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The effects of Al on the neutral Mg acceptor impurity in $Al_xGa_{1-x}N$

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Received ZZZ, revised ZZZ, accepted ZZZ
Published online ZZZ (Dates will be provided by the publisher.)

Keywords AlGaN, Mg-doping, activation, EPR

High hole concentrations in $Al_xGa_{1-x}N$ become increasingly difficult to obtain as the concentration of Al increases. It is well known in GaN and related alloys that hole concentration is directly affected by compensation and extended defects. Using electron paramagnetic resonance (EPR) spectroscopy, we studied the amount of neutral Mg in $Al_xGa_{1-x}N$ with x = 0 to 0.28. 0.4-0.9 μm thick Mg-doped $Al_xGa_{1-x}N$ films were grown by metal-organic chemical vapour deposition and annealed at 900 °C anneal in N_2. EPR measurements indicate that the amount of neutral Mg decreased by 60% in $Al_xGa_{1-x}N$ films for x =0.18 and 0.28 as compared to x=0.00 and 0.08. Experiments also showed that the lower neutral Mg for higher Al compositions trend did not depend on threading dislocation densities in the range of 3-20x10^9 cm^{-2}, capping the surface with 5 nm of P+ GaN, or detailed annealing conditions. Additional studies show that oxygen and carbon concentrations are insufficient to account for the decrease in neutral Mg observed in the samples. Although the study cannot isolate the cause for the decrease in neutral Mg, the results clearly demonstrate that the acceptor concentration decreases with increasing Al, providing an additional limitation to achieving high hole densities.

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1 Introduction GaN and its alloys have a variety of applications in optoelectronics, most notably light emitting diodes. Al or In is added to GaN for tuning the bandgap so that a wide range of wavelengths can be achieved [1]. Unfortunately, there are many problems plaguing GaN advancement. One is the compensation of the acceptor site through unintentional incorporation of impurities such as H, Si, O, and possibly nitrogen vacancies or carbon [2-4]. Another concern is that high dislocation densities in GaN can affect device efficiency [5]. A partial solution to the first problem is a post-growth thermal anneal in a nitrogen or oxygen rich environment at a sufficiently high temperature [2]. This process drives out hydrogen and "activates" the Mg sites, making the Mg neutral and the GaN p-type .Two additional problem specific to $Al_xGa_{1-x}N$ alloys is the increase in oxygen [6,7] and the decrease in hole concentration due to increasing acceptor ionization energy with increasing Al mole fraction.

Electron paramagnetic resonance (EPR) is a use-ful way to characterize the acceptor in GaN because the spectroscopy probes the local environment of a specific charge state of an impurity. In p-type GaN, for example, an EPR signal is commonly detected which reflects a de-fect related to the neutral Mg acceptor [8]. However, cen-ters passivated by impurities such as hydrogen produce no EPR signal. Another benefit of EPR spectroscopy is that the intensity of the signal is proportional to the total amount of spins within a sample. For p-type nitrides this corresponds to the amount of neutral Mg-related acceptors. Although the acceptor in GaN has been heavily studied, less is known about the role of Mg in $Al_xGa_{1-x}N$. Our work investigates the effect of Al alloying on the number of neutral Mg acceptors.

2 Experimental Details

2.1 Samples 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. These films were deposited on a template consisting of a 2.7 μm undoped $Al_{0.3}Ga_{0.71-x}N$ layer on a sapphire substrate. These films had a dislocation density of 3-5x10^9 cm^{-2}, and are referred to here as low dislocation density (LDD) samples. In addition, identical growth conditions were used to grow films with higher dislocation density (2x10^{10} cm^{-2}), by growing on a 1.3 μm thick AlN layer. These are referred to as high dislocation density (HDD). Composition and threading dislocation density were determined by x-ray diffraction measurements of symmetric (00.2) and asymmet-

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ric (10.1) reflections [9]. 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 0.5 um thick (sample 1) and 0.9 μm thick (sample 2) on 3 μm of undoped GaN on sapphire. The 0.9 μm thick sample was capped with a 5 nm film doped with 6-8x10^{19} cm^{-3} Mg.

Table 1 lists all the samples used in this study. Secondary ion mass spectroscopy (SIMS) experiments were performed on samples 1, 4, and 8. The Mg concentration in other samples in this study are expected to range between 2-4 x10^{19} cm^{-3}.

Table 1 List of samples used in study

Sample number	Al%	Mg Concentration (10^{19} cm^{-3})	O Concentration (10^{16} cm^{-3})	Dislocation Density (10^{9} cm^{-2})
1	0	4	3	2-3
2	0	4*		14
3	8	2-3*		3-5
4	8	2-3	15	20
5	18	2-3*		3-5
6	18	2-3*		20
7	28	2-3*		3-5
8	28	2-3	30	20

*Samples were grown in a similar fashion and are expected to have similar Mg concentration as x=0.08 & x=0.28.

2.2 Annealing Procedure Two different annealing procedures were used to activate the Mg in the as-grown samples. For one, annealing was performed in a conventional tube furnace with flowing 99.999% pure dry (< 1 ppm H_20) N_2 at temperatures from 300-900 ^oC. After the samples were annealed, they were quenched to approximately 150 ^oC and remained in cooling zone for 15 min with dry N_2 flowing. The second type of anneal is a 5 min rapid thermal anneal (RTA) at 900 ^oC in high purity N_2. Only LDD uncapped samples received a RTA.

2.2 EPR Parameters 9.4 GHz EPR spectroscopy was performed at 4 K with the c-axis rotated in the plane of the magnetic field. Measurements were taken after each anneal and the double integral of the spectral intensity was compared to a calibrated Si:P powder to obtain the amount of activated Mg. The concentrations quoted below assume a uniform distribution of centers, and have an accuracy of no more than a factor of two. Relative EPR intensities are typically accurate to within 5%. They were obtained by comparing EPR peak-to-peak height for each sample to that found in RTA sample 1.

3 Results and Discussion The Mg-related EPR signal is shown in Fig. 1 for $Al_xGa_{1-x}N$:Mg samples with x=0.00 (a), 0.08 (b), and 0.28 (c) after a 900 ^oC 15 min N_2 anneal. The additional signal seen around 3400 G in (a) and (c) originate from the sample tube.

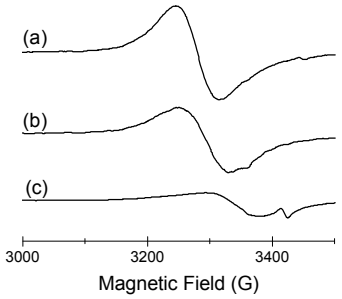

Figure 1 Mg-related EPR signal measured in $Al_xGa_{1-x}N$ for (a) x=0.00, (b) x=0.08, and (c) x=0.28 after a 900 ^oC 15 min N_2 anneal. Measurements were made at 3.5 K with the c axis oriented at an angle of 30^o with respect to the magnetic field.

The concentration of defects related to neutral Mg is shown as the unfilled red circles in Figure 2, where the decrease in EPR intensity seen in Fig. 1 is reflected by the 60% drop in the concentration of neutral Mg for samples with the x > 0.08. Also shown are the SIMS results for Mg (filled black squares). Unlike the EPR detected neutral Mg, the total amount of Mg differs among the samples by no more than the uncertainty of the SIMS measurement. Thus, the data suggest that the fraction of total Mg incorporated as neutral acceptors decreases as Al is added to the films.

Earlier investigations by others indicate that unintentional incorporation of O and C increases as the Al mole fraction increases [7]. Separate studies suggest that the increase in O contributes to the decrease of free carriers [6] due to compensation of the Mg acceptor. Prompted by such conclusions, O and C were measured by SIMS for three of the $Al_xGa_{1-x}N$ samples. Figure 2 shows that, as expected, both impurities increase with x. However, the concentration of O is at least an order of magnitude less than that of the neutral Mg detected by EPR. Thus, although introduction of O may compensate some of the Mg sites. As suggested by Kim and co-workers, the concentration of O in these samples is not high enough to account for the difference between total Mg and neutral Mg-related acceptors.

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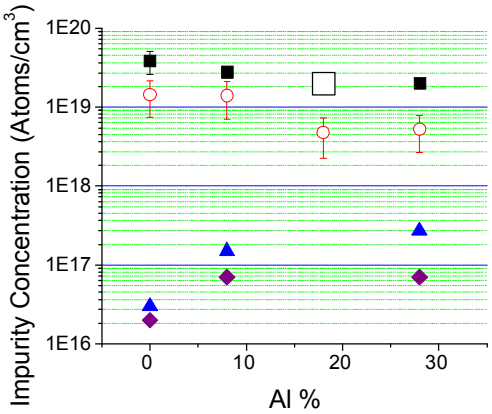

Figure 2 Concentration of Mg (filled black squares), O (filled blue triangles), and C (filled green diamonds) obtained from SIMS on 900 °C 15 min N_2 annealed samples and Mg-related (unfilled red circles) from EPR analysis on RTA $Al_xGa_{1-x}N$:Mg samples. The unfilled black square represents an estimated Mg concentration based on SIMS for $Al_{0.18}Ga_{0.82}N$ samples grown under similar conditions.

The effect of threading dislocations was investigated as a possible cause of the decrease in Mg concentration with Al incorporation. Fig. 3 shows relative intensities of the Mg-related EPR signal for three sets of samples: 900 °C RTA films with low dislocation density (green triangles) and furnace annealed films with low (3-5x10^9 cm^{-2}) and high (2x10^{10} cm^{-2}) dislocation density. The furnace anneals were performed at 900 °C for 15 min. The Mg-related EPR signal intensity decreases as Al increases in all 3 sets. The data illustrate two significant points. First, a variation in the threading dislocation density by a factor of at least 4 does not alter the number of neutral Mg acceptors in each sample. Second, the detailed annealing procedures in this study do not affect the resulting number of neutral acceptors. The last point is further emphasized by the results of isochronal and isothermal annealing experiments, which were performed between 300 and 900 °C until the Mg-related EPR intensity approached saturation at each temperature. Throughout the anneals, the EPR intensity in high (x=0.18, 0.28) Al mole fraction films was consistently at less than that in the low (x=0.00, 0.08) Al samples.

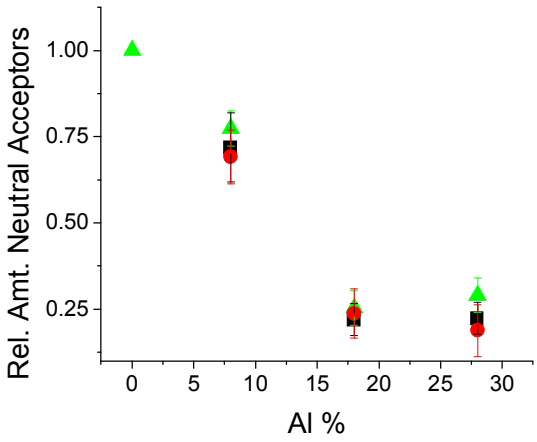

Figure 3 Relative Mg-Related EPR intensities in $Al_xGa_{1-x}N$ samples after a 15 min 900 °C N_2 Furnace anneal for LDD (black), HDD (red), and RTA samples (green triangles).

Removal of hydrogen from the nitride surface is the critical step in activating Mg acceptors. Hence we compared the concentration of neutral Mg in uncapped AlGaN samples to those capped with a P+ GaN layer. Although the additional surface layer tended to increase the amount of neutral Mg in all samples, in most cases the increase was within the uncertainty of the measurement. However, in the 18% Al film, an increase by as much as a factor of two was seen. Even considering this singular increase, the presence of a p-type GaN capping layer did not alter the trend seen in Figure 3 showing that the amount of neutral Mg decreases for samples with high Al fraction. This suggests that changes in the film surface do not have a significant effect on the amount of activated Mg in $Al_xGa_{1-x}N$.

Although the investigations discussed here do not determine why the number of Mg-related centers decrease as Al concentration increases, angular dependent EPR data reported earlier hints at a possible cause [10, 11]. Data extracted from rotation of an EPR sample with the c-axis in the plane of the magnetic field provides information about the symmetry and local environment of the defect. For the samples studied here, the angular variations in the spectra gradually reduce as the Al fraction increases. Such behavior suggests that Al perturbs the Mg site. Further discussion of this topic will be reported in a future publication.

In summary, this 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 is increases from 0 to 0.28. SIMS measurements indicate that O and C concentrations are too low to explain the significant difference between neutral Mg and total Mg in high Al samples, and exhaustive annealing studies indicate that the trend is not altered by modified annealing procedures. Further, the data indicate that neither dislocation density nor surface conditions

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contribute to the decreased amount of neutral Mg in samples with the higher Al concentration.

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.

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