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Oxygen diffusion into SiO_2-capped GaN during annealing

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SiO_2 layers were deposited on *p*-GaN (hole concentration $9\times10^{17}\,cm^{-3}$) by inductively coupled plasma chemical vapor deposition using an ^{17}O-enriched O_2 precursor. The samples were then annealed at 500–900 °C and the SiO_2 was removed. Secondary ion mass spectrometry profiling showed significant indiffusion of ^{17}O into the GaN under these conditions, with an incorporation depth of $\sim0.18\,\mu m$ after the 900 °C anneal. The ^{17}O diffusion profiles indicate that the high dislocation density in the GaN strongly affects the effective penetration depth. The GaN remained *p* type upon incorporation of the oxygen. © *1999 American Institute of Physics.* [S0003-6951(99)00445-3]

Oxygen is one of the most important residual impurities in GaN, and is generally believed to be responsible for the *n*-type conductivity of unintentionally doped material.[1–16] The source of the residual oxygen is generally as an impurity in NH_3 used as a precursor for metal organic chemical vapor deposition (MOCVD) or the remnant water vapor in molecular beam epitaxy (MBE) chambers. In the latter case, oxygen may also be leached from the SiO_2 or Al_2O_3 plasma containment sections used in some plasma sources for creating atomic nitrogen from N_2 feedstock. It has also been reported that bulk GaN grown at high temperatures (1700 °C) and high N_2 pressures (20 k bar) from Ga solutions typically contains $\geqslant10^{18}$–$10^{19}\,cm^{-3}$ of oxygen.[9] Implantation of O^+ ions creates shallow donor levels (~30 meV) in GaN after activation annealing and under these conditions the oxygen diffusivity is very small ($<10^{-14}\,cm^2\,s^{-1}$ at 1400 °C).[6] Intentional oxygen doping during MOCVD growth produced a donor level at E_c-78 meV, with banding occurring at high concentrations.[1] Theoretically, O_N in GaN was found to create a shallow donor level with low formation energy.[2,3] Oxygen may also be important in co-doping with acceptors to increase the effective concentration in GaN.[17–20]

There has been little work on understanding the role of oxygen during thermal processing of GaN. It is know that the temperature at which surface dissociation becomes significant during annealing of GaN is several hundred degrees lower in O_2-containing ambients relative to pure N_2 ambients.[21] The strong affinity of O for GaN may lead to autodoping in situations such as epitaxial regrowth over SiO_2 windows, as in the epitaxial lateral overgrowth technique, or during annealing with SiO_2 encapsulant layers. However, if the acceptor concentration in the GaN were low ($<10^{17}\,cm^{-3}$), it is clear that indiffused oxygen could even cause type conversion if a significant fraction of it was electrically active. In this letter we report on the observation of ^{17}O diffusion into *p*-type GaN during SiO_2-capped annealing. We employed isotopically enriched O_2 as a precursor for SiO_2 deposition, and were able to follow the ^{17}O diffusion with high sensitivity using secondary ion mass spectrometry (SIMS). The activation energy and prefactor for ^{17}O diffusion were determined over the temperature range 500–900 °C.

Epitaxial layers of GaN consisting of 1 μm undoped ($n\sim10^{16}\,cm^{-3}$) followed by 0.3 μm of Mg-doped (hole concentration, $p\sim9\times10^{17}\,cm^{-3}$) were grown on *c*-plane Al_2O_3 substrates by radio frequency plasma activated MBE.[22] These layers were capped with 1800 Å of SiO_2 grown by inductively coupled plasma chemical vapor deposition (ICP–CVD) at 50 °C using SiH_4 and ^{17}O-enriched (50%) O_2 in a Plasma-Therm 790 reactor. The ICP source power was 300 W (2 MHz), while the sample position was biased at -5 V using 5 W of 13.56 MHz power. Under these conditions there is minimal change in the electrical or optical properties of the GaN as measured by Hall and cathodoluminescence measurements, due to the low energy of the incident ions (<30 eV). Sections of these samples were annealed for 5 min at 500, 700, or 900 °C under N_2 in a Heatpulse 610 furnace. SIMS measurements were performed on the as-deposited and annealed samples both before and after removal of the SiO_2 in buffered HF solution at 25 °C.

Figure 1 shows SIMS depth profiles of the as-deposited structure. There is a high concentration of ^{17}O in the SiO_2 film and the interface with the GaN is abrupt. Samples annealed up to 900 °C showed no change in the profiles of the lattice elements, including the Mg in the GaN. The SiO_2 was selectively removed in buffered HF and there was little difference in its etch rate before and after annealing, indicating

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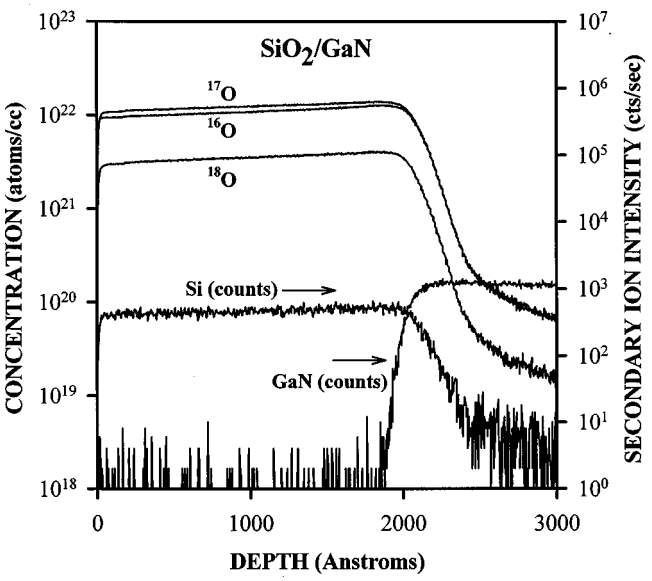

FIG. 1. SIMS profiles of as-deposited SiO_2 layer on GaN.

that there was little densification resulting from the high temperature process.

Figure 2 shows SIMS profiles of ^{17}O in the GaN after different annealing temperatures. Note that there is the usual high concentration, near-surface ($\leqslant 200$ Å) signal characteristic of SIMS profiling through a surface or interface and which is basically an artifact of the measurement. In the as-deposited sample the ^{17}O signal is returned to the background level of $\sim 10^{17}\,cm^{-3}$ at a distance of 400–500 Å. By sharp contrast, in the samples annealed prior to removal of the SiO_2, the ^{17}O concentration and depth of incorporation show clear increases for higher annealing temperatures. The ^{17}O clearly diffuses from the SiO_2 into the GaN during annealing. There is no indication of pairing of oxygen with Mg to form Mg–O complexes, which should be evident as a plateau in the O profile. There are some obvious implications of these results: First, the use of SiO_2 masks for ELO of GaN could produce *n*-type autodoping of the material by oxygen

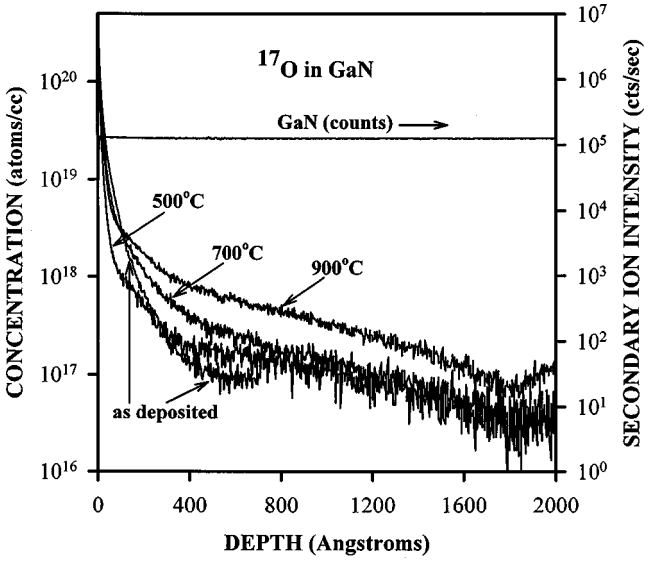

FIG. 2. SIMS profiles of ^{17}O in GaN annealed at different temperatures for 5 min prior to removal of the SiO_2 layer.

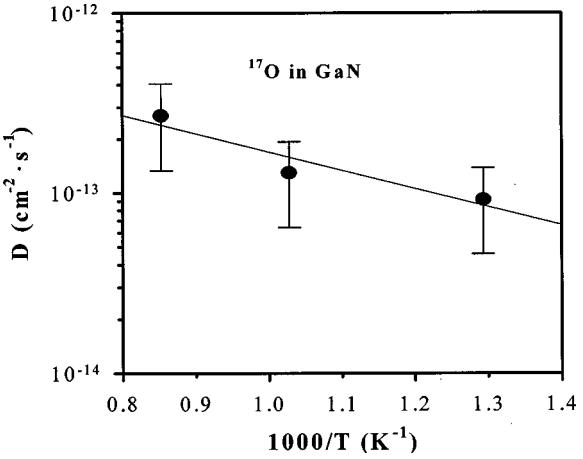

FIG. 3. Arrhenius plot of ^{17}O diffusivity in *p*-GaN.

incorporation. Second, SiO_2 is not a suitable choice as an encapsulant or annealing of implanted GaN, for the same reason.

The ^{17}O diffusion profiles in Fig. 2 clearly do not follow an error function (erfc) distribution and the fact the logarithm of the concentration is almost linear in penetration depth is a clear signature of pipe diffusion.[23–26] The expanded regions around threading dislocations provide an easy path for diffusion of impurities, with an activation energy typically half that for diffusion in the bulk of the material.[27] In a simple picture one can consider the bulk and pipe diffusion to be independent, with the square of the diffusion distance given by[23]

$$X^2 = 2D_d t + 2D_b t,$$

where $D_{d,b}$ are the diffusivities in the dislocations or bulk, respectively, and t is the diffusion time. If $D_d \gg D_b$ and the oxygen-dislocation binding energy forward partitioning to the dislocation then the overall mass transport of the oxygen would be dominated by the pipe diffusion. Since this appears to be the case from Fig. 2, we can obtain a rough estimate of D_d from $X^2/2t$, where X is the depth at which the oxygen concentration falls to $10^{17}\,cm^{-3}$ and $t = 300$ s. Figure 3 shows the resulting values of D in Arrhenius form. At least squares fit to the data yielded the relationship

$$D = 4.5 \pm 2.2 \times 10^{-12} \exp(-0.23 \pm 0.12 eV/kT),$$

where k is Boltzmann's constant. The activation is approximately half that expected for diffusion of interstitials in bulk material. We do not know the final lattice position of the oxygen, but can estimate that $<30\%$ is substitutional based on the fact that we could not measure any change in the carrier concentration, obtained by Hall effect using a two band model[28] in the 900 °C diffused sample.

The diffusion behavior of oxygen originating from SiO_2 encapsulant layers is obviously quite different from implanted oxygen.[6] In the latter situation the high vacancy concentration created by the implanted O^+ ions may enhance the occupation probability of substitutional sites, i.e., there is a higher efficiency for creation of O_N. There are still many unanswered questions concerning the effect of strain induced in the near-surface region by the SiO_2 cap (which is known to enhance point defect diffusion in other compound semi-

conductor systems)[29] and of the exact role of threading dislocations in the GaN on the diffusivity of oxygen. The latter can be answered by repeating the experiments in bulk substrates when they become available, while the former will require comparison of diffusion profiles from SiO_2 films of varying stress.

In summary, the use of isotopically labeled O_2 for deposition of SiO_2 layers on GaN has allowed the unambiguous observation of oxygen diffusion into the GaN during annealing in the range 500–900 °C, which are typical contact alloying temperatures. Based on the measured activation energy for the oxygen diffusivity, it migrates in interstitial form along dislocations. In addition to the more widely recognized ability of atomic hydrogen to migrate rapidly into GaN at moderate temperatures, our results show that one must also be aware of the possibility of oxygen indiffusion during thermal treatments.

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[1] B.-C. Chung and M. Gershenzon, J. Appl. Phys. **72**, 651 (1992).
[2] J. Neugebauer and C. G. Van de Walle, in *Proceedings of the 22nd International Conference on Phys. of Semiconductors*, edited by D. J. Lockwood (World Scientific, Singapore, 1994), Vol. III, p. 2327.
[3] T. Mattila and R. M. Nieminen, Phys. Rev. B **54**, 16676 (1996).
[4] W. Götz, N. M. Johnson, C. Chen, H. Liu, C. Kuo, and W. Imler, Appl. Phys. Lett. **68**, 3144 (1996).
[5] T. L. Tansley, E. M. Goldys, M. Godlewski, B. Zhou, and H. Y. Zuo, in *GaN and Related Materials*, edited by S. J. Pearton (Gordon and Breach, New York, 1997).
[6] J. C. Zolper, R. G. Wilson, S. J. Pearton, and R. A. Stall, Appl. Phys. Lett. **68**, 1945 (1996).
[7] C. Wetzel and I. Akasaki, in *Properties, Processing and Applications of GaN and Related Semiconductors*, edited by J. H. Edgar, S. Strite, I. Akasaki, H. Amano, and C. Wetzel (INSPEC, IEE, London, 1999).
[8] W. Seifert, R. Franzheld, E. Butter, H. Sobotta, and V. Riede, Cryst. Res. Technol. **18**, 383 (1983).
[9] P. Perlin, T. Suski, A. Polian, J. C. Chervin, E. L. Staszewska, I. Grzegory, S. Porowski, and J. W. Erickson, Mater. Res. Soc. Symp. Proc. **449**, 519 (1997).
[10] C. Wetzel, T. Suski, J. W. Ager III, W. Walukiewicz, S. Fischer, and B. K. Meyer, *Proceedings of the 23rd International Conference Phys. Semiconductors* (World Scientific, Singapore, 1996), p. 2929.
[11] C. H. Park and D. J. Chadi, Phys. Rev. B **55**, 12995 (1997).
[12] C. C. Van de Walle, Phys. Rev. B **57**, R2033 (1998).
[13] J. I. Pankove, S. Bloom, and G. Harbeke, RCA Rev. **36**, 163 (1975).
[14] S. Koynov, M. Topf, S. Fischer, B. K. Meyer, P. Radojkovic, E. Hartman, and Z. Lilienthal-Weber, J. Appl. Phys. **82**, 1890 (1997).
[15] C. R. Abernathy, S. J. Pearton, J. MacKenzie, J. W. Lee, C. B. Vartuli, R. G. Wilson, R. J. Shul, J. C. Zolper, and J. M. Zavada, Mater. Res. Soc. Symp. Proc. **395**, 685 (1996).
[16] S. J. Pearton, J. W. Lee, C. R. Abernathy, R. G. Wilson, J. M. Zavada, and J. C. Zolper, Proc.-Electrochem. Soc. **97–34**, 209 (1998).
[17] D. Brandt, H. Yang, H. Kostial, and K. H. Ploog, Appl. Phys. Lett. **69**, 2767 (1996).
[18] T. Yamamoto and H. Katayama-Yoshida, Jpn. J. Appl. Phys., Part 2 **36**, L180 (1997).
[19] J. I. Pankove, J. T. Torvik, C.-H. Qui, I. Grzegory, S. Porowski, P. Quigley, and B. Martin, Appl. Phys. Lett. **74**, 416 (1999).
[20] T. Yamamoto and H. Katayama-Yoshida, Mater. Sci. Forum **258–263**, 1185 (1997).
[21] J. C. Zolper, R. J. Shul, and F. Ren, J. Appl. Phys. **86**, 1 (1999).
[22] J. M. Van Hove, R. Hickman, J. J. Klaassen, P. P. Chow, and P. P. Ruden, Appl. Phys. Lett. **70**, 282 (1997).
[23] R. J. Borg and G. J. Dienes, *An Introduction to Solid State Diffusion* (Academic, San Diego, 1988), pp. 139–144.
[24] J. C. Fisher, J. Appl. Phys. **22**, 74 (1951).
[25] A. D. LeClaire and A. Rabinovitch, in *Diffusion in Crystalline Solids*, edited by G. E. Murch and A. S. Nowick (Academic, San Diego, 1984), pp. 259–316.
[26] G. B. Abdullaev and T. D. Dzhafarov, *Atomic Diffusion in Semiconductor Structures* (Harwood, New York, 1987), pp. 19–25.
[27] J. P. Schaffer, A. Saxena, S. D. Antolovich, T. H. Sanders, Jr., and S. B. Warner, *The Science and Design of Engineering Materials* (Irwin, Chicago, 1995).
[28] D. C. Look, *Electrical Characterization of GaAs Materials and Devices* (Wiley, New York, 1985).
[29] See for example, R. M. Cohen, Mater. Sci. Eng., R. **20**, 167 (1997).