Magnesium incorporation in GaN grown by molecular-beam epitaxy

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A pronounced dependence of Mg incorporation on surface polarity was observed in a series of Mg step-doped epitaxial GaN layers grown by rf-plasma-assisted molecular-beam epitaxy. Incorporation was studied for both (0001), or Ga-polarity and $(000\bar{1})$ or N-polarity orientations. Up to a factor of 30 times more Mg was incorporated in Ga-polarity layers under certain conditions, as determined by secondary ion mass spectrometry. Measurements indicate surface accumulation of Mg occurs during growth, with stable accumulations of close to a monolayer of Mg on the Ga-polarity surface. The presence of atomic hydrogen during growth significantly increased incorporation of Mg without also incorporating potentially compensating hydrogen. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1339255]

At present, the only technologically feasible *p*-type dopant for GaN is Mg, which exhibits a large thermal activation energy of ~200 meV.[1] This results in the ionization of only a few percent of the acceptor atoms at room temperature. Thus, large concentrations of Mg are required to achieve the *p*-type conductivity necessary for many device applications. Further complications occur when Mg is used as the *p*-type dopant for metalorganic chemical vapor deposition (MOCVD) growth of GaN since the Mg must be activated by either electron irradiation[2] or thermal annealing,[3] which dissociates Mg–H complexes to electrically activate the Mg. In addition, the high growth temperatures (>1000 °C) and severe ''Mg memory'' effect in MOCVD growth lead to broad doping profiles, making careful junction placement difficult.[4]

Molecular beam epitaxy (MBE) is an alternate growth technique that may ameliorate these problems. For example, high *p*-type activation in as-grown MBE GaN layers has recently been reported for conditions that also give sharp interfaces.[4] While there have been several studies of Mg doping during MBE growth of GaN,[5–7] many effects remain poorly understood. In addition, both (0001), or Ga polar, and $(000\bar{1})$, or N polar, GaN can be grown by MBE depending upon the nucleation conditions. The different surface polarities can yield vastly different results, with some researchers obtaining *p*-type conduction with Mg only for Ga polarity.[6]

Our study of Mg incorporation indicates there is a significant difference in Mg incorporation between Ga-and N-polar surfaces. This difference can explain many of the puzzling results obtained for Mg doping by MBE, particularly when combined with Mg-induced surface polarity inversion. Our results also provide strong evidence that surface segregation of Mg occurs during growth. In addition, we report results supporting theoretical predictions[8] that hydrogen enhances Mg incorporation in GaN.

Mg-doped GaN layers were grown by rf plasma-assisted MBE using an EPI Unibulb nitrogen plasma source. Conventional effusion cells were used for Ga and Mg. N-polarity GaN was obtained by nucleating GaN buffer layers directly onto sapphire.[9] Incorporation in Ga-polarity GaN was studied by growth on MOCVD GaN templates on (0001) sapphire substrates. The doped layers were grown at a rate of 0.25 μm/h, which corresponds to a nitrogen flow rate of 0.85 sccm and rf power of 200 W. The samples were grown under Ga-stable conditions that result in high quality GaN growth.[9–11] Mg step-doped structures were produced by sequentially opening and closing a Mg shutter. Importantly, the *in situ* growth rate was monitored using laser interferometry, allowing a precise correlation between source shuttering and Mg incorporation profiles. All changes in oven and substrate temperatures occurred with the Mg shutter closed. Atomic hydrogen was produced using a thermal cracker (EPI-AHS, EPI Vacuum Products, Inc.). Secondary ion mass spectrometry (SIMS) determination of Mg and H concentrations was performed at Charles Evans and Associates (Sunnyvale, CA).

Figure 1 contains the SIMS measurement of the Mg concentration profile for a Ga-polarity Mg step-doped structure. The general features observed in this profile are representa-

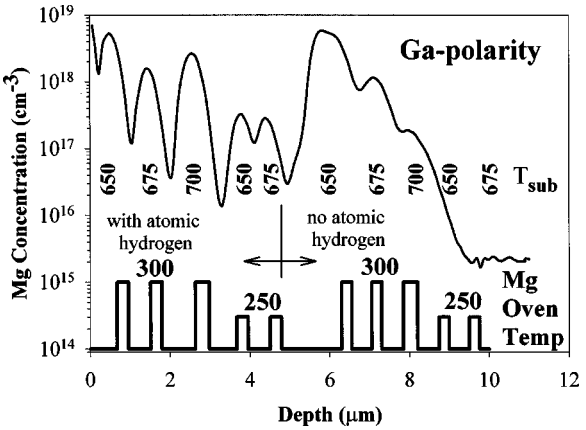

FIG. 1. Mg concentration in a Ga-polarity step-doped GaN layer. The Mg shutter opening and closing are shown schematically.

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TABLE I. Mg concentrations [Mg] for various growth and doping conditions. The [Mg] dependence on polarity (the last two columns) is compared for similar growth conditions from layers grown in similar time periods. Comparison of Mg incorporation for growth with and without atomic H is also given (ND: Not detected.)

Film	T_{sub}	T_{Mg}	Surface polarity	[Mg]	[Mg]:H	[Mg] ratio with/ without H	[Mg] Ratio between Ga/N polarity	
							Without H	With H
9942	705	250	N	ND	ND			
	705	300	N	1.0×10^{18}	2.0×10^{18}	2.0		
	705	350	N	4.5×10^{18}	6.0×10^{18}	1.3		
	705	400	N	8.0×10^{18}	1.0×10^{19}	1.3		
9950	700	350	Ga	7.0×10^{19}	2.0×10^{20}	2.9	16[a]	33[a]
	725	350	Ga	9.0×10^{18}	2.3×10^{19}	2.6		
9973	650	250	N	ND	8.1×10^{16}	>200		
	675	250	N	ND	1.0×10^{17}	>250		
	650	300	N	3.3×10^{17}	2.1×10^{17}	0.6		
	675	300	N	2.3×10^{17}	5.4×10^{17}	2.3		
	700	300	N	6.5×10^{16}	5.9×10^{17}	9.1		
9974	650	250	Ga	ND	3.3×10^{17}	>165		4.1[b]
	675	250	Ga	ND	2.8×10^{17}	>140		2.8[b]
	650	300	Ga	5.8×10^{18}	5.3×10^{18}	0.9	18[b]	25[b]
	675	300	Ga	1.1×10^{18}	1.5×10^{18}	1.4	4.8[b]	2.8[b]
	700	300	Ga	1.9×10^{17}	2.7×10^{18}	14	2.9[b]	4.6[b]

[a]Comparison between films 9950 and 9942.
[b]Comparison between films 9974 and 9973.

tive of all the structures investigated. The opening and closing of the Mg shutter are indicated schematically along the bottom of Fig. 1, with the associated Mg oven temperature listed. By monitoring the growth rate throughout layer growth and by combining with other chemical markers measured in SIMS, the correlation with the shutter is accurate within an uncertainty of 100 nm. The various substrate temperatures investigated are also listed in the appropriate regions. A summary of the results measured for all the Mg step-doped structures is given in Table I.

Several features are immediately obvious. First, at the lower Mg oven temperatures and higher substrate temperatures there is no evidence of Mg incorporation. It does appear that Mg may start to incorporate for a Mg oven temperature of 250 °C and a substrate temperature of 650 °C, but at a gradually increasing rate rather than an abrupt onset. Mg is seen to incorporate at larger Mg flux, with strong substrate temperature dependence as reported previously.[7] A key feature is that incorporation is out of phase with the opening and closing of the shutter, with the peak in incorporation occurring either when or after the Mg shutter was closed. This is shown for the most significant cases in Fig. 2 for nitrogen-polarity and gallium-polarity growth. Note that significant amounts of Mg are incorporated **after** the Mg shutter was closed, strongly indicative of surface segregation and accumulation of Mg. Indeed, for the Ga-polar growth shown in Fig. 2(b) the SIMS result indicates that approximately 3.3×10^{14} Mg atoms/cm^2 were incorporated after the shutter was closed, corresponding to between 1/4 and 1/2 monolayer of Mg on the surface of the growing layer. This is consistent with calculations[12,13] which predict stable surface configurations involving either 1/4 or 3/4 monolayers of Mg in substitutional sites on the GaN surface. By assuming about a monolayer of Mg on the surface, the measured concentration would indicate approximately 3×10^{-4} of the Mg incorporates into each monolayer of growth while the remainder segregates to the new surface. This fraction is quite close to the number of surface sites available for capturing Mg atoms estimated previously through indirect means to be $\sim5\times10^{-4}$ using a surface segregation model for similar growth conditions.[14] Other reported evidence for surface accumulation of Mg for Mg-doped GaN has been based on Auger spectroscopy of layers after growth[15] and on the observation that Mg acts as a persistent surfactant for the growth of GaN.[16] In the latter case, the surfactant effect of Mg remains for a significant period of time after closing the Mg shutter, indicating that Mg remains on the surface in the absence of Mg flux.

Of particular interest are the results summarized in Table I that also indicate a strong dependence of Mg incorporation on surface polarity for identical growth conditions. In par-

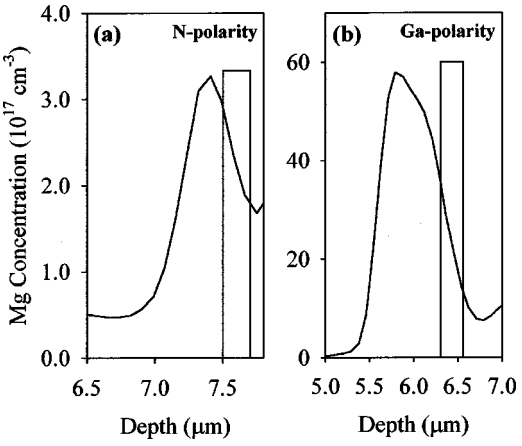

FIG. 2. Mg concentration profiles for (a) N polarity and (b) Ga polarity exhibiting evidence of surface accumulation layers. The Mg shutter opening and closing are shown schematically. Both layers were grown at a substrate temperature of 650 °C and a Mg source temperature of 300 °C.

ticular, at higher Mg flux and growth temperatures, Mg incorporation is found to be approximately 15–20 times less for N-polar GaN. A significant difference was observed for each set of comparable conditions examined, with larger incorporation always occurring for the Ga polarity.

Lower Mg-incorporation rates for N-polar material explains one of the puzzling results obtained for large Mg flux conditions associated with Ga-polarity growth. The presence of greater than a monolayer of Mg on the Ga-polarity GaN surface during growth results in the surface inverting to N polarity.[13] SIMS measurement of a Ga-polarity step-doped sample indicated a dramatic **decrease** in Mg incorporation, from $\sim 10^{20}$ to $\sim 10^{18}\,\mathrm{cm}^{-3}$, upon increasing the Mg oven temperature from 350 to 400 °C. The latter oven temperature should result in a flux of approximately 1 monolayer/s or greater of Mg arriving at the surface of the growing sample in our system. Subsequent transmission electron microscopy characterization indicated inversion from Ga to N polarity occurred when the growing layer was exposed to this large Mg flux.[17] That is, the large Mg flux at the growing surface led to polarity inversion, which then resulted in a dramatic decrease in Mg incorporation since the sample was now N polarity. Thus, the decrease in electrical activation reported previously[4,5] for a large Mg flux on Ga-polar material can be understood in terms of surface polarity inversion followed by reduced Mg incorporation. Additionally, this polarity-dependent incorporation is consistent with the lower electrical activation observed for N-polar growth compared to Ga-polar growth for the same growth conditions.[6]

The results shown in Fig. 1 and Table I also represent verification of the prediction[8] that the presence of hydrogen will enhance Mg incorporation. Without hydrogen, no incorporation was observed for low Mg flux. The addition of atomic hydrogen caused incorporation at levels more consistent with higher Mg flux incorporation rates. The effect of hydrogen on maximum Mg incorporation was less pronounced at higher Mg flux or lower substrate temperature. Atomic hydrogen has little effect or may slightly lower the maximum incorporation at 650 °C for reasonable Mg flux. Although diffusion effects are also present in our samples, the presence of atomic hydrogen appeared to sharpen the interfaces. However, the profiles still indicate that surface accumulation layers form, suggesting that the increase in sharpness is due to enhanced incorporation as opposed to the suppression of surface accumulation. Note also that while hydrogen generally enhances incorporation for both polarities, it does not eliminate the polarity dependence of Mg incorporation and in most cases accentuates this effect. SIMS indicated that, while hydrogen significantly increases Mg incorporation, hydrogen itself is not incorporated at significant levels. That is, if hydrogen is incorporated at the growing surface, it anneals out during growth at the temperatures used.

The concentration profiles of the Mg step-doped structures show the effects of both surface accumulation and diffusion during the long growth times used. Although complicated by the surface accumulation effects, analysis of the profiles yields an estimate for an upper limit of the Mg diffusion coefficient. For growth temperatures between 650 and 700 °C, we estimate the Mg diffusion coefficient to be about $1\times 10^{-15}\,\mathrm{cm}^2/\mathrm{s}$, which is large enough that Mg diffusion may be of concern in the growth of multilayer structures.

In conclusion, a dramatic difference for Mg incorporation rates was observed between the N- and Ga-polarity surfaces during Mg doping of GaN by rf-plasma MBE. The decrease in electrical activation previously reported for higher Mg flux conditions during doping of Ga-polar material can now be understood in terms of a combination of surface polarity inversion coupled with the lower incorporation rate for N-polarity GaN. Difficulties in Mg doping of N-polarity GaN can also be better understood in terms of the reduced incorporation rate. The presence of hydrogen was shown to enhance Mg incorporation rates for most growth conditions. Strong evidence for surface accumulation of Mg was also observed.

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[1] W. Gotz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, Appl. Phys. Lett. **68**, 667 (1996).
[2] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **28**, L2112 (1989).
[3] S. Nakamura, T. Mukai, and M. Senoh, Jpn. J. Appl. Phys., Part 2 **30**, L1998 (1991).
[4] I. P. Smorchkova, E. Haus, B. Heying, P. Kozodoy, P. Fini, J. P. Ibbetson, S. Keller, S. P. Den Baars, J. S. Speck, and U. K. Mishra, Appl. Phys. Lett. **76**, 718 (2000).
[5] M. A. L. Johnson, Z. Yu, C. Boney, W. C. Hughes, J. W. Cook, Jr., J. F. Schetzina, H. Zhao, B. J. Skromme, and J. A. Edmond, Mater. Res. Soc. Symp. Proc. **449**, 215 (1997).
[6] L. K. Li, M. J. Jurkovic, W. I. Wang, J. M. Van Hove, and P. P. Chow, Appl. Phys. Lett. **76**, 1740 (2000).
[7] S. Guha, N. A. Bojarczuk, and F. Cardone, Appl. Phys. Lett. **71**, 1685 (1997).
[8] J. Neugebauer and C. G. Van de Walle, Phys. Rev. Lett. **75**, 4452 (1995).
[9] T. H. Myers, L. S. Hirsch, L. T. Romano, and M. R. Richards-Babb, J. Vac. Sci. Technol. B **16**, 2261 (1998).
[10] A. R. Smith, V. Ramachandra, R. M. Feenstra, D. W. Greve, A. Ptak, T.Myers, W. Sarney, L. Salamanca-Riba, M. Shin, and M. Skowronski, MRS Internet J. Nitride Semicond. Res. **3**, 12 (1998).
[11] E. J. Tarsa, B. Heying, X. H. Wu, P. Fini, S. P. DenBaars, and J. S. Speck, J. Appl. Phys. **82**, 5472 (1997).
[12] C. Bungaro, K. Rapcewicz, and J. Bernholc, Phys. Rev. B **59**, 9771 (1999).
[13] V. Ramachandran, R. M. Feenstra, W. L. Sarney, L. Salamanca-Riba, J. E. Northrup, L. T. Romano, and D. W. Greve, Appl. Phys. Lett. **75**, 808 (1999).
[14] J. W. Orton, C. T. Foxon, T. S. Cheng, S. E. Hooper, S. V. Novikov, B. Ya. Ber, and Yu. A. Kudriavtsev, J. Cryst. Growth **197**, 7 (1999).
[15] T. S. Cheng, S. V. Novikov, C. T. Foxon, and J. W. Orton, Solid State Commun. **109**, 439 (1999).
[16] V. Ramachandran, R. M. Feenstra, J. E. Northrup, and D. W. Greve, MRS Internet J. Nitride Semicond. Res. **5S1**, W3.65 (2000).
[17] L. T. Romano, J. E. Northrup, T. Myers, and A. Ptak, Appl. Phys. Lett. **77**, 2479 (2000).