14. Y. H. Lee, H. S. Kim, W. S. Kwon, G. Y. Yeom, J. W. Lee, M. C. Yoo, and T. I. Kim, J. Vac. Sci. Technol., in press.
15. C. B. Vartuli, S. J. Pearton, J. W. Lee, J. Hong, J. D. MacKenzie, C. R. Abernathy, and R. J. Shul, Appl. Phys. Lett. 69, 1426 (1996).

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