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Reduction in the Number of Mg Acceptors with Al Concentration in $Al_xGa_{1-x}N$

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High hole concentrations in $Al_xGa_{1-x}N$ become increasingly difficult to obtain as the Al mole fraction increases. The problem is believed to be related to compensation, extended defects, and the band gap of the alloy. Whereas electrical measurements are commonly used to measure hole density, in this work we used electron paramagnetic resonance (EPR) spectroscopy to investigate 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 for films with different dislocation densities and surface conditions. EPR measurements indicated 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 with $x = 0.00$ and 0.08. A decrease in the angular dependence of the EPR signal accompanied the increased x, suggesting a change in the local environment of the Mg. Neither dislocation density nor annealing conditions contribute to the reduced amount of neutral Mg in samples with the higher Al concentration. Rather, compensation is the simplest explanation of the observations, because a donor could both reduce the number of neutral acceptors and cause the variation in the angular dependence.

Key words: Nitride, *p*-type, GaN, Mg, magnetic resonance

INTRODUCTION

GaN, and 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, many materials problems are limiting advances in nitride-based technology. One issue is the compensation of Mg, the only effective acceptor, by unintentional incorporation of such impurities as Si, O, and possibly nitrogen vacancies or carbon.[1–3] For nitride films grown by chemical vapor deposition, hydrogen incorporation during growth is an additional concern, because hydrogen passivates the Mg acceptor. Post-growth thermal annealing in a nitrogen-rich atmosphere is required to remove the hydrogen and activate the acceptor.[1] Another problem of all nitride-based materials is the dislocation density, which is several orders of magnitude higher than that found in such traditional semiconductors as Si or GaAs. Other 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, because of increasing acceptor ionization energy with increasing Al mole fraction.[3,4]

These problems are often investigated by monitoring hole densities by use of 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 by use of such techniques as secondary ion mass spectroscopy (SIMS). Pertinent to this work, Parish et al. used SIMS measurements to demonstrate that the amount of compensating oxygen increases as the number of holes decreases in $Al_xGa_{1-x}N$ with a high percentage of Al.[5] Although measurements of hole density and impurity concentrations are directly relevant to device applications, the studies do not directly investigate

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the neutral Mg impurity or the charge state of the acceptor necessary to generate the holes. Photoluminescence studies provide some insight, but they cannot be used for quantitative monitoring of changes in Mg concentration. To address these limitations, we used electron paramagnetic resonance (EPR) spectroscopy, which enables direct investigation of the amount and charge state of a defect known to be related to the Mg acceptor. Because the technique detects only those centers with an "unpaired" electron, 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 et al. show that the number of centers is approximately the same as the total Mg concentration as measured by SIMS.[7] In addition, angle-dependent EPR measurements are indicative of axial symmetry, as expected for the Mg acceptor in the hexagonal lattice. A series of hydrogen and nitrogen annealing studies suggested that the EPR-detected centers may be passivated and activated as expected for the neutral acceptor in GaN.[6] On the basis of these studies, the EPR signal obtained for *p*-type nitrides is referred to as that from the Mg-related acceptor. It is important to note that the EPR spectral profile represents the neutral state of the acceptor, with the hole on the Mg rather than in the valence band. Although many magnetic resonance studies have been conducted on *p*-type nitrides, few reports address the critically important *p*-type alloys, AlGaN, or InGaN. In this work we investigated the effects of Al alloying on the amount of neutral Mg-related acceptors and the changes induced in the local environment of the impurity.

MATERIALS AND METHODS

Mg-doped $Al_xGa_{1-x}N$ samples, with x ranging from 0.08 to 0.28, were grown 0.4–0.5 μm thick by metal–organic chemical vapor deposition. 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 3–5 $\times 10^9$ 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 $\sim 2 \times 10^{10}$ 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 100 kohm/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 was capped with a 10 nm P + GaN layer. As a control for this study, two Mg-doped GaN samples were grown on 3 μm undoped GaN on sapphire. Sample 1, 0.9 μm thick, was capped with a 5-nm film doped with twice the concentration of Mg as in the films. The second was 0.5 μm thick and had no cap. Impurity and dislocation densities measured for the different samples are listed in Table I.

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

EPR spectroscopy measurements (9.4 GHz) 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 with that found in RTA sample 1. These are typically accurate to within 5%. The total number of centers was obtained by comparison of the spectra with that obtained from a standard, Si:P powder. The concentrations reported in Table I were determined assuming uniform distribution of centers; the accuracy is no more than a factor of two.

One of the characteristics of an EPR signal is the *g*-factor, values of which are obtained by use of the equation:

$$g = hf/\mu_b B_o. \quad (1)$$

where h is Plank's constant, f is the microwave frequency, and μ_b is the Bohr magneton. EPR spectra were 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, because of the symmetry of the Mg-related EPR site in GaN, only two unique values, $g_{||}$, and $g_\perp$, are required to fully describe the defect. The former is obtained when the principle axis is parallel to the magnetic field, and the latter is obtained when the orientation is perpendicular. 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:

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

Table I. The samples used in this study. SIMS was performed on samples 1, 4, and 8

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 ± 0.75	4	3
2	0	14		4[a]	
3	8	3–5	1.4 ± 0.7	2–3[a]	
4	8	20		2–3	15
5	18	3–5	0.475 ± 0.238	2–3[a]	
6	18	20		2–3[a]	
7	28	3–5	0.526 ± 0.263	2–3[a]	
8	28	20		2–3	30

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

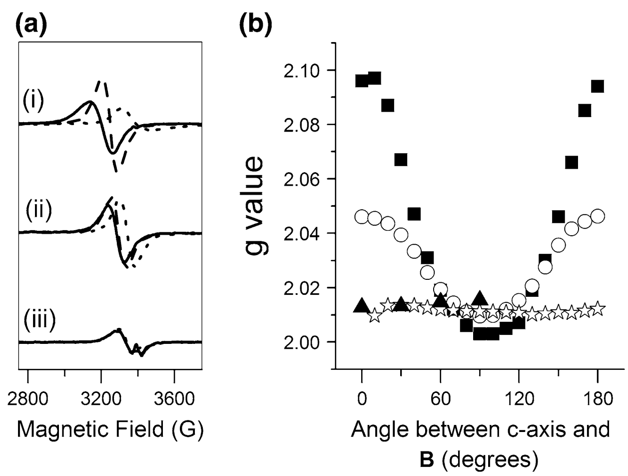

Fig. 1. (a) 4 K Mg-related EPR spectra of RTA $Al_xGa_{1-x}N$ with the magnetic field oriented at 0° (solid), 30° (dashed), and 90° (dotted) to the c-axis for (i) $x = 0$, (ii) $x = 0.08$, and (iii) $x = 0.18$. (b) g values obtained from RTA $Al_xGa_{1-x}N$ for $x = 0$ (filled squares), $x = 0.08$ (unfilled circles), $x = 0.18$ (unfilled stars), and $x = 0.28$ (filled triangles).

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

RESULTS AND DISCUSSION

The Mg-related EPR signals for $Al_xGa_{1-x}N$ samples treated by rapid thermal annealing are shown in Fig. 1a with the magnetic field parallel to (solid), and at 30° (dashed) and 90° (dotted) to 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; as x increases, however, 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 g-values for the $x = 0.18$ film as 2.010 and for $x = 0.28$ as 2.014.

The results shown in Fig. 1 lead to the central conclusion of this work. The reduction in the signal intensities seen in Fig. 1a indicate that the number of neutral Mg-related acceptors decreases with increasing Al mole fraction. In Fig. 1b, Δg is seen to decrease from 0.093 in GaN to approximately zero for $x = 0.18$ $Al_xGa_{1-x}N$ 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 enable 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 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 for $Al_xGa_{1-x}N$ was attributed to the increase in average bond strength which accompanies the formation of AlN. However, other factors likely contribute also, because Δg is known to vary substantially for the Mg-related acceptor 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 reduce Δg.[10,12] In our current 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, for example 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 acceptors detected by EPR (Table I), 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 I, the amount remains at least an order of magnitude smaller than that needed to cause 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.

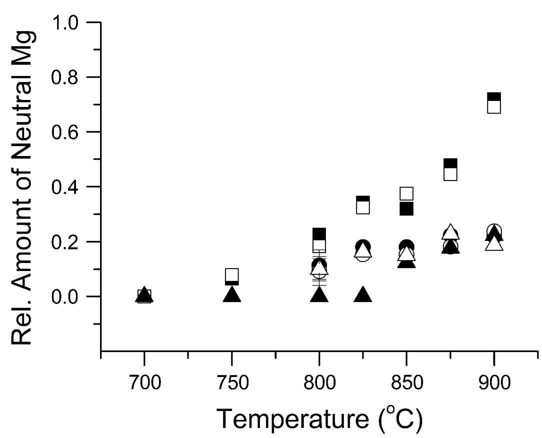

Fig. 2. Relative intensity of EPR signals after N_2 annealing for 30 min (300–825°C) or 15 min (850–900°C) for LDD (filled symbols) and HDD (unfilled symbols) $Al_xGa_{1-x}N$ for $x = 0.08$ (squares), $x = 0.18$ (stars), $x = 0.28$ (triangles).

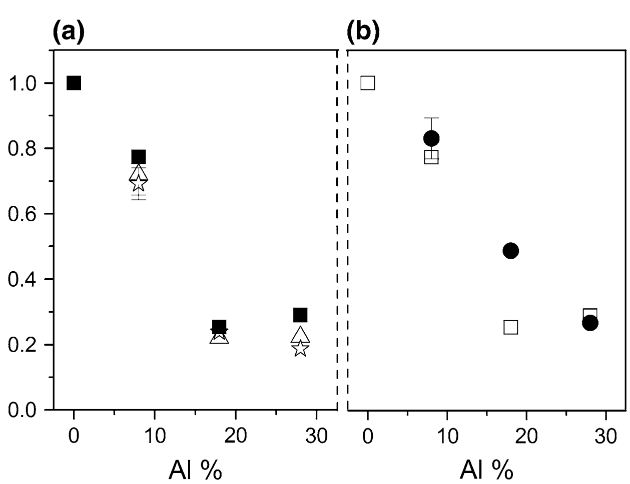

Fig. 3. (a) Relative intensity of Mg-related EPR signals from $Al_xGa_{1-x}N$ after annealing for 15 min at 900°C under N_2 for LDD (unfilled triangles) and HDD (unfilled stars) samples. RTA GaN (filled squares) is included as a reference. (b) Relative intensity of Mg-related EPR signals from $Al_xGa_{1-x}N$ after RTA of uncapped (unfilled squares) and capped (filled circles) samples.

One of the most common concerns about 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 affect the number 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 intensity of the EPR signal for $x = 0.08$ (squares), $x = 0.18$ (stars), and $x = 0.28$ (triangles) is shown in Fig. 2. As expected, the EPR signal increases with increasing annealing 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°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 other data, for all temperatures, the number of Mg-related acceptors in the $x = 0.18$ and 0.28 films is less that in films with $x = 0.08$. A similar trend is observed when monitoring the intensity of the Mg-related acceptor signal during isothermal annealing performed at temperatures between 700 and 900°C for times up to 60 min. Thus, modifying the annealing 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 Fig. 3 for a variety of different conditions. The figure shows the relative amount of acceptors extracted from a comparison of the EPR signal from 900°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°C RTA (filled squares). Clearly, the 60% decrease in acceptor density is not dependent on the detailed annealing conditions. Because hydrogen diffusion in GaN is believed 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 RTA of capped (filled circles) and uncapped (unfilled square) samples. The Mg-related signal decreases as Al increases for both capped and uncapped samples. This trend agrees with the results obtained from uncapped superlattice $Al_xGa_{1-x}N$ films subjected to a series of activation and passivation annealing.[11] The only significant change is seen for $x = 0.18$ $Al_xGa_{1-x}N$, for which the amount of neutral Mg differs by at least a factor of two for 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, this 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 percentage of Al 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 reduced 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 reduce the number of neutral acceptors and cause the variation in the angular dependence. Because SIMS measurements indicate that O concentrations are too low to explain the significant difference between neutral and total Mg in samples with a 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.

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