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Magnesium and Beryllium Doping During rf-Plasma MBE Growth of GaN

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A series of Mg and Be step-doped epitaxial GaN layers was grown by rf-plasma assisted molecular beam epitaxy to study dopant incorporation for various conditions. Incorporation was studied for both (0001), or Ga-polarity and (000-1), or N-polarity, orientations. Dopant concentrations were determined by secondary ion mass spectrometry. A significant dependence on polarity of Mg incorporation was observed, with up to a factor of 30 times more Mg incorporated on the Ga-polarity under certain conditions. Any surface polarity-related differences were less pronounced for Be. Measurements support surface accumulation of both Mg and Be during growth, with stable accumulations of close to a monolayer. The presence of atomic hydrogen during growth was found to have a pronounced influence on Mg incorporation, increasing incorporation of Mg without also incorporating potentially compensating hydrogen. Photoluminescence measurements indicate an optical activation energy of about 100 meV for Be in GaN.

KEYWORDS: GaN, p-type doping, magnesium, beryllium, surface segregation

1. Introduction

While magnesium is currently the most technologically important p-type dopant for GaN, Be also shows promise. Although Mg, and to some extent Be, have been extensively studied in the last several years, incorporation mechanisms during growth by molecular beam epitaxy (MBE) remain unclear. For example, previous studies have presented results that indicate Mg incorporation is independent of Mg flux over a wide flux range but is quite sensitive to substrate temperature,[1)] and there is evidence for significant surface accumulation of Mg.[2)] Two competing models have been put forth to explain much of the observed behavior. The first assumes the presence of a surface accumulation layer, with dopant incorporation driven by segregation effects. The second model assumes the presence of a finite concentration of sites on the growing surface where the Mg is strongly incorporated. We present the results of a study of both Mg and Be incorporation for both N- and Ga-polarity GaN that strongly indicates surface accumulation occurs for both dopants under Ga-rich growth conditions.

2. Details of Growth

The 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 while Be was evaporated from a dopant effusion cell (EPI-5-D). N-polarity GaN was obtained by nucleating GaN buffer layers directly on sapphire under heavily Ga-rich conditions, as reported previously.[3)] 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/hr, which corresponded to a nitrogen flow rate of 0.85 sccm and rf power of 200 W. The samples were grown under Ga-stable conditions (Ga/N flux ratio >1) which results in high quality GaN growth.[3,4,5)] Step-doped structures were produced by opening and closing the dopant shutter. In-situ growth rates were monitored using laser interferometry. All changes in oven and substrate temperatures occurred with the dopant shutter closed. Atomic hydrogen was produced using a thermal cracker (EPI-AHS, EPI Vacuum Products, Inc). Typically, $2x10^{-6}$ Torr beam equivalent pressure of hydrogen was passed through the source operating at 9.5 A. Secondary ion mass spectrometry (SIMS) measurements were performed at Charles Evans and Associates (Redwood, Ca). Photoluminescence (PL) measurements were performed at 4.5K using a He-Cd laser at 325 nm as the excitation source. The PL was dispersed by a 0.64-m monochromator and detected by a GaAs photomultiplier tube working in photon counting mode. All spectra were corrected for the measurement system response, and energies were corrected for strain by using low temperature reflectance measurements to identify free excitonic transitions.

3. Mg Incorporation Studies

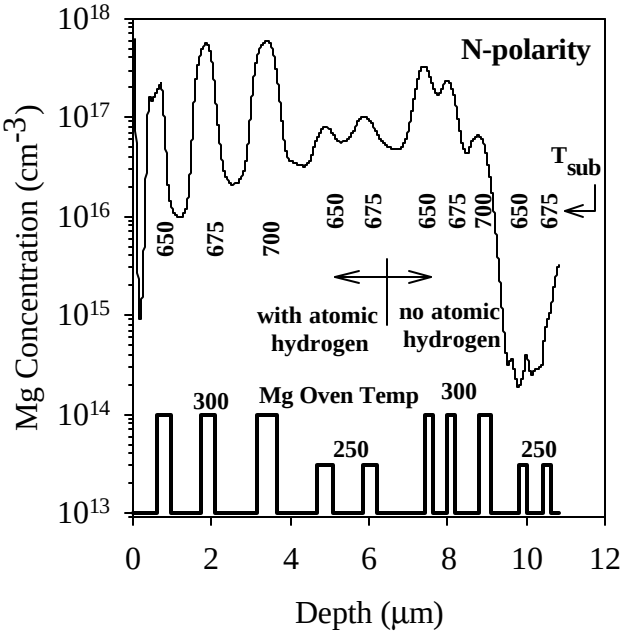

Figure 1. Mg-incorporation in N-polarity GaN for various conditions.

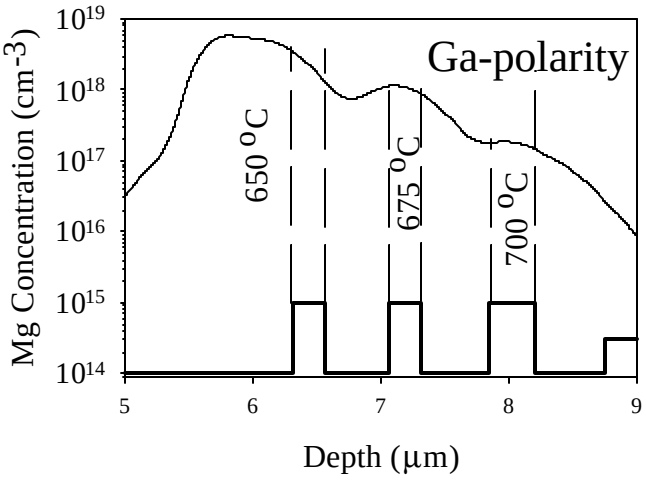

Figure 2. Mg concentration in Ga-polarity GaN.

Figure 1 contains the SIMS measurement of Mg made on a N-polarity Mg step-doped structure. The general features observed here are representative of all the structures investigated. The opening and closing of the Mg shutter is indicated schematically along the bottom of the figure, with the associated Mg oven temperature listed. The various substrate temperatures investigated are also listed in the appropriate regions. 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 an oven temperature of 250 °C and a substrate temperature of 650 °C, but at a gradually increasing rate rather than an abrupt turn-on. Mg is seen to incorporate at larger Mg flux, with strong substrate temperature dependence as reported previously.[1)]

The incorporation is also out of phase with the opening and closing of the shutter, generally increasing while the shutter is open, consistent with the observations of Orton *et al.*[6)] This is shown for the most significant case in Figure 2 for gallium polarity growth. Importantly, significant amounts of Mg are incorporated **after** the Mg shutter was closed, strongly indicative of surface segregation and accumulation of Mg. Cheng *et al.*[2)] report evidence for surface accumulation of Mg for Mg-doped GaN based on Auger spectroscopy of layers after growth. Ramachandran *et al.*[7)] report a significant persistence of the surfactant effect of Mg after closing the Mg shutter, indicating that Mg remains on the surface in the absence of a Mg flux.

Indeed, for the Ga-polar growth shown in Figure 2 the SIMS result indicates that approximately 3.3 $x10^{14}$ Mg atoms/cm^2 were incorporated after the shutter was closed, corresponding to between ¼ and ½monolayer of Mg on the surface of the growing layer. This is consistent with calculations[7,8)] which predict stable surface configurations involving either ¼ or ¾monolayers 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 $3x10^{-4}$ of the Mg incorporates in each monolayer of growth while the remainder segregates to the new surface. This number is quite close to the fraction of surface sites available for capturing Mg atoms estimated by Orton *et al.*[6)] to be ~$5x10^{-4}$ using a surface segregation model for a similar growth temperature.

Our results also indicate a strong dependence of Mg incorporation on polarity for identical growth conditions. In particular, at higher Mg flux and higher temperatures, Mg incorporation is found to be approximately twenty to thirty times less in N-polar GaN. A significant difference was observed for each set of comparable conditions examined, with larger incorporation always occurring for the Ga-polarity. This observation is consistent with the lower electrical activation observed for N-polar growth compared to Ga-polar growth observed by Li *et al.*[9)]

A final important point is that a dramatic decrease in Mg incorporation (as determined by SIMS) was observed for Ga-polarity GaN when the Mg flux was increased to produce more than a monolayer/sec flux on the surface. The incorporation after this abrupt decrease was more consistent with that observed for the N-polarity. The observed change in incorporation suggested surface inversion had occurred, changing from Ga-polarity to N-polarity. This has been verified by TEM.[10)] The observed polarity inversion is consistent with the prior results of Ramachandran *et al.*[11)] Such a surface inversion, coupled with the concomitant decrease in Mg incorporation, represents a potentially serious issue with heavy Mg-doping of GaN by MBE at higher growth temperatures.

Calculations by Neugebauer and Van de Walle[12)] suggested that the presence of hydrogen would enhance Mg incorporation. The results shown in Figure 1 verify this prediction. In particular, without hydrogen, no incorporation was observed for low Mg flux. The addition of atomic hydrogen caused incorporation at levels more consistent with projections from higher Mg-flux incorporation rates. The effect of hydrogen on Mg incorporation was less pronounced at higher Mg flux or lower substrate temperature. Indeed, the atomic hydrogen has little effect or may slightly inhibit 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 interfaces and bring incorporation more in sequence with the Mg oven shutter opening and closing. These effects imply that hydrogen may suppress the formation of the Mg surface accumulation layer. Note also that while hydrogen enhances incorporation for both polarities, it does not eliminate the polarity dependence of Mg incorporation. SIMS on the Mg-doped layers grown with atomic hydrogen indicated that while hydrogen has a significant effect on 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.

4. Be Incorporation Studies

Similar samples were grown and analyzed by SIMS to specifically study Be-incorporation kinetics. The effect of

atomic hydrogen on incorporation was also studied. As indicated in Figure 3 for a Ga-polar sample, at low concentrations the Be incorporation profile appears to be that expected for classic surface accumulation/segregation. While diffusion effects are undoubtedly present as well, the pronounced lack of any step-like structure relating to the opening and closing of the Be shutter is consistent with surface accumulation. Again, similar to the Mg case, the presence of atomic hydrogen enhances incorporation at low fluxes and sharpens the profiles at higher fluxes. There also seems to be a significant substrate temperature dependence on incorporation at lower flux.

SIMS results were also obtained for Ga-polarity GaN for higher concentrations of Be. Again, the profiles were offset with respect to the opening and closing of the dopant shutter, consistent with surface accumulation. Unlike the low concentration case, atomic hydrogen did not seem to influence Be incorporation. Atomic hydrogen was not observed to significantly change Be incorporation for any N-polarity samples investigated. In general, there seemed to be a larger incorporation of Be on N-polarity GaN with little discernible difference in incorporation due to atomic hydrogen. Although not shown, additional SIMS indicated that Be incorporation at higher flux is typically a factor of two larger on N-polarity than Ga-polarity for the same Be flux; that unlike Mg, incorporation is not a strong function of temperature at higher concentrations although some temperature dependence is present at low concentrations; and incorporation rates do not change significantly (~25% increase) when going from very Ga-rich growth conditions to N-stable growth.

In addition to the Be-profile shapes, most of the SIMS measurements were also suggestive of a higher concentration of Be at the surface. Auger measurements were made on several step-doped and uniformly doped layers. Although quantitative interpretation was complicated, the presence of Be was measured to be at levels representing a significant fraction of a monolayer. This surface layer of Be metal may have a significant influence on the as-grown properties.

SIMS measurements made on the Be-doped samples indicated a low background for both oxygen and carbon, less than the background (low-to-mid 10^{16} cm^{-3}) for these measurements. Measurements also indicate that hydrogen is incorporated at levels at or above the Be concentration when grown under atomic H. An increase in the background oxygen and carbon was also observed for growth under atomic H; the origin of this effect needs further investigation.

5. Photoluminescence Characterization of Be-doped Layers

Figures 4 and 5 show low-temperature photoluminescence spectra from two of the Be-doped GaN layers. All Be-doped GaN exhibited a strong feature near 3.38 eV, which is the most prominent feature for most samples as shown in Figure 4. Temperature and power dependence studies consistently indicate that the 3.38 PL is donor-acceptor pair luminescence. Previous studies of Be-doped GaN have also reported the same feature with a similar interpretation.[13] The only other features are phonon replicas of this feature and a bound-exciton at 3.475 eV. Using the typical shallow donor energy in GaN of 20 to 35 meV, this indicates an acceptor ionization level at about 100 meV. The previously unreported feature at 3.397 eV shown in Figure 5 was observed on several of the p-type samples, and has a temperature and power dependence characteristic of an electron-acceptor transition. The transition lineshape obtained using weak below-gap illumination was consistent with this interpretation. Again, this would indicate an acceptor level ~100 to 110 meV above the valence band. The feature at 3.472 eV in Figure 5 is

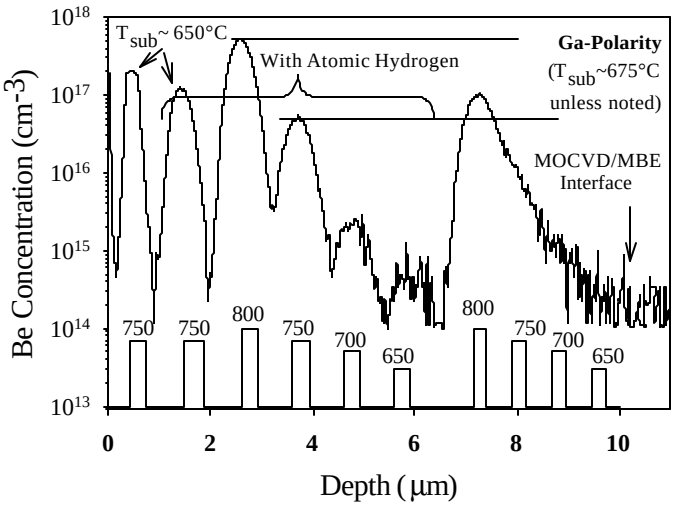

Figure 3. Be concentration vs. growth conditions in a step-doped structure. Be shutter opening and closing is shown schematically.

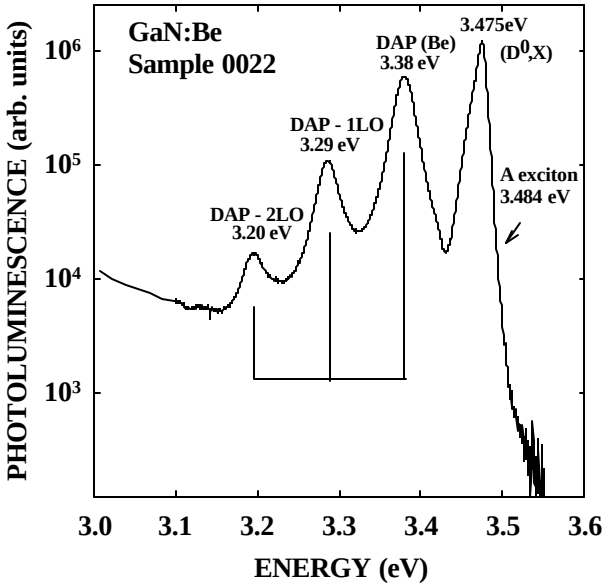

Figure 4. Low temperature PL of Be-doped GaN.

tentatively assigned to an acceptor-bound exciton with a binding energy of 9 to 10 meV. This binding energy is again consistent with Be having a smaller ionization energy than Mg, which has a binding energy of 12.6 meV.

The feature at 3.27 eV has also been previously reported for Be-doped material and also has donor-acceptor pair characteristics.[14] There is also a transition near 3.14 eV that has previously been labeled the I_4 transition. Interestingly, these latter two features were removed after etching the surface of the GaN, indicating they may be related to the surface accumulation layer.

6. Conclusions

In summary, there is a significant difference in Mg incorporation depending on polarity with the Ga-polarity incorporating a factor of up to thirty times more Mg than the N-polarity under the Ga-rich growth conditions used while only a small fraction of the actual Mg flux is incorporated. There is a very strong substrate temperature dependence on Mg incorporation with a distinct increase in Mg incorporation in the presence of atomic hydrogen. There is also an indication that a surface-accumulation layer of Mg may be forming during doping. The decrease in both Mg incorporation and 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.

Be incorporation in GaN grown by rf plasma MBE is much better behaved than Mg, showing significantly less dependence on growth conditions. Strong evidence was observed for surface accumulation of Be during growth. Atomic hydrogen only seemed to significantly affect incorporation at low Be concentrations on Ga-polarity material.

Temperature and power-dependent PL spectra show strong evidence for donor-to-acceptor and electron-to-acceptor transitions, which indicate a Be acceptor level about 100 meV above the valence band, much shallower than the Mg acceptor level (~225 meV).

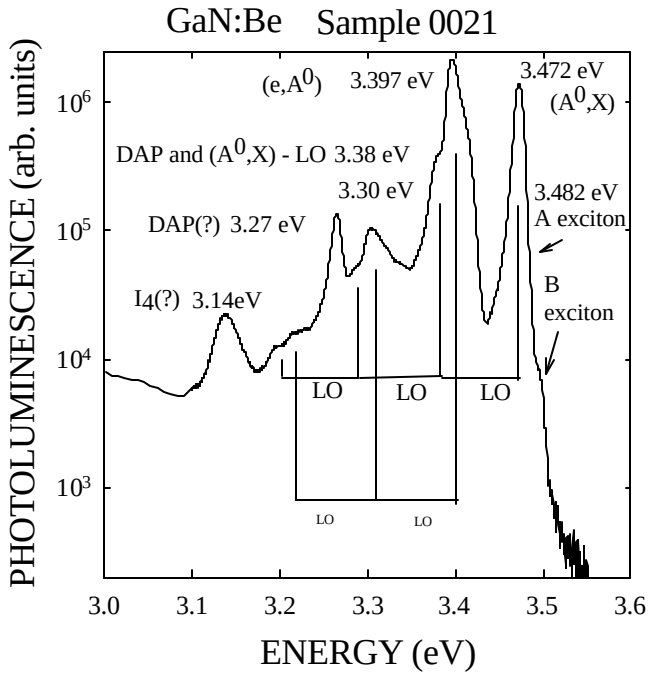

Figure 5. Low temperature photoluminescence of a Be-doped GaN sample.

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