Journal of Electronic Materials

SAND2014-17634J

The reduction in the number of Mg acceptors with Al concentration in AlxGa1-xN

--Manuscript Draft--

Manuscript Number:	
Full Title:	The reduction in the number of Mg acceptors with Al concentration in AlxGa1-xN
Article Type:	S.I. : EMC 2014
Keywords:	nitride; p-type; GaN; Mg; magnetic resonance
Corresponding Author:	Ustun Sunay Birmingham, AL UNITED STATES
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	
Corresponding Author's Secondary Institution:	
First Author:	Ustun Sunay
First Author Secondary Information:	
Order of Authors:	Ustun Sunay
	M E Zvanut, PhD
	A A Allerman, PhD
Order of Authors Secondary Information:	
Abstract:	High hole concentrations in AlxGa1-xN become increasingly difficult to obtain as the Al mole fraction increases. The problem is thought to be related to compensation, extended defects, and the band gap of the alloy. While electrical measurements are commonly used to measure the hole density, the present work utilizes electron paramagnetic resonance (EPR) spectroscopy to probe a defect related to the neutral Mg acceptor. The amount and symmetry of neutral Mg in MOCVD grown AlxGa1-xN with x=0 to 0.28 was monitored in films with varying dislocation densities and surface conditions. EPR measurements indicate that the amount of neutral Mg decreased by 60% in 900 oC annealed AlxGa1-xN films for x=0.18 and 0.28 as compared to x=0.00 and 0.08. A decrease in the angular dependence of the EPR signal accompanied the increased x, suggesting a change in the Mg local environment. Neither dislocation density nor anneal conditions contribute to the decreased amount of neutral Mg in samples with the higher Al concentration. Rather, compensation is the simplest explanation for the observations because a donor could both decrease the number of neutral acceptors as well as effect the variation in the angular dependence.
Suggested Reviewers:	Alan Doolittle
	Dave Look
	Gary Gerardi
	Leonard Brillson

The reduction in the number of Mg acceptors with Al concentration in $Al_xGa_{1-x}N$

U.R. Sunay[1], M.E. Zvanut[1], and A.A. Allerman[2]

[1] Department of Physics, University of Alabama at Birmingham, 1530 3rd Ave S, 35294-1170 Birmingham, USA
[2] Sandia National Laboratory, 1515 Eubank S.E., 81723 Albuquerque, USA

Abstract

High hole concentrations in $Al_xGa_{1-x}N$ become increasingly difficult to obtain as the Al mole fraction increases. The problem is thought to be related to compensation, extended defects, and the band gap of the alloy. While electrical measurements are commonly used to measure the hole density, the present work utilizes electron paramagnetic resonance (EPR) spectroscopy to probe a defect related to the neutral Mg acceptor. The amount and symmetry of neutral Mg in MOCVD grown $Al_xGa_{1-x}N$ with x=0 to 0.28 was monitored in films with varying dislocation densities and surface conditions. EPR measurements indicate that the amount of neutral Mg decreased by 60% in 900 °C annealed $Al_xGa_{1-x}N$ films for x=0.18 and 0.28 as compared to x=0.00 and 0.08. A decrease in the angular dependence of the EPR signal accompanied the increased x, suggesting a change in the Mg local environment. Neither dislocation density nor anneal conditions contribute to the decreased amount of neutral Mg in samples with the higher Al concentration. Rather, compensation is the simplest explanation for the observations because a donor could both decrease the number of neutral acceptors as well as effect the variation in the angular dependence.

Introduction

GaN, together with the alloys $Al_xGa_{1-x}N$ and $In_xGa_{1-x}N$, have a variety of applications in optoelectronics and high power, high frequency device electronics. Unfortunately, there are many materials problems plaguing the advancement of nitride-based technology. One issue is the compensation of Mg, the only effective acceptor, through unintentional incorporation of impurities such as Si, O, and possibly nitrogen vacancies or carbon [1, 2,3]. For nitride films grown by a chemical vapor deposition method, hydrogen incorporation during growth is an additional concern because hydrogen passivates the Mg acceptor. A post-growth thermal anneal in a nitrogen-rich ambient is required to remove the hydrogen and activate the acceptor [1]. Another problem plaguing all nitride-based materials is the dislocation density, which is several orders of magnitude higher than that found in traditional semiconductors like Si or GaAs. Additional issues specific to $Al_xGa_{1-x}N$ alloys are the increase in oxygen incorporation during growth [4,5] and the decrease in hole concentration due to increasing acceptor ionization energy with increasing Al mole fraction [3,4].

The problems listed above are often investigated by monitoring hole densities using electrical techniques. For example, the dependence of acceptor level on Al mole fraction is determined from temperature-dependent Hall measurements [6]. The total amount of Mg is also monitored using techniques such as secondary ion mass spectroscopy (SIMS). Pertinent to the present work, Parish and coworkers used SIMS measurements to demonstrate that the amount of compensating oxygen increases as the number of holes decreases in high Al percentage $Al_xGa_{1-x}N$ [5]. While measurements of the hole density and impurity concentrations are directly relevant to device applications, the studies do not directly probe the neutral Mg impurity, the charge state of the acceptor necessary to generate the holes. Photoluminescence studies provide some insight, but they cannot quantitatively monitor changes in Mg concentration. To address these limitations, we use electron paramagnetic resonance (EPR) spectroscopy, which directly probes the amount and charge state of a defect known to be related to the Mg acceptor. Since the technique detects only those centers with an 'unpaired' electron, the passivation by hydrogen or compensation by donors appears as a decrease in the EPR signal intensity.

Several studies have identified an EPR center associated with Mg in GaN. For example, Glaser and co-workers show that the number of centers is approximately the same as the total Mg concentration as measured by SIMS [7]. In addition, angular dependent EPR measurements indicate axial symmetry, as expected for the Mg acceptor in the hexagonal lattice. A series of hydrogen and nitrogen annealing studies suggest that the EPR detected centers may be passivated and activated as expected for the neutral acceptor in GaN [6]. Based on these studies, the EPR signal seen in p-type nitrides is referred to as the Mg-related acceptor. It is important to note that the EPR spectral finger print represents the neutral state of the acceptor, with the hole on the Mg rather in the valence band. While there are many magnetic resonance studies of p-type nitrides, only a few reports exists which address the critically important p-type alloys, AlGaN or InGaN. The present work investigates the effects of Al alloying on the amount the neutral Mg-related acceptors and the changes induced in the local environment of the impurity.

Experimental Details

Mg-doped $Al_xGa_{1-x}N$ samples were grown 0.4-0.5 µm thick by metal-organic chemical vapor deposition with x ranging from 0.08 to 0.28. The films were grown on two different templates during the same growth run. One template consisted of a 2.7 µm thick undoped $Al_{0.3}Ga_{0.71-x}N$ layer grown on a 1.3 µm thick AlN layer on a sapphire substrate. These films have a dislocation density of 3-5x10^9 cm^{-2}, and are referred to here as low dislocation density (LDD) samples. The other template consisted of a 0.8 µm thick undoped $Al_{0.3}Ga_{0.71-x}N$ layer grown on a 0.3 µm thick AlN layer on a sapphire substrate. These films have a dislocation density of ~2x10^{10} cm^{-2}, and are referred to here as high dislocation density (HDD) samples. The dislocation of the AlGaN layer was controlled by changing the growth process of the AlN layer on sapphire. The sheet resistance of the undoped AlGaN templates exceeded 100kohm/sqr. confirming the templates had no intrinsic conductivity. Composition and threading dislocation density were determined by x-ray diffraction measurements of symmetric (00.2) and asymmetric (10.1) reflections [8]. To study surface effects, a second set of samples grown by the same method as those described above were capped with a 10 nm P+ GaN layer. As a control for this study, two Mg-doped GaN samples were grown on 3 µm of undoped GaN on sapphire. Sample 1, 0.9 um thick, was capped with a 5 nm film doped with twice the conconcentration of Mg as in the films. The second is 0.5 µm thick and has no cap. Impurity and dislocation densities measured in the various samples are listed in Table 1.

Two different annealing methods were used to activate the samples. One consisted of a thermal heat treatment in a conventional tube furnace with flowing 99.999% pure dry (< 1 ppm H_20) N_2 at temperatures from 300-900 ^oC for 30 min (300-825 ^oC) or 15 min (850-900 ^oC). After the samples were annealed, they were quenched to approximately 150 ^oC and remained in a cooling zone for 15 min with dry N_2 flowing. The other process was a rapid thermal anneal (RTA) at 900 ^oC in high purity N_2. All of the samples listed in Table 1, both capped and uncapped, were furnace annealed. Separate wafers, with low dislocation $Al_xGa_{1-x}N$ and no cap received a RTA.

9.4 GHz EPR spectroscopy measurements were performed at 4 K with the c-axis rotated in the plane of the magnetic field. Relative EPR intensities were obtained by comparing EPR peak-to-peak heights for each sample to that found in RTA sample 1. They are typically accurate to within 5%. The total number of centers was obtained by comparison of the spectra to that obtained from a standard, a Si:P powder. The concentrations reported in Table 1 were determined assuming a uniform distribution of centers and have an accuracy of no more than a factor of two.

One of the characteristics of an EPR signal is the g-factor, where the values are obtained from the equation

$$g = {}^{hf}/_{\mu_b B_o} \qquad \text{Eq. 1}$$

Here h is Plank's constant, f is the microwave frequency, and μ_b is the Bohr magneton. EPR spectra are recorded as the derivative of absorption [9]. Therefore, the magnetic field at resonance, $B_{o,}$ which is defined as the point of maximum absorption, is obtained where the spectral intensity passes through zero. In general, g is a second rank tensor, but due to the symmetry of the Mg-related EPR site in GaN only two unique parameters, $g_{||}$, and $g_{\perp}$, are required to fully describe the defect. The former is found when the principle axis is parallel to the magnetic field, and the latter is determined at perpendicular orientation. Defining θ as the angle between the magnetic field and the principle axis, which is the c-axis for Mg in GaN, the angular dependence of g is described by

$$g = \sqrt{g_{\parallel}^2 \cos^2(\theta) + g_{\perp}^2 sin^2(\theta)}. \qquad \text{Eq. 2}$$

The variable Δg, defined as $g_{\parallel} - g_{\perp}$, is used to quantify the range of the angular dependence.

Results

The Mg-related EPR signals for $Al_xGa_{1-x}N$ samples which received the rapid thermal anneal are shown in Fig. 1a with the magnetic field parallel (solid), 30° (dashed) and 90° (dotted) from the c-axis. Comparison of spectra for x=0 (i), x=0.08 (ii) and x=0.18 (iii) show that both the intensity and the angular dependence of the signal varies with the percentage of Al in the alloy. Using Eq. 1, g-values are obtained from the zero crossings as the sample is rotated with the c-axis in the plane of the magnetic field. The results are plotted in Fig. 1b for x=0 (filled squares), x=0.08 (unfilled circles), x=0.18 (unfilled stars), and x=0.28 (filled triangles). As expected, the data reflect axial symmetry about the c-axis; however, as x increases Δg decreases from 0.093(x=0) to 0.037 (x=0.08). For higher x, Δg varies by no more than 0.0015, which is within the resolution of the measurement. We report the g-values for the x=0.18 film as 2.010 for x=0.28 as 2.014.

The data shown in figure 1 form the central conclusion of this work. The reduction in the signal intensities seen in Figure 1a indicate that the number of neutral Mg-related acceptors decreases with increasing Al mole fraction. In figure 1b, Δg is seen to decrease from 0.093 in GaN to approximately zero for the x=0.18 $Al_xGa_{1-x}N$ films, indicating a change in the local environment of the center. Consideration of both the change in the magnitude and angular dependence of the EPR signal is necessary to form an understanding of the effect of Al on the Mg-related acceptor.

The effect of Al on the angular dependence has been observed by others studying $Al_xGa_{1-x}N$ for x= 0 to 0.12 [10], and was reported in our earlier studies of $Al_xGa_{1-x}N$ films grown on AlN/$Al_{0.3}Ga_{0.7}N$ superlattices [11]. In the former work, the change in Δg in $Al_xGa_{1-x}N$ was attributed to the increase in average bond strength which accompanies the formation of AlN. However, other factors likely contribute also since Δg is known to vary significantly for the Mg-related acceptor seen in nominally similar GaN films. In general, the crystal field ultimately determines the g value, so that local strain and/or near neighbor charged defects could alter the crystal field and decrease Δg [10,12]. In the present work, the reduction in the intensity of the Mg-related acceptor signal suggests that charged defects, which act as compensating centers, may be partially responsible. The increase of donors, such as nitrogen vacancies and oxygen, with Al incorporation supports the compensation hypothesis [3,4]. However, as indicated by the differences between the total Mg measured by SIMS and Mg-related acceptor detected by EPR (Table 1), the number of such compensating centers must be similar to the number of acceptors to account for the decreasing EPR signal intensity obtained in our work.

Despite the increase in oxygen with increasing Al seen in Table 1, the amount remains at least an order of magnitude smaller than what is needed to effect the observed changes in the neutral Mg concentration. Nitrogen vacancies, on the other hand, are predicted to have a formation energy less than that for neutral Mg and could provide efficient compensation [13,14]. Once compensated, the charged acceptors and donors could perturb the crystal field near the remaining neutral Mg and reduce Δg, as observed. Unfortunately, V_N has not yet been conclusively observed experimentally, and the number of vacancies is difficult to predict from the formation energy. However, below we show that other potential mechanisms cannot account for our observations. Specifically, dislocation density, surface conditions, and annealing procedure do not affect the number or angular dependence of Mg-related acceptors. The presence of compensating impurities, on the other hand, is consistent with both the reduction of Δg and neutral acceptor density.

One of the most common concerns in nitrides that could affect the density of the acceptor centers are dislocations. Threading dislocations decorated by Mg could alter the defect structure of the acceptor and eliminate the EPR signal. Typically, electrical studies address the effect of dislocations on conductivity or mobility [15,16]. Here, we investigate whether threading dislocations influence the amount of Mg-related acceptors, which ultimately determine the conductivity. Two sets of $Al_xGa_{1-x}N$ films with low and high dislocation densities were activated by annealing over a range of temperatures. The relative intensity of the EPR signal for $x=0.08$ (squares), $x=0.18$ (stars), and $x=0.28$ (triangles) are shown in Fig. 2. As expected, the EPR signal increases with increased anneal temperature as the acceptors are activated by removal of hydrogen. EPR intensities obtained from samples with low (filled symbols) and high (unfilled symbols) dislocation density are seen to deviate from one another by no more than the accuracy of the measurement (± 5%), except for the $x=0.28$ sample in the temperature range 800-825 ^{o}C. The discrepancy between LDD and HDD at these temperatures may be an artifact caused by inaccuracies in the background subtraction for small signals. For the remainder of the data, for all temperature, the number of Mg-related acceptors in the $x=0.18$ and 0.28 films is less that that seen in films with $x = 0.08$. A similar trend is observed when monitoring the intensity of the Mg-related acceptor signal during isothermal anneals performed at temperatures between 700 and 900 ^{o}C for times up to 60 min. Thus, modifying anneal conditions does not eliminate the reduced acceptor density. Furthermore, the Mg-related EPR signal intensity decreases as Al increases for both HDD and LDD samples, showing that dislocations are not responsible for the decrease in the number of Mg-related acceptors.

The effect of Al mole fraction on the concentration of neutral Mg is clearly illustrated in Figure 3 for a variety of different conditions. The figure shows the relative amount of acceptors extracted from a comparison of the EPR signal in 900 ^{o}C annealed GaN and the three different $Al_xGa_{1-x}N$ samples. In Fig. 3a, the furnace annealed samples (unfilled triangles, LDD; unfilled stars, HDD) are compared with films which were activated by a conventional 5 min 900 ^{o}C RTA (filled squares). Clearly, the 60% decrease in acceptor density is not dependent on the detailed anneal conditions. Since hydrogen diffusion in GaN is thought to be significantly affected by surface conditions, samples were studied in which the surface was intentionally altered by growing a 10 nm thick P+ layer on top of the $Al_xGa_{1-x}N$ film. Figure 3b shows the relative intensity of the Mg-related EPR signals from $Al_xGa_{1-x}N$ after a RTA of capped (filled circles) and uncapped (unfilled square) samples. The Mg-related signal decreases as Al increases in both capped and uncapped samples. The only significant change is seen in x=0.18 $Al_xGa_{1-x}N$ where the amount of neutral Mg differs by at least a factor of two between the capped and uncapped samples. The difference in neutral Mg concentration for x=0.18 is consistently seen in the HDD, LDD, furnace annealed, and RTA samples. The apparent effect of surface conditions for 18% Al alloys is not yet clear.

In summary, the EPR study has shown that the number of neutral Mg-related acceptors decreases by more than 60% in $Al_xGa_{1-x}N$ films as x increases from 0 to 0.28. In addition, the angular dependence of the g factor reduces to zero as the Al percentage increases. Annealing studies indicate that the trend does not depend on the activation procedure. Further, the data indicate that dislocation density does not contribute to the decreased amount of neutral Mg in samples with the higher Al concentration, and surface conditions alter only samples with 18% Al. Compensation is the simplest explanation for the observations because a donor could both decrease the number of neutral acceptors as well as effect the variation in the angular dependence. Since SIMS measurements indicate that O concentrations are too low to explain the significant difference between neutral and total Mg in samples with high Al fraction, the nitrogen vacancy is suggested as the donor. However, additional studies are required to determine whether a sufficient number could be generated to account for decrease in neutral Mg indicated by the EPR data.

Acknowledgements This work is funded by the National Science foundation DMR1006163. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under Contract No. DE-AC04-94AL85000.

References

[1] S.Nakamura, N. Iwasa, M. Senoh, and T. Mukai, Jpn. J Appl. Phys. **31**, Pt. 1 1258 (1992)

[2] M. D. McCluskey, N. M. Johnson, C. G. Van de Walle, D. P. Bour, and M. Kneissl, Phys. Rev. Lett. **80** 4008 (1998)

[3] C. Stamphfl and C.G. Van de Walle, Phys. Rev. B **65** 155212 (2002)

[4] J. Kim, E. Waldron, and Y. Li et al., Appl. Phys. Lett. **84**, 3310 (2004)

[5] G. Parish, S. Keller, S.P. Denbaars, and U.K. Mishra, J. Electron. Mater. **3**, 15 (2000)

[6] A. Y. Polyakov, N. B. Smirnov, A. V. Govorkov, E. A. Kozhukhova, A. M. Dabiran, P. P. Chow, A. M. Wowchak,
In-Hwan Lee, Jin-Woo Ju, and S. J. Pearton, J. Appl. Phys. 106, 073706 (2009)

[7] E.R. Glaser, W. E. Carlos, G.C.B. Braga, J.A. Freitas, Jr. W.J. Moore, B.V. Shanabrook, R.L. Henry, A.E. Wickenden, and D.D. Koleske, Phy. Rev. **B65**, 085312 (2002)

[8] S. R. Lee, A. M. West, A. A. Allerman, K. E. Waldrip, D.M. Follstaedt, P. P. Provencio, D. D. Koleske and C. R. Abernathy, Appl. Phys. Lett. **86** (2005) 241904

[9] John A. Weil and James R. Bolton, Electron Paramagnetic Resonance: Elementary Theory and Particle Applications, 2nd edn., (John Wiley & Sons, Inc., Hoboken, 2007) pp. 6-7

[10] H. Alves, F. Leiter, D. Pfisterer, D.M. Hofmann, B.K. Meyer, S. Einfeld, H. Heinke, and D. Hommel, Phys. Stat. Sol. **C 0**, 1770 (2003)

[11] M.E. Zvanut, U.R. Sunay, J. Dashdorj, W.R. Willoughby, and A.A. Allerman, in: Proceedings SPIE, San Francisco, USA, 2012, **8262** (SPIE, Bellingham, 2012), pp. 82620L-1 – 82620L-6

[12] G.N.Aliev, S. Zeng, J.J. Davies, D. Wolverson, and S.J. Bingham, Phys. Rev. B **71** 195204 (2005)

[13] John L. Lyons, Anderson Janotti, and Chris G. Van de Walle, Phys. Rev. Lett. **108**, 156403 (2012)

[14] Qimin Yan, Anderson Janotti, Matthias Scheffler, and Chris G. van de Walle, Appl. Phys Lett. **100** 142110 (2012)

[15] Stephen W. Kaun, Man Hoi Wong, Umesh K. Mishra, James S. Speck, Appl. Phys. Lett. **100**, 262102 (2012)

[16] Wong, Yuen-Yee et. al., J. Elect. Chem Soc. **157** (7) H746 (2010)

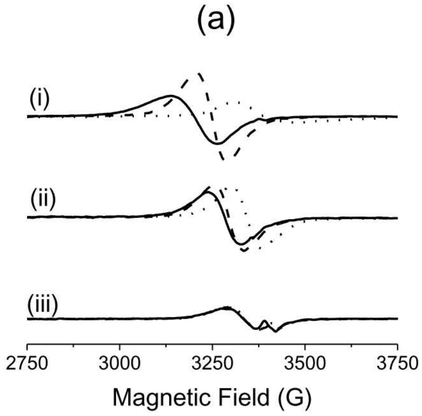

Fig 1(a) 4 K Mg-related EPR spectra of RTA $Al_xGa_{1-x}N$ with the magnetic field oriented at 0° (solid), 30° (dashed), and 90° (dotted) from the c-axis for (i) x=0, (ii) x=0.08, (iii) x=0.18.

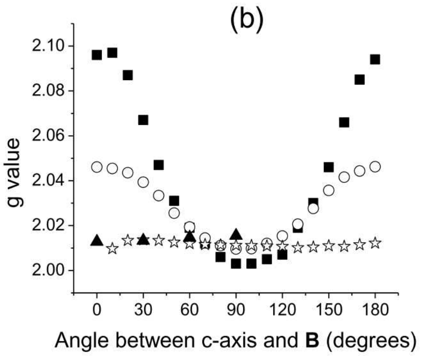

Fig 1(b) g values obtained from RTA $Al_xGa_{1-x}N$ for x=0 (filled squares), x=0.08 (unfilled circles), x=0.18 (unfilled stars), x=0.28 (filled triangles).

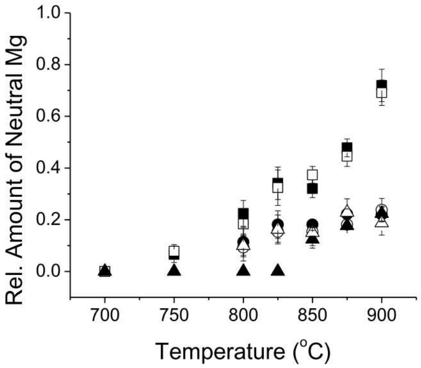

Fig 2 Relative intensity of EPR signals after N_2 anneals for 30 min (300-825 °C) or 15 min (850-900 °C) of LDD (filled symbols) and HDD (unfilled symbols) $Al_xGa_{1-x}N$ for x=0.08 (squares), x=0.18 (stars), x=0.28 (triangles).

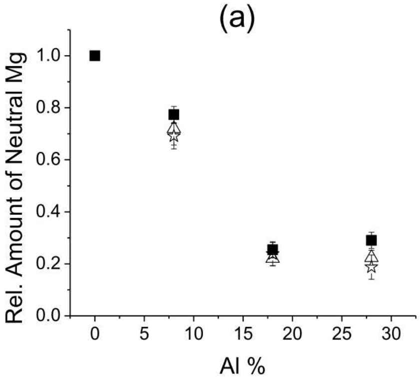

Fig 3(a) Relative intensity of Mg-related EPR signals from $Al_xGa_{1-x}N$ after 15 min 900 ^oC N_2 anneal for LDD (unfilled triangle) and HDD (unfilled star), and RTA LDD (filled square) samples.

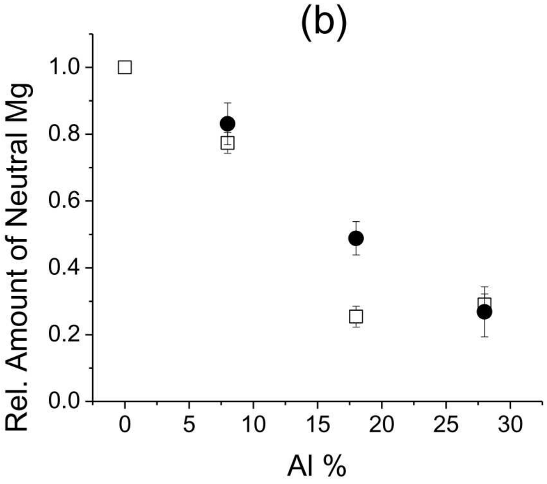

Fig 3(b) Relative intensity of Mg-related EPR signals from $Al_xGa_{1-x}N$ after RTA of uncapped (unfilled square) and capped (filled circle) samples.

Sample number	Al%	Dislocations (10^9 cm^{-2})	EPR Mg (10^{19} cm^{-3})	SIMS Mg (10^{19} cm^{-3})	O (10^{16} cm^{-3})
1	0	2-3	1.5±0.8	4	3
2	0	14		4*	
3	8	3-5	1.4±0.7	2-3*	
4	8	20		2-3	15
5	18	3-5	0.5±0.2	2-3*	
6	18	20		2-3*	
7	28	3-5	0.5±0.3	2-3*	
8	28	20		2-3	30

Table 1 List of all the samples used in this study. SIMS was performed on samples 1, 4, and 8. *Samples were grown in a similar fashion and are expected to have similar Mg concentration as x=0.08 and x=0.28. Two wafers of samples 3-8 were grown: one with a 10 nm P+ GaN capping layer and one without the cap.