

Compositional Changes in Erbium-Implanted GaN Films Due To Annealing

J.M. ZAVADA,^{1,5} R.G. WILSON,² U. HÖMMERICH,³ M. THAIK,³ J.T. SEO,³
C.J. ELLIS,⁴ J.Y. LIN,⁴ and H.X. JIANG⁴

1.—U.S. Army Research Office, Durham, NC 27709. 2.—Consultant, Stevenson Ranch, CA 91381.
3.—Hampton University, Hampton, VA 23668. 4.—Kansas State University, Manhattan, KS
66506. 5.—E-mail: john.zavada@us.army.mil

We have conducted a study of the material and infrared-luminescence properties of Er-implanted GaN thin films as a function of annealing. The GaN films, grown by metal-organic chemical-vapor deposition, were coimplanted with Er and O ions. After implantation, the films were furnace annealed at temperatures up to 1,100°C. Following each annealing stage, the samples were examined by photoluminescence (PL) measurements and secondary ion-mass spectrometry (SIMS) analysis. In the as-implanted samples, no PL signal near 1,540 nm could be detected with either above-bandgap or below-bandgap excitation. Only after annealing at temperatures above 900°C was the 1,540-nm luminescence detectable. Annealing at higher temperatures resulted first in an increase and then a decrease in the PL-signal intensities. The SIMS data showed that large concentrations of Al, O, and C atoms entered into the GaN films with high-temperature annealing. The stoichiometric changes in the GaN appear responsible for the changes in the Er-related luminescence.

Key words: GaN, erbium, implantation, annealing, photoluminescence, SIMS

INTRODUCTION

Ion implantation has been widely applied in the doping of semiconductor materials used in integrated-electronic circuits and optoelectronic devices.¹ Because implantation is a nonequilibrium process, doping is limited neither by solubility nor by surface-chemistry constraints. A high concentration of dopant atoms can be formed in localized regions of the semiconductor host. Consequently, a number of research groups have used ion implantation to dope III-V nitride semiconductors with rare-earth (RE) atoms.^{2–5} However, ion implantation of RE atoms can lead to considerable damage to the GaN crystal, and postimplantation annealing is usually required to observe luminescence from the trivalent ion.

Wilson et al. were the first to observe luminescence at $\sim 1.54 \mu\text{m}$ from Er^{3+} after implantation into III-V nitride thin films.⁶ The GaN films were coimplanted with Er and O ions and then annealed at $\sim 650\text{--}700^\circ\text{C}$ for 20 min. Several prior studies had indicated that codoping the semiconductor with impurity elements, such as O or F, enhances the in-

frared emission.^{7,8} Using an Ar-ion laser, at a wavelength of 458 nm, strong infrared luminescence was measured from 6 K to 300 K. The spectra were centered at $1.54 \mu\text{m}$ and displayed many distinct lines, indicative of the allowed transitions between the $^4\text{I}_{13/2}$ and the $^4\text{I}_{15/2}$ manifolds of the Er^{3+} system. In addition, the integrated- Er^{3+} luminescence intensity at room temperature was nearly 50% that at 77 K.

Torvik et al. performed a similar photoluminescence (PL) study of GaN films grown by chemical-vapor deposition on R-plane sapphire substrates.⁹ Different combinations of fluences for the Er + O implants and annealing temperatures were examined. Using laser excitation at a wavelength of $0.980 \mu\text{m}$, they reported that the samples implanted with the highest Er fluence ($\sim 10^{15} \text{ cm}^{-2}$) yielded the strongest PL intensity. Furthermore, there was an optimum annealing temperature above which the luminescence of the Er-doped GaN film decreased rapidly. While this decrease has been attributed to changes in the local environment of the Er^{3+} ions, no detailed explanation was given.

In this paper, we present evidence that high-temperature annealing of the Er-implanted GaN film

(Received July 19, 2002; accepted September 2, 2002)

changes the stoichiometric composition of the film and alters the local environment of the Er^{3+} ions. Using secondary ion-mass spectrometry (SIMS) analysis,¹⁰ we have obtained atomic-depth profiles for Er atoms in the GaN film as well as for Al, C, and O atoms in-diffusing during annealing. The SIMS measurements show that significant stoichiometric changes can occur with high-temperature annealing. The PL spectra also changed after each annealing stage. The experimental data indicate that in order to achieve efficient Er^{3+} luminescence a sensitive tradeoff between implantation parameters and annealing procedures is necessary.

EXPERIMENTAL DETAILS

The GaN films used in these experiments were grown by metal-organic chemical-vapor deposition on c-plane sapphire (Al_2O_3) substrates. The epilayers were approximately 0.8- μm thick and were coimplanted with Er and O ions. The Er implantation was done at an energy of 300 keV to a dose of $5.7 \times 10^{13}/\text{cm}^2$. The O implantation was done at an energy of 40 keV to a dose of $1.2 \times 10^{15}/\text{cm}^2$. The implantation energies were chosen to produce a large overlap of the Er- and O-atom profiles. After implantation, the samples were cut into small pieces that were then furnace annealed for 10 min in an N ambient at various temperatures ranging from 800°C to 1,100°C. The PL measurements were performed on each of the GaN pieces after each annealing stage.

The PL spectra near 1,540 nm were measured using the ultraviolet Ar-ion laser lines (336–363 nm) for above-bandgap excitation and using a visible, HeCd laser line (442 nm) for below-bandgap excitation. The infrared spectra were recorded using a 1-m monochromator equipped with a liquid-nitrogen-cooled Ge detector. The signal was processed using lock-in techniques. The obtained-PL spectra were not corrected for the spectral response of the setup.

The SIMS analysis of the implanted-GaN film was used to determine the Er and O profiles after implantation and to monitor any compositional changes with annealing. The SIMS measurements for the Er, Al, and Ga atoms were made using O_2^+ -ion bombardment and positive secondary-ion detection. The SIMS measurements for impurity elements, such as O and C atoms, were made using Cs^+ -ion bombardment and negative secondary-ion detection. The SIMS measurements were quantified using implanted standards of implanted-GaN films.

INFRARED-PHOTOLUMINESCENCE SPECTROSCOPY

Photoluminescence spectroscopy has been the principal technique used to characterize the optical emission of rare-earth (RE) ions in semiconductor materials. In a wide-bandgap semiconductor host, there are at least three different methods for optical excitation of the RE ions. The first consists of using an optical source having above-bandgap energy.

This method leads to generation of electron-hole pairs; some of which transfer energy to RE ions, leading to excitation of the 4f electrons. In the second method, RE ions can be excited directly by the optical-source radiation, provided that the energy of the radiation is resonant with one of the higher energy states of the RE ion. A third method involves an indirect excitation of the RE ions through a process involving defects in the host crystal.^{11,12} Defects and impurity elements in the GaN host lead to broad, below-bandgap absorption bands that provide an effective excitation channel of the Er^{3+} ions.

In Fig. 1 are shown room-temperature Er^{3+} -PL spectra over the range of 1,400–1,700 nm for the Er + O implanted-GaN samples annealed up to 1,100°C. The Er^{3+} ions were excited using a HeCd laser at a wavelength of 442 nm, corresponding to below-bandgap excitation. As shown in Fig. 1, no PL signal was detected in the as-implanted sample. After annealing at 800°C, there was a small, but detectable, PL signal near 1,540 nm, indicative of the transitions between the $^4I_{13/2}$ and the $^4I_{15/2}$ manifolds. The PL signal became more intense with annealing at higher temperatures and reached a maximum after annealing at 900°C. Annealing above 900°C resulted in a diminished Er^{3+} -PL signal and could not be observed after annealing at 1,100°C.

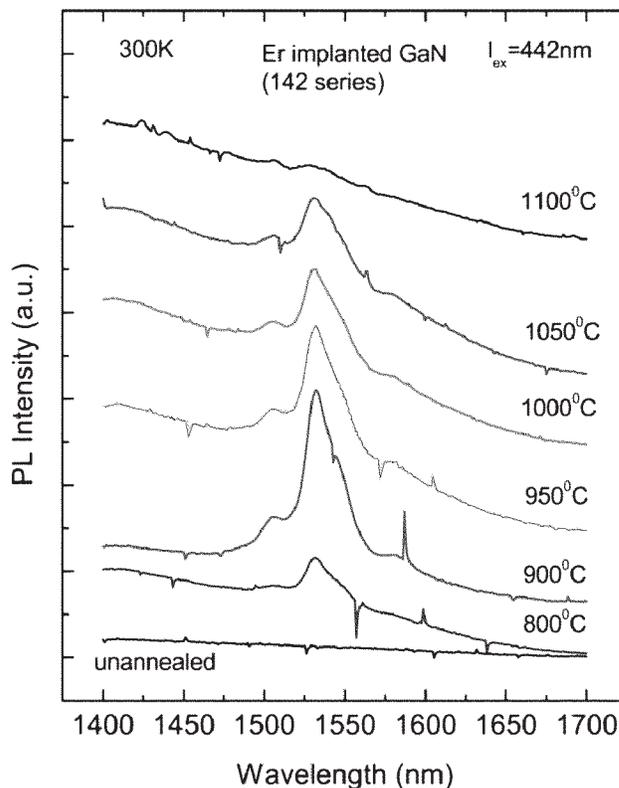


Fig. 1. The room-temperature, infrared PL spectra of Er + O-implanted GaN as a function of annealing temperature. The Er^{3+} ions were excited using a laser source (442 nm) corresponding to below-bandgap excitation. The spectra are displaced to permit easier viewing.

In general, after implantation, the Er atoms can occupy a number of different sites in the GaN matrix. The locations of the implanted-Er atoms in the GaN host can also change with annealing as well as the local configuration of the Er^{3+} complex. Prior studies have shown that different Er^{3+} complexes have different absorption characteristics and lead to different PL spectra near 1,540 nm.^{11,12} Alves et al. have shown that after annealing at 600°C, nearly 80% of the Er ions are on the Ga sublattice.¹³ Implantation-induced damage in the GaN host may also produce absorption of the luminescence near 1,540 nm. Annealing at temperatures above 800°C may be required to reduce the damage-related absorption to low enough levels to permit detection of the PL near 1,540 nm.

The room-temperature PL spectra, obtained using an above-bandgap excitation laser (336–363 nm), are shown in Fig. 2. As with below-bandgap excitation, no PL signal was detected in the as-implanted sample. After annealing at 800°C, there was a broad PL signal centered at $\sim 1,530$ nm. The intensity of the PL spectrum increased with annealing at higher temperatures and became more indicative of the transitions between the $^4I_{13/2}$ and the $^4I_{15/2}$ manifolds. The PL signal reached a maximum after annealing at 1,050°C, and a detectable Er^{3+} -PL signal was present even after annealing at 1,100°C.

The PL spectra shown in Fig. 2 may be due to a different set of Er^{3+} complexes than the ones leading to

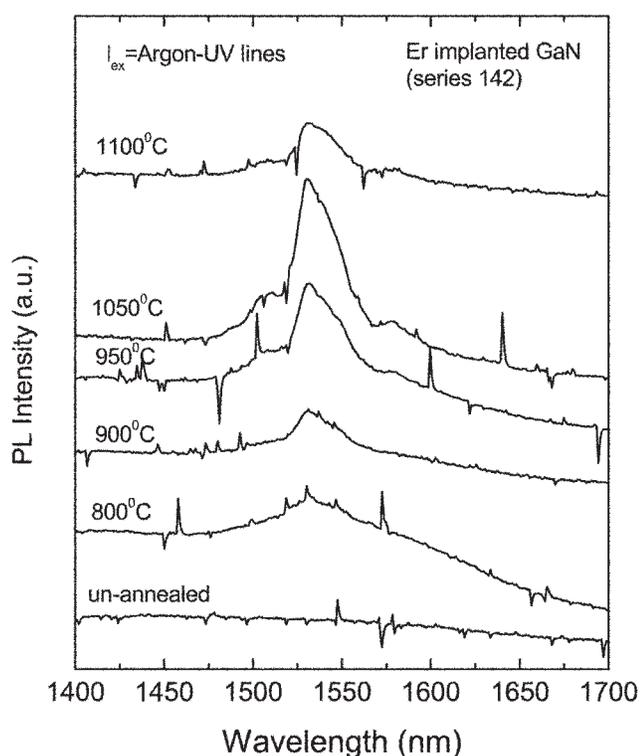


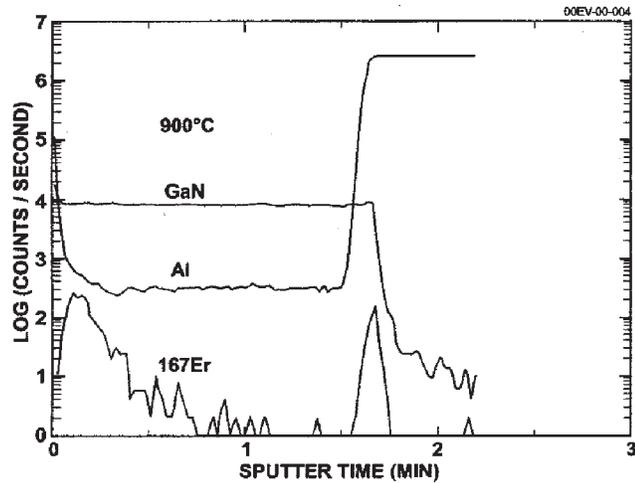
Fig. 2. The room-temperature PL spectra of Er + O-implanted GaN as a function of annealing temperature. The Er^{3+} ions were excited using a laser source (336–363 nm) corresponding to above-bandgap excitation. The spectra are displaced to permit easier viewing.

the spectra shown in Fig. 1. Because above-bandgap excitation produces a large number of electron-hole pairs, it is possible that several different Er^{3+} complexes may be excited in the process. However, the implantation-induced damage reduces the generation rate of electron-hole pairs and provides nonradiative-recombination channels. Consequently, the optimum-annealing temperature for above-bandgap excitation is likely to be different than that for below-bandgap excitation, and the spectra are likely to differ. Again, some minimum annealing temperature appears necessary to reduce the damage-related absorption to low enough levels to permit detection of the Er^{3+} spectra.

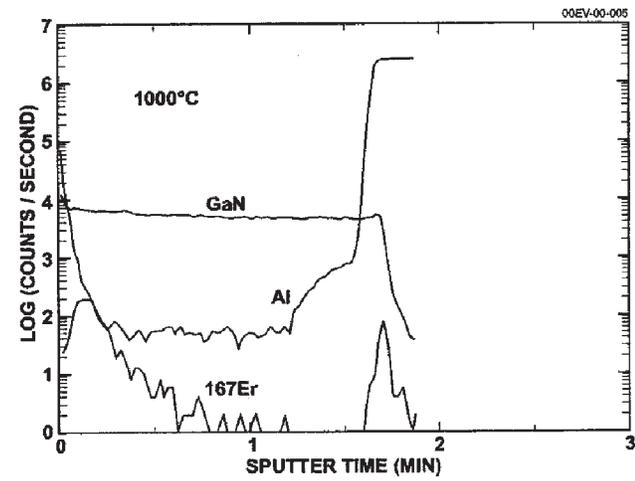
SECONDARY ION-MASS SPECTROSCOPY ANALYSIS

The SIMS profiles for Er, Al, and Ga atoms in the implanted-GaN film after annealing at 900°C, 1,000°C, and 1,100°C are shown in Fig. 3. The measurements were made using O_2^+ -ion bombardment and positive secondary-ion detection. The atomic profiles in Fig. 3a are nearly identical to those in the as-implanted film. The peak of the Er profile is at $\sim 0.1 \mu\text{m}$ with a maximum concentration of $\sim 2 \times 10^{19}/\text{cm}^3$. The Al profile is at the background level, and the accumulation at the surface is probably a SIMS artifact. After annealing at 1,000°C, the Er and Ga profiles (Fig. 3b) are still basically the same. However, the Al profile shows a definite shoulder at the film/substrate interface, indicating Al in-diffusion from the Al_2O_3 substrate. The Al concentration in this region is almost an order of magnitude higher than the background level. These changes are even more pronounced after annealing at 1,100°C. As shown in Fig. 3c, the peak-Al concentration is ~ 3 – 4 orders of magnitude higher than the background level, and Al atoms have reached to the surface. The Ga profile has also changed throughout the entire film. There appears to be a substitution of Al for Ga throughout most of the film. In addition, the Er profile has been slightly modified with some diffusion deeper into the film. At this stage, the basic character of the film has been changed; the stoichiometry is no longer that of GaN.

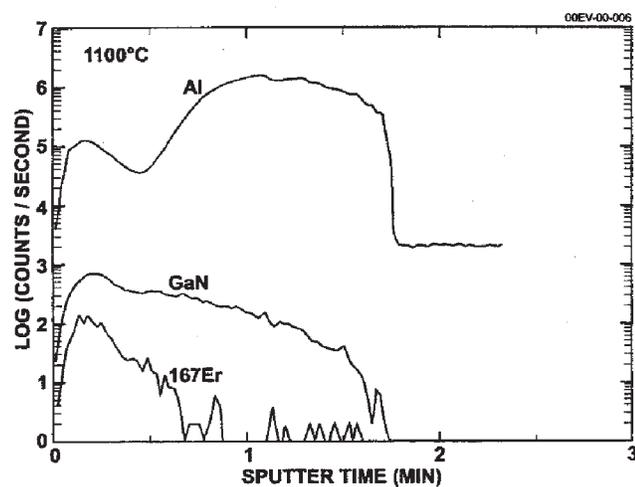
The data from SIMS measurements for the impurity elements O and C are shown in Fig. 4. These profiles were taken using Cs^+ -ion bombardment and negative secondary-ion detection. Following the annealing at 900°C, the Ga-atomic profile is nearly identical to the as-prepared profile. However, there are already high levels of O and C in the GaN film, as shown in Fig. 4a. The SIMS profiles indicate that these impurities have entered the film from the surface during annealing in the N ambient. The O and C in-diffusion is even more noticeable after annealing at 1,000°C. As shown in Fig. 4b, the O and C concentrations near the surface are ~ 3 – 4 orders of magnitude higher than the background levels. In addition, the increase in O and C levels is accompanied by a decrease in the Ga profile at the surface. After



a



b

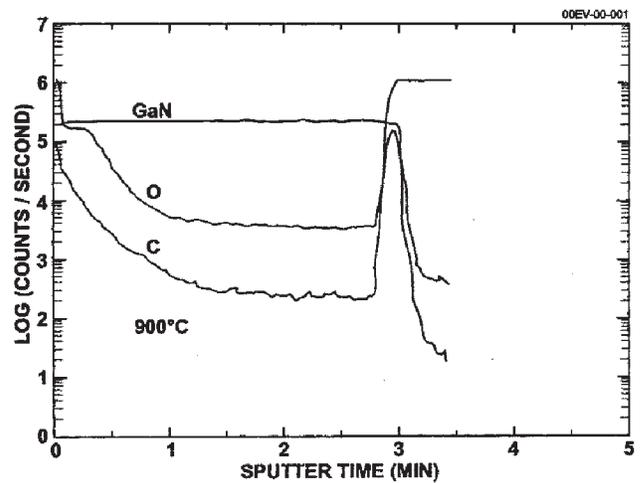


c

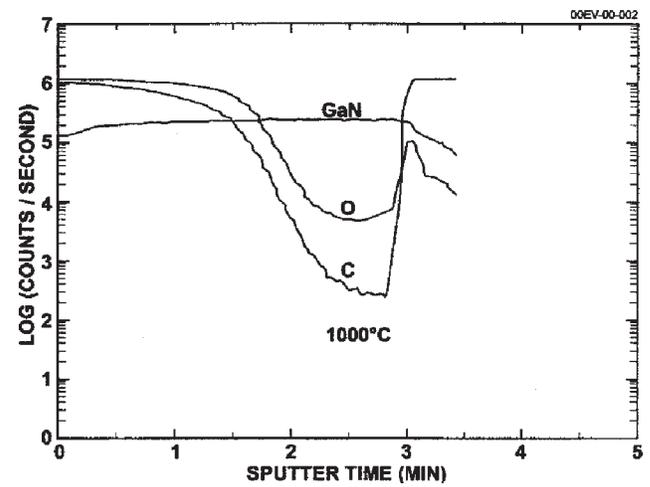
Fig. 3. The SIMS profiles for Er, Al, and Ga atoms in the implanted-GaN film after annealing at (a) 900°C, (b) 1,000°C, and (c) 1,100°C.

annealing at 1,100°C (Fig. 4c), the O and C impurities have penetrated through most of the GaN film, and there is a further decrease in Ga near the surface.

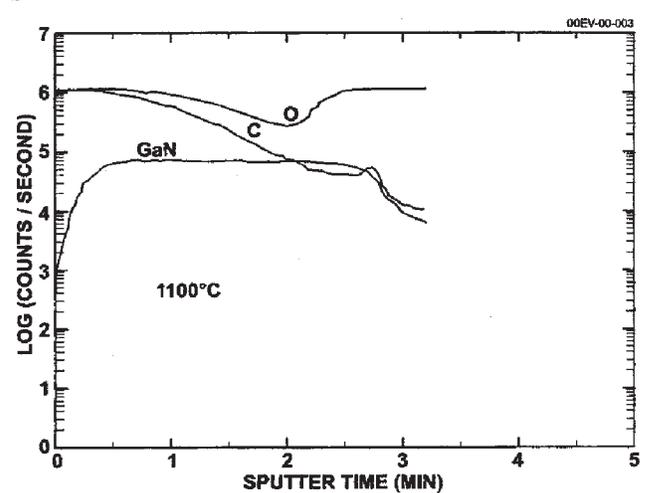
Based on these SIMS analyses, there are major changes in the composition of the GaN film with



a



b



c

Fig. 4. The SIMS profiles for the impurity elements O and C in the implanted-GaN film after annealing at (a) 900°C, (b) 1,000°C, and (c) 1,100°C.

annealing in an N ambient at temperatures above 900°C. High concentrations of O and C have entered the film from the surface and a large amount of Al from the sapphire substrate. After annealing at

1,100°C, there are such high concentrations of Al, O, and C within the GaN film that it is probably in some amorphous phase. On the other hand, the Er-atomic profile is nearly unchanged even after annealing at 1,100°C.

As a check on the validity of the data, SIMS measurements were performed on an unimplanted sample of GaN thin film grown on sapphire. Profiles for Ga atoms and the impurity elements Al, O, and C are displayed in Fig. 5. Following annealing at 900°C, the Ga-atomic profile is nearly identical to the as-prepared profile (Fig. 5a). In addition, the levels of O and C in the GaN film are quite low, indicating that these impurity elements have not entered the film from the surface during annealing as was the case with the implanted sample (Fig. 4a). Even after annealing at 1,100°C (Fig. 5b), the O and C concentrations within the film are still at the background levels. However, at this stage, there is evidence of Al and O in-diffusion from the Al₂O₃ substrate. The thin film/substrate interface has been degraded, and there is a shoulder in both the Al and O profile in this region (Fig. 5b). Nevertheless, the extent of impurity in-diffusion is significantly less than in the as-implanted film.

SUMMARY AND DISCUSSION

Ion implantation is a convenient method for doping GaN-semiconductor films with Er atoms. However, implantation with such a massive ion causes considerable damage to the GaN film. Coimplantation with O increases the damage, and postimplantation annealing is required to observe the infrared PL signal from the Er³⁺ ions. Only after annealing at 800°C was an Er³⁺ signal near 1,540 nm detectable at room temperature. Using below-bandgap excitation, the intensity of the Er³⁺-PL signal reached a maximum with annealing at 900°C. Annealing at higher temperatures resulted in a diminished-PL signal. With above-bandgap excitation, the intensity of the Er³⁺ PL reached a maximum with annealing at 1,050°C. Based on SIMS analysis, the Er-atomic profile was unchanged even after annealing at such high temperatures. However, annealing in an N ambient at temperatures above 900°C resulted in high concentrations of Al, O, and C being introduced into the film.

The model that emerges based on the data presented previously involves several stages. First, implantation produces damage to the crystal, and a wide number of sites are available for the implanted-Er atoms. Generation of electron-hole (e-h) pairs, with above-bandgap excitation, is greatly reduced at this stage, and numerous defects are present within the GaN crystal. Annealing at ~600°C leads to rearrangement of the Er ions whereby most are situated on the Ga sublattice,¹³ which is probably the preferred location for luminescence. However, the damage to the crystal has not been fully removed at this stage, and it is probable that there is significant optical absorption near 1,540 nm.

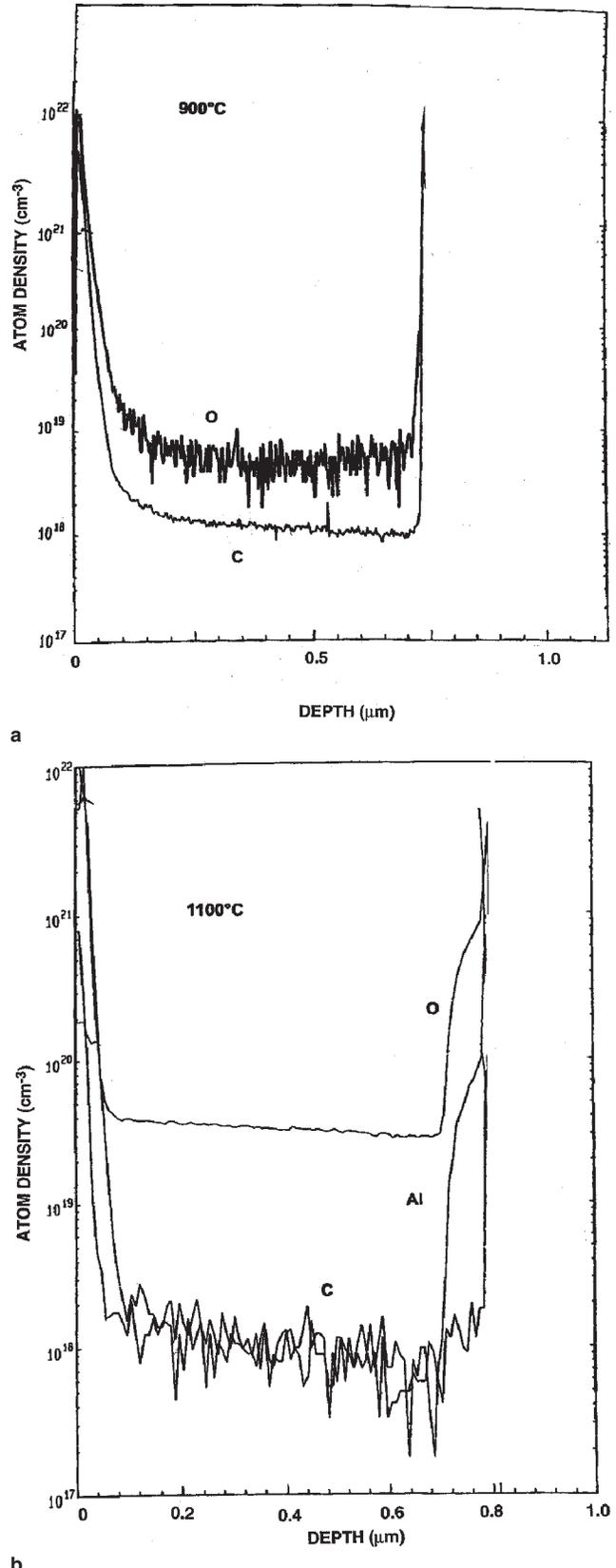


Fig. 5. The SIMS profiles for Ga atoms and the impurity elements Al, O, and C in an unimplanted-GaN film grown on sapphire: (a) unannealed and after annealing at 900°C and (b) after annealing at 1,100°C.

Annealing at $\sim 700\text{--}900^\circ\text{C}$ increases the e-h pair generation and reduces the optical absorption. At this stage, a PL signal at 1,540 nm can be observed with either above- or below-bandgap excitation. However, significant amounts of O and C have entered the film from the surface. Because these impurity elements tend to improve the below-bandgap excitation of Er,¹⁴ the Er signal increases, as shown in Fig. 1. For above-bandgap excitation, the increase in O and C levels in the Er-doped region has only a minor effect on the PL signal.

After annealing at $1,000^\circ\text{C}$, there are further increases in the O and C levels near the surface. At this stage, the Er signal with below-bandgap excitation begins to decrease. This may be due to a reduction in the defect levels within the bandgap that provide a channel for the Er excitation. With above-bandgap excitation, the Er signal rises at this stage. This may be due to an improved efficiency of e-h pair generation with higher annealing temperatures.

With annealing at $1,100^\circ\text{C}$, additional O and C impurities have entered the film. The Al has penetrated the entire film, and the Er profile shows some redistribution, as indicated in Fig. 3. The basic character of the film has been radically changed. Apparently, there are so many nonrecombination centers at this stage that no Er signal could be detected with below-bandgap excitation. With above-bandgap excitation, a small Er signal was still present. However, the film now contains a large mole fraction of Al, C, and O impurities. The optical absorption, the e-h pair generation, and the Er complexes have all been altered. Further annealing did not yield any improvement.

An important conclusion from these experiments is that stoichiometric degradation may occur with high-temperature annealing of GaN thin films grown on sapphire substrates. Impurity elements can enter the film either from the N ambient or from the substrate during annealing. This is especially true for GaN thin films that have been ion implanted. The surface damage created by implantation may be forming pathways that increase the impurity in-diffusion from the ambient. Protection of the surface may be afforded by

deposition of protective caps, such as SiN. However, in-diffusion of Al from the sapphire substrate may still occur with annealing at temperatures of $1,000^\circ\text{C}$ or higher. It may be necessary to use rapid-thermal annealing procedures to preserve the stoichiometric integrity of the GaN film for optoelectronic-device performance.

ACKNOWLEDGEMENTS

This work was supported in part by the U.S. Army Research Office.

REFERENCES

1. S.J. Pearton, *Mater. Sci. Rep.* 4, 313 (1990).
2. J.M. Zavada and D. Zhang, *Solid State Electron.* 38, 1285 (1995).
3. G.S. Pomeroy, P.B. Klein, and D.W. Langer, eds., *Rare Earth Doped Semiconductors I* (Pittsburgh, PA: Materials Research Society, 1993).
4. S. Coffa, A. Polman, and R.N. Schwartz, eds., *Rare Earth Doped Semiconductors II* (Pittsburgh, PA: Materials Research Society, 1996).
5. J. Zavada, T. Gregorkiewicz, and A.J. Steckl, eds., *Rare Earth Doped Semiconductors III* (Amsterdam, Elsevier, 2001).
6. R.G. Wilson, R.N. Schwartz, C.R. Abernathy, S.J. Pearton, N. Newman, M. Rubin, T. Fu, and J.M. Zavada, *Appl. Phys. Lett.* 65, 992 (1994).
7. J. Michel, J.L. Benton, R.F. Ferrante, D.C. Jacobson, D.J. Eaglesham, E.A. Fitzgerald, Y. Xie, J.M. Poate, and L.C. Kimerling, *J. Appl. Phys.* 70, 2672 (1991).
8. J.E. Colon, D.W. Elsaesser, Y.K. Yeo, R.L. Hengehold, and G.S. Pomeroy, *Mater. Res. Soc. Symp. Proc.* 301, 169 (1993).
9. J.T. Torvik, R.J. Feuerstein, C.H. Qui, M.W. Leksono, F. Namavar, and J.I. Pankove, *Mater. Res. Soc. Symp. Proc.* 422, 199 (1996).
10. R.G. Wilson, F.A. Stevie, and C.M. Magee, *Secondary Ion Mass Spectrometry: A Practical Guide for Depth Profiling and Bulk Impurity Analysis* (New York: Wiley, 1989).
11. S. Kim, S.J. Rhee, D.A. Turnbull, E.E. Reuter, X. Li, J.J. Coleman, and S.G. Bishop, *Appl. Phys. Lett.* 71, 231 (1997).
12. M. Thaik, U. Hömmerich, R.N. Schwartz, R.G. Wilson, and J.M. Zavada, *Appl. Phys. Lett.* 71, 2641 (1997).
13. E. Alves, M.F. DaSilva, J.C. Soares, J. Bartels, R. Vianden, C.R. Abernathy, S.J. Pearton, *MRS Internet J. Nitride Semicond. Res.* 4S1, G11.2 (1999).
14. U. Hömmerich, J.T. Seo, M. Thaik, J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, R.G. Wilson, and J.M. Zavada, *MRS Internet J. Nitride Semicond. Res.* 4S1, G11.6 (1999).