A Comparison of Magnesium and Beryllium Acceptors in GaN Grown by rf-Plasma Assisted Molecular Beam Epitaxy

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ABSTRACT

Step-doped structures of both magnesium and beryllium were grown in GaN and analyzed using secondary ion mass spectrometry. Dopant incorporation was studied as a function of substrate temperature and dopant flux for Ga-polarity and N-polarity GaN. Incorporation is different for each polarity, with Mg incorporating by up to a factor of 20 times more (30 times more with atomic hydrogen) on the Ga-face, while Be incorporates more readily on the N-face. The effect of atomic hydrogen on the incorporation kinetics of both Mg and Be is also discussed. Mg and Be both undergo surface segregation during growth. Photoluminescence measurements suggest that Be is a p-type dopant with an optical activation energy of approximately 100 meV.

INTRODUCTION

While magnesium is currently the most technologically important p-type dopant for GaN, Be also shows promise. Although Mg, and Be have been 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] 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, and that surface polarity can have a dramatic influence on incorporation.

DETAILS OF GROWTH

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. 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). Secondary ion mass spectrometry (SIMS) measurements were performed at

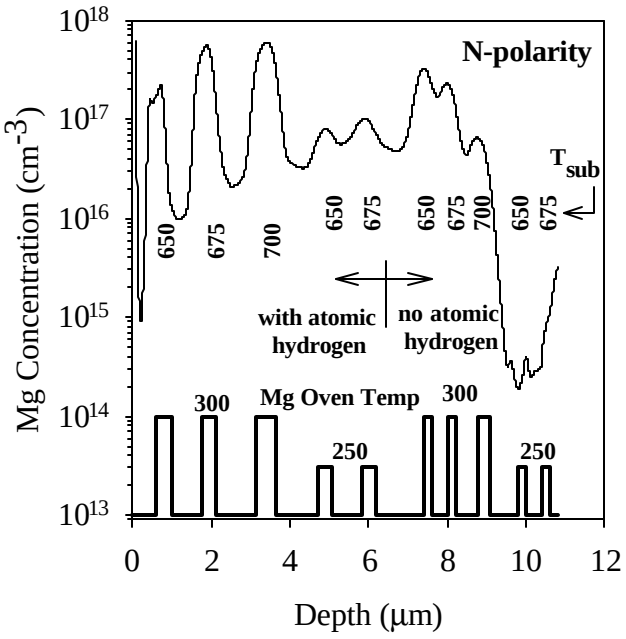

Figure 1. Mg-incorporation in N-polarity GaN for various conditions. The opening and closing of the Mg shutter is shown schematically.

Evans Analytical Group (Sunnyvale, Ca). Photo-luminescence (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 mono-chromator and detected by a GaAs photo-multiplier 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.

INCORPORATION STUDIES

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 Mg structures investigated. 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 ^{o}C and a substrate temperature of 650 ^{o}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]

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.*[6]

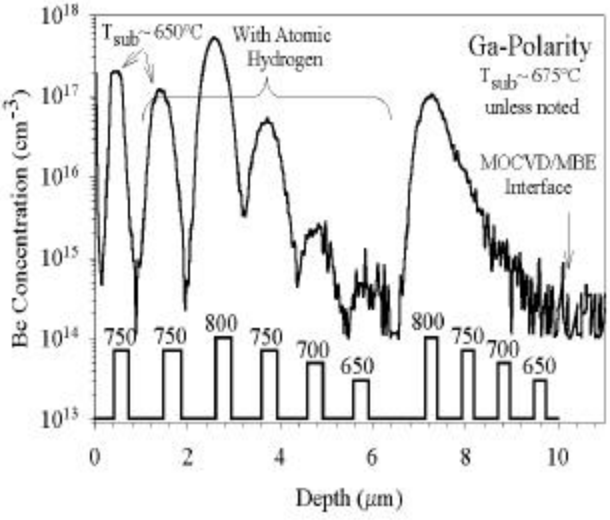

Figure 2. Be incorporation for various growth conditions on Ga polar GaN. Be shutter opening and closing is shown schematically.

A final important point for Mg 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 dramatic change in incorporation suggested surface inversion had occurred, changing from Ga-polarity to N-polarity and was subsequently verified by TEM. [7] The observed polarity inversion is consistent with the prior results of Ramachandran *et al*. [8] and can be understood to be a result of a Mg-induced surface reconstruction as discussed by Romano *et al.* [7] 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.

Similar samples were grown and analyzed by SIMS to specifically study Be-incorporation kinetics. Figure 2 shows the SIMS measurement for a Ga-polar Be step doped sample grown on MOCVD GaN. At low concentrations, the SIMS profile is that of classic surface accumulation/segregation. SIMS results were also obtained for Ga-polarity GaN for higher concentrations of Be. Although not shown, the following general characteristics for Be incorporation have been observed: there seemed to be a larger incorporation of Be on N-polarity GaN than on the Ga-polarity, typically by a factor of two for the same Be flux; 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 when going from very Ga-rich growth conditions to N-stable growth.

EVIDENCE FOR SURFACE ACCUMULATION

As can be seen in Figure 1 for Mg and Figure 2 for Be, 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*.[9] for Mg doped GaN. Importantly, as clearly shown in Figure 3 for Mg on both polarities, significant amounts of Mg are incorporated **after** the Mg shutter was closed, with a profile strongly indicative of non-classical surface segregation and accumulation of Mg. This behavior, particularly the increase after the shutter is closed, may be due to the presence of a stable surface reconstruction involving Mg. [10,11] 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.*[10] 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.

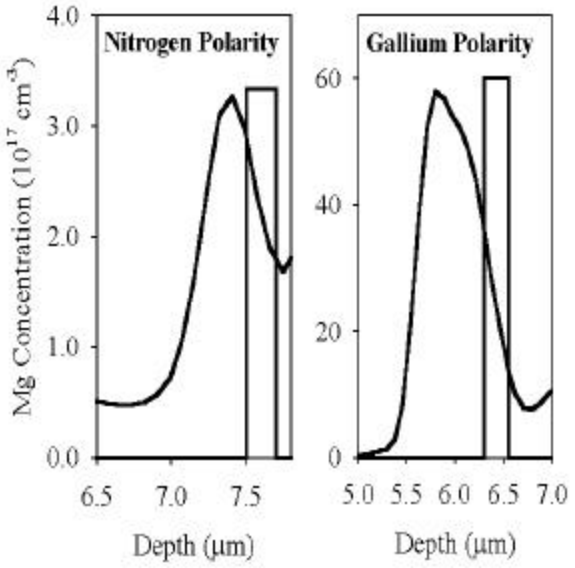

Figure 3. Significant Mg incorporation can occur after closing the shutter. The initial Mg concentration is from the previous doping step.

Indeed, for the Ga-polar growth shown in Figure 3 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 ½ monolayer of Mg on the surface of the growing layer. This is consistent with calculations[10,11] 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.

There is also strong evidence for surface accumulation of Be as again, the profiles were offset with respect to the opening and closing of the dopant shutter. As indicated in Figure 2 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.

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, and surface accumulation in general may be an endemic problem for the p-type doping of GaN.

EFFECTS OF ATOMIC HYDROGEN

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 ^{o}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. 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.

The effect of atomic hydrogen on incorporation was also studied for the case of Be. Again, similar to the Mg case, the presence of atomic hydrogen enhances incorporation at low fluxes and sharpens the profiles at higher fluxes on the Ga polarity. There also seems to be a significant substrate temperature dependence on incorporation at lower flux. Unlike the low concentration case, atomic hydrogen did not seem to influence Be incorporation at higher fluxes. Atomic hydrogen was not observed to significantly change Be incorporation for any N-polarity samples investigated.

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.

PHOTOLUMINESCENCE CHARACTERIZATION OF DOPED LAYERS

Low temperature photoluminescence on low doped ($<10^{17}$ cm^{-3}) GaN:Mg layers (not shown) exhibit strong excitonic emission including the A and B free excitons, as well as the familiar donor and acceptor bound excitons seen by others (See, for example, [13]). The localization for the Mg bound exciton determined from our measurements is 12.6 meV. In addition, a donor–acceptor pair transition is clearly visible that yields an acceptor activation energy of ~225 meV when a donor energy of ~ 30 meV is assumed.

Figure 4 shows 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. While the so-called yellow luminescence (~2.3 – 2.5 eV) was observed (not shown), it was typically a factor of ten to 100 less than the near edge luminescence. Temperature and power dependence studies consistently indicate that the 3.38 eV PL is donor-acceptor pair luminescence. Previous studies of Be-doped GaN have also reported the same feature with a similar interpretation.[14] 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 4a) 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 4a) is 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. The feature at 3.27 eV has also been previously reported for Be-doped material and also has donor-acceptor pair characteristics.[15] There is also a transition near 3.14 eV Interestingly, these latter two features were removed after etching the surface of the GaN, indicating they may be related to the surface accumulation layer.

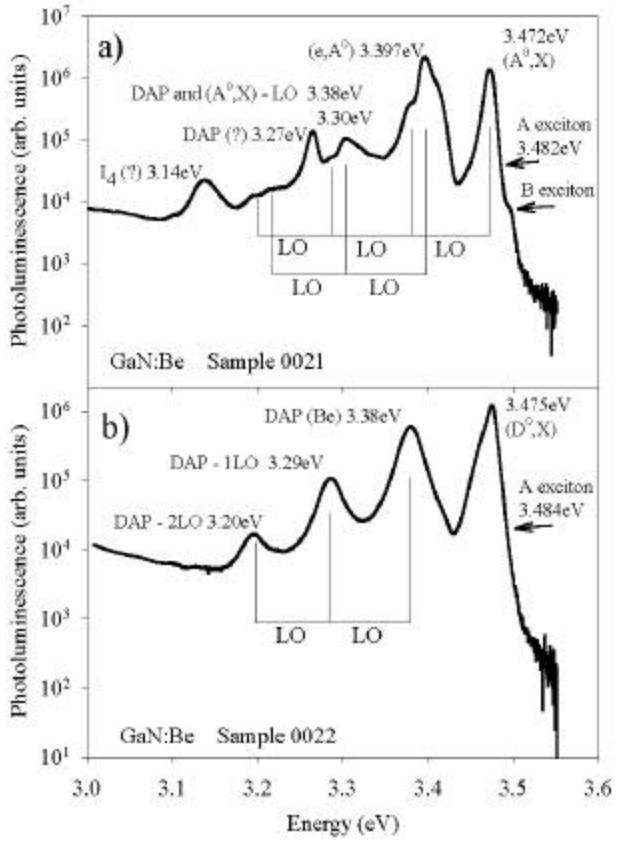

Figure 4. Low temperature PL of Be-doped GaN.

CONCLUSIONS

Mg and Be both show a difference in incorporation depending on polarity with Mg incorporating up to 30 times more on the Ga polarity, and Be incorporating slightly more on the N polarity under Ga rich growth conditions. Only a small fraction of the actual Mg flux is

incorporated, and there is a very strong substrate temperature dependence on Mg incorporation with a distinct increase in the presence of atomic hydrogen. Be incorporation in GaN is much better behaved than Mg, showing significantly less dependence on growth conditions. Atomic hydrogen only seemed to significantly affect incorporation at low Be concentrations on Ga-polarity material. Strong evidence was observed for surface accumulation of both Mg and Be during growth. 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. Temperature and power-dependent PL spectra show strong evidence for donor-to-acceptor and electron-to-acceptor transitions indicating a Be acceptor level ~100 meV above the valence band, much shallower than the Mg acceptor level (~225 meV).

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