DEPTH AND THERMAL STABILITY OF DRY ETCH DAMAGE IN GaN SCHOTTKY DIODES

X. A. Cao, H. Cho and S. J. Pearton

Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611

G. T. Dang, A. P. Zhang and F. Ren

Department of Chemical Engineering, University of Florida, Gainesville, FL 32611

R. J. Shul, L. Zhang and A.G. Baca

Sandia National Laboratories, Albuquerque, NM 87185

R. Hickman and J. M. Van Hove

SVT Associates, Eden Prairie, MN 55344

ABSTRACT

GaN Schottky diodes were exposed to N_2 or H_2 Inductively Coupled Plasmas prior to deposition of the rectifying contact. Subsequent annealing, wet photochemical etching or $(NH_4)_2S$ surface passivation treatments were examined for their effect on diode current-voltage characteristics. We found that either annealing at 750 ^{o}C under N_2, or removal of ~500-600 Å of the surface essentially restored the initial I-V characteristics. There was no measurable improvement in the plasma-exposed diode behavior with $(NH_4)_2S$ treatments.

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GaN-based devices are being developed for two basic classes of applications, namely blue/green/UV emitters and high power/high temperature electronics.[1-5] The high bond energy, 8.92 eV/atom, of GaN has necessitated use of dry etching technologies for device patterning. Plasma induced damage to GaN may take several forms, all of which lead to changes in its electrical and optical properties, as follows:

1. Ion induced creation of lattice defects which generally behave as deep level states and thus produce compensation, trapping or recombination in the material. Due to channeling of the low energy ions that strike the sample, and rapid diffusion of the defects created, the effects can be measured as deep as 1000 Å from the surface, even though the projected range of the ions is only ≤10 Å.

2. Unintentional passivation of dopants by atomic hydrogen. The hydrogen may be a specific component of the plasma chemistry, or may be unintentionally present from residual water vapor in the chamber or from sources such as photoresist mask erosion. The effect of the hydrogen deactivation of the dopants is a strong function of substrate temperature, but may occur to depths of several thousand angstroms.

3. Deposition of polymeric film from plasma chemistries involving CH_x radicals, or from reaction of photoresist masks with Cl_2-based plasma.

4. Creation of non-stoichiometric surfaces through preferential loss of one of the lattice elements. This can occur because of strong differences in the volatility of the respective etch products, leading to enrichment of the less volatile species, or by preferential sputtering of the lighter lattice element if there is a strong physical component to the etch mechanism. Typical depths of this non-stoichiometry are <100 Å.

Usikov et al.[6] studied the effect of Ar and Ar/N_2 collimated ion beam etching on GaN p-n junctions. On undoped GaN epilayers, Ar^+ ion beam etching increased the near-surface electron concentration from 10^{16} cm^{-3} to 10^{18} cm^{-3}. In the PL spectrum an intense broad band appeared at 3.05 eV, and there was an increase in intensity of the yellow band at 2.20 eV. The latter is thought to involve defects such as Ga_v in some models. Use of Ar^+/N_2^+ ion beams produced less degradation of both optical and electrical properties.

Saotome at al.[7] studied the effects of RIBE/ECR etching with pure Cl_2 on GaN properties. Etch rates up to ~1000 Å-min^{-1} at 500 V beam voltage were obtained. He-Cd (325 nm) laser irradiation was used to measure PL from RIBE GaN samples before and after photo-assisted wet etching in an 85% $KOH:H_2O$ (1:3) solution. The RIBE treatment decreased near band-edge PL intensity by a factor of approximately five, whereas subsequent photo-assisted wet etching restored this to about half of the original value.

Several groups have found that the n-type ohmic contact resistance was significantly improved on GaN if the surface were initially plasma etched, leading to a near-surface N_2 deficiency and a higher n-type surface doping level.[8-10] In contrast, Schottky contacts fabricated on reactively ion etched (RIE) n-GaN showed severe degradation.[11] The sheet resistance of the GaN below this surface region may increase substantially due to deep level creation by ion bombardment,[12,13] while the optical properties may also be degraded.[14]

In this work, we report on a study of current-voltage (I-V) and reverse breakdown voltage (V_B) characteristics in GaN Schottky diodes exposed to H_2 or N_2 Inductively Coupled Plasmas (ICP). The depth and thermal stability of the damage has been determined.

The layer structure consisted of 0.5 μm of n^+ (10^{18} cm^{-3}) GaN grown on a c-plane Al$_2$O$_3$ substrate, followed by 3 μm of nominally undoped (n~10^{17} cm^{-3}) GaN. The samples were grown by rf plasma-assisted Molecular Beam Epitaxy.[15] Ohmic contacts were formed with Ti/Au annealed at 600 °C. The exposed GaN surface was then exposed to ICP H$_2$ or N$_2$ discharges, and either annealed or photoelectrochemically etched in 0.2 M KOH solutions prior to deposition of the Pt/Au Schottky contacts through a stencil mask. The diameter of these contacts was 250 μm. In some case a mesa structure was formed by Cl$_2$/Ar ICP etching down to the n^+-GaN layer, followed by 750 °C annealing to remove etch damage. These samples were then treated in (NH$_4$)$_2$S solution at 25 °C for 20 mins.[16] Schematics of the planar and mesa diodes are shown in Figure 1.

The typical effect of either H$_2$ or N$_2$ plasma exposure was a severe decrease in reverse breakdown voltage and much more forward leakage current as the barrier height (Φ_B) was decreased. An example is shown in Figure 2, where V_B decreases from –5 V to approximately –1 V after exposure to a 500 W source power, 150 W rf chuck power (dc self-bias –221 V), 5 mTorr N$_2$ discharge. Under similar plasma conditions we always observed somewhat worse degradation of diode properties with N$_2$ compared to H$_2$ discharges, probably due to the greater mass of the impinging N$_2^+$ ions.

As the samples were annealed for 30 secs under a 1 atm N$_2$ ambient at different temperatures, there was significant improvement in the I-V characteristics, as also shown in Figure 2. However at 850 °C, the quality of the diode behavior began to degrade. This has been ascribed to the onset of preferential N$_2$ loss from the GaN surface, which requires use of a stable encapsulating layer such as AlN to prevent.[17] Figure 3 shows the variation of V_B with annealing temperature – clearly at 750 °C there is almost complete restoration of the initial V_B value.

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A similar set of I-V characteristics were recorded for diodes in which we removed various amount of the plasma-damaged surface by photochemical etching [18] prior to deposition of the Schottky contact. Figure 3 also shows the variation of V_B with depth removed for samples exposed to the same discharge as in the annealing experiments (N_2, 500 W source power, 150 W rf chuck power, 5 mTorr). After removal of ~250 Å, the V_B value is restored to about half of its initial value. For larger removal depths it becomes increasingly difficult to accurately measure the etch depth because of the surface roughening typical of PEC etching, but we estimated that 500 – 600 Å of GaN must be removed to completely restore V_B.

Figure 4 shows I-V characteristics from control and $(NH_4)_2S$ treated mesa diodes. For diodes not exposed to the ICP discharges, there was little improvement in V_B (Figure 4), but the forward section of the I-V characteristic showed a decrease in ideality factor (Figure 5). Note that the 2kT leakage current in a diode of this type has contributions from both the bulk space-charge region and the mesa surface, and that sulfide passivation would only affect the latter. On diodes damaged by plasma exposure, we did not observe any improvement in I-V characteristics with the $(NH_4)_2S$ treatment. In this case the diode behavior is clearly dominated by the 500 – 600 Å thick damaged region and not by the surface recombination velocity.

In summary, the Schottky diode characteristics of ICP plasma exposure GaN were investigated. The main conclusions of the study are:

1. N_2 discharges produce more degradation in V_B than H_2 discharges, which implicates ion mass as the main factor.

2. The electrical damage depth is 500-600 Å.

3. The diode characteristics are almost restored by post-plasma annealing at 750 $^{\circ}$C. Higher annealing temperatures produce degraded I-V properties due to N_2 loss.

4. $(NH_4)_2S$ passivation is relatively ineffective on GaN, and has no effect on plasma damaged material.

References

1. See for example, GaN and Related Materials, ed. S. J. Pearton (Gordon and Breach, NY, 1997); GaN, ed. J. I Pankove and T. D. Movstakas (Academic Press, San Diego, 1998).

2. S. Nakahama, IEEE J. Selected Topics in Quantum Electronics, 4 483 (1998).

3. S. Nakamura and G. Fasol, The Blue Laser Diode (Springer, Berlin 1998).

4. S. N. Mohammad and H. Morkoc, Prog. Quantum Electron. 20 361 (1996).

5. F. A. Ponce and D. P. Bour, Nature 386 351 (1997).

6. A. S. Usikov, W. L. Lundin, U. I. Ushakov, B. V. Pushnyi, N. M. Schmidt, Y. M. Zadiranov and T. V. Shubtra, Proc. ECS 98-14, 57 (1998)

7. K. Satore, A. Matsutani, T. Shirasawa, M. Mori, T. Honda, T. Sakaguchi, F. Koyama and K. Iga, Mat. Res. Soc. Symp. Proc. 449 1029 (1997).

8. Z. F. Fan, S. N. Mohammad, W. Kim, Ö. Aktas, A. E. Botchkarev and H. Morkoç, Appl. Phys. Lett. 69 1672 (1996).

9. A. T. Ping, Q. Chen, J. W. Yang, M. A. Khan and I. Adesida, J. Electron. Mater. 27 261 (1998).

10. J. Y. Chen, C. J. Pan and G. C. Chi, Solid-State Electron. 43 649 (1999).

11. A. T. Ping, A. C. Schmitz, I. Adesida, M. A. Khan, Q. Chen and J. W. Yang, J. Electron. Meter. 26 266 (1997).

12. S. J. Pearton, J. W. Lee, J. D. MacKenzie, C. R. Abernathy and R. J. Shul, Appl. Phys. Lett. 67 2329 (1995).

13. C. R. Eddy, Jr. and B. Molnar, Mat. Res. Soc. Symp. Proc. 395 745 (1996).

14. R. J. Shul, J. C. Zolper, M. H. Crawford, R. J. Hickamn, R. D. Briggs, S. J. Pearton, J. W. Lee, R. F. Karlicek Jr., C. Tran, M. Schurman, C. Constantine and C. Barratt, Proc. Electrochem. Soc. 96-15 232 (1996).

15. J. M. Van Hove, R. Hickman, J. J. Klaassen, P. P. Chow and P. P. Ruden, Appl. Phys. Lett. 70 282 (1997).

16. V. Malhotra and C. W. Wilmsen, in Handbook of Compound Semiconductors, ed. P. H. Holloway and G. E. McGuire (Noyes Publications, Park Ridge, NJ 1995).

17. J. C. Zolper, D. J. Rieger, A. G. Baca, S. J. Pearton, J. W. Lee and R. A. Stall, Appl. Phys. Lett. 69 538 (1996).

18. C. Youtsey, G. Bulman and I. Adesida, J. Electron. Meter. 27 282 (1998).

Figure Captions

Figure 1. Schematic of the planar (top) and mesa (bottom) diodes.

Figure 2. I-V characteristics from GaN planar diodes before and after ICP N_2 plasma exposure (500 W source power, 150 W rf chuck power, 5 mTorr), and after subsequent annealing at different temperatures.

Figure 3. Variation of V_B in N_2 plasma exposed (500 W source power, 150 W rf chuck power, 5 mTorr) GaN planar diodes as a function of either annealing temperature (top) or depth of damaged material removed (bottom).

Figure 4. I-V characteristics from GaN mesa diodes before and after $(NH_4)_2S$ treatment.

Figure 5. Forward I-V characteristics from GaN mesa diodes before and after $(NH_4)_2S$ treatment. Ideality factors are ~2.3 and 1.7, respectively.

Ti/Au   Pt/Au   Ti/Au

3 μm undoped (n~10^{17} cm^{-3}) GaN

0.5 μm n$^+$ (10^{18} cm^{-3}) GaN

Al$_2$O$_3$ substrate

Pt/Au

Ti/Au   3 μm GaN   Ti/Au

0.5 μm n$^+$-GaN

Al$_2$O$_3$ substrate