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The free hole carriers in GaN have been limited to concentrations in the low 10^{18} cm^{-3} range due to the deep activation energy, lower solubility, and compensation from defects, therefore, limiting doping efficiency to about 1%. Herein, we report an enhanced doping efficiency up to ~10% in GaN by a periodic doping, metal modulation epitaxy growth technique. The hole concentrations grown by periodically modulating Ga atoms and Mg dopants were over $\sim 1.5 \times 10^{19}$ cm^{-3}. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3005640]

The attainment of high hole concentration[1–3] has been a major road block in nitride based solid state lighting technologies. The major challenges related to *p*-type doping include the following: (1) deep acceptor activation energies, as large as ~170 meV for Mg in GaN,[1] which activates only about 1% of the Mg acceptors at room temperature; (2) solubility limits for Mg, in the low 10^{20} cm^{-3} range;[4] (3) compensation by native defects such as nitrogen vacancies,[5] which have a low formation energy in *p*-type GaN; and (4) pyramidal extended defects due to inversion domains[3,6] which also lead to compensation in *p*-type material. Numerous growth techniques over the last 2 decades have been developed for *p*-type doping. Representative growth techniques developed to overcome the technical barriers mentioned above include Mg δ-doping,[7] codoping,[8] superlattice doping,[9] and doping with an alternative acceptor, Be.[10] However, none of the above growth techniques have provided a reliable growth technology able to overcome the current low hole concentration in III-nitride materials. As a result, the present maximum hole concentration in GaN that is consistently obtainable by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition, with Mg doping, is generally limited to $\sim(1-2)\times 10^{18}$ cm^{-3}.

In this letter, we report on the improvement in hole conductivity in GaN by the metal modulation epitaxy (MME) growth technique.[11] MME is a technique wherein only the metal fluxes (Ga and Mg dopants) are modulated, in a short periodic fashion in a rf MBE system, while maintaining a continuous nitrogen plasma flux. This technique has demonstrated dramatic improvements in hole concentrations, 4.5×10^{18} cm^{-3} published previously[11] and over 1.5×10^{19} cm^{-3} in the present report.

To understand why MME provides such a significant enhancement in hole concentration, we first must review Mg incorporation behavior and the formation of compensating donor-type defects. The widely accepted underlying dynamic mechanism of Mg incorporation involves "surface segregation and accumulation at the surface," which forces the Mg to remain at high surface concentration levels, and creates Mg-related defects at the growing surface.[6,12,13] The degree of the surface segregation and accumulation is dependent upon the substrate temperature, Mg flux, and III/V ratios.[14]

Under N-rich conditions, Mg will preferentially incorporate into readily available Ga substitutional sites; however, these substitutional Mg can then easily exchange with impinging Ga, forcing the Mg to largely remain segregated on the surface. When the Mg concentration reaches more than 1.2 ML (monolayer),[3] polarity inversion domains[3,15] are formed and can trap free holes. Additionally, nitrogen vacancies, which have been proposed as the dominant compensating defects in Mg-doped GaN,[16] have higher formation energies under N-rich conditions than under Ga-rich conditions.[17] Therefore, the useful aspects of N-rich growth are (i) Mg dopants can be incorporated into Ga substitutional sites; and (ii) compensating N-vacancy concentrations are reduced due to their higher formation energy. However, a detrimental aspect is (iii) an increase in surface faceting that can create extended defects (grain boundaries and dislocations). Therefore, effective Mg doping under N-rich conditions is a balance of the beneficial aspects of (i) and (ii) versus the detrimental effects of (iii).

Next we consider slight Ga-rich conditions, in which the Ga coverage (or Ga bilayers) slightly exceeds the N coverage; in this case, more Mg accumulates on the surface due to the limited availability of Ga substitutional sites, and less is incorporated into the epitaxial layer.[18] Attempts to solve this problem with higher Mg fluxes cause the local polarity to invert from Ga-polar to N-polar,[3,15] and results in reduced Mg incorporation. Furthermore, the formation energy of nitrogen vacancies decreases under slightly Ga-rich conditions and as a result more nitrogen vacancies are available to compensate the free holes.[17]

Even though slight Ga-rich conditions reduce Mg incorporation into III-nitride materials, it is found that *extreme* Ga-rich conditions, i.e., metal droplet growth conditions, lead to enhanced Mg incorporation.[19] Under such conditions, the enhancement of Mg incorporation is attributed to the fact that the Mg dissolves into the metallic Ga and consequently is prevented from re-evaporating.[19] Therefore, extreme Ga-rich conditions enhance the incorporation of Mg. Moreover, polarity inversion can be avoided by completely covering the

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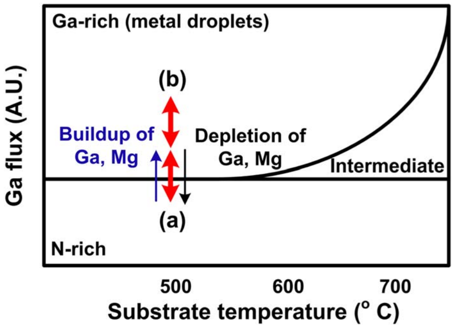

FIG. 1. (Color online) Schematic of the MME growth technique: the periodic cycling of buildup and depletion of surface-accumulated Ga and Mg dopants (a) during the transitions between Ga- and N-rich conditions and (b) under Ga-rich growth conditions.

growing surface with metallic Ga bilayers.[15] Unfortunately, however, the formation energy of nitrogen vacancies is lowest in this condition[17] and as mentioned above, these defects will compensate free holes.

Based on the considerations discussed above, *p*-type growth of GaN is not ideal under either Ga-rich or N-rich conditions alone. The best strategy is a periodic growth with abrupt transitions between Ga-rich and N-rich conditions, Ga-rich to smooth the surface and to prevent compensating extended defects resulting from faceting, and N-rich to promote Mg incorporation onto the Ga-substitutional site without the production of compensating N-vacancies. Such an "oscillation" of growth conditions can be achieved by periodic modulation of the metal fluxes while maintaining a constant nitrogen flux. During the growth, metallic buildup occurs under Ga-rich conditions but depletion of both the metallic Ga bilayers and the surface-accumulated Mg dopants occur during the transition from Ga-rich to N-rich conditions. A detailed schematic is shown in Fig. 1(a) and growth parameters can be adjusted according to the GaN epitaxy phase diagram.[20] However, as indicated in Fig. 1(b), conventional growth or even nonoptimal modulation growth, leads to incomplete depletion of the surface-accumulated Ga and Mg when the modulation growth occurs under Ga-rich conditions. It is found that nonoptimal modulation growth of Mg-doped GaN limits the hole concentration to the low 10^{18} cm^{-3} range.

In this work, both the Ga and Mg shutters are modulated [the Mg being delivered from a Veeco corrosive series valved cracker with a flux of $(4-5)\times 10^{-10}$ Torr beam equivalent pressure (BEP)] at a growth temperature of 500 °C.[11,18] The Ga fluxes used are large enough that droplets rapidly form when the Ga shutter opens and are subsequently depleted when the Ga shutter closes. Figure 2(a) shows Mg concentrations in alternating Mg-doped/undoped GaN with different periodic (open/close) duty cycles of metal shutters while maintaining the same Ga fluxes. The opening cycles for the Mg and Ga shutters are changed from no modulation to 30 s while the closing cycles are maintained for 10 s. The resultant Mg concentrations from secondary ion mass spectrometry (SIMS) measurements show constant values of $(1-2)\times 10^{20}$ cm^{-3} (within factors of 2) regardless of different shutter duty cycles, supporting the assumption of saturated Mg through surface accumulation. It should be noted that the oxygen concentrations are found to be about $\sim 3\times 10^{17}$ cm^{-3} in the Mg-doped GaN except for the initial growth, which contains about 1×10^{18} cm^{-3}. Individual Mg-doped samples grown with different periodic duty cycles of the metal shutters are also confirmed to have similar Mg concentrations of $(1-2)\times 10^{20}$ cm^{-3}.

However, it is found that the hole concentration is increased, from 2×10^{18} to 1.4×10^{19} cm^{-3}, by employing shorter shutter opening times (more N-rich average conditions), as shown in Fig. 2(b). One of the key observations is that the doping efficiency increases up to ~10% for the highest hole concentration of 1.4×10^{19} cm^{-3}. Since the SIMS-determined Mg concentrations are almost the same (within a factor of 2) for all samples grown under a variety of different growth conditions, the increased hole concentrations can be attributed to optimal incorporation of surface-accumulated Mg dopants into Ga substitutional sites with minimal formation of compensating defects (i.e., point defects, mainly N-vacancies, and extended defects, mainly faceting). Doping efficiency around 10% is also reported by Bhattacharyya *et al.*[19] with extreme Ga-rich growth conditions at much higher growth temperature of 770 °C, producing hole concentrations varying from 2×10^{17} to 3×10^{18} cm^{-3} and corresponding mobilities varying from 30 to 2 cm^2/V s. However, the higher growth temperature limited the incorporation of Mg concentrations to low 10^{19} cm^{-3}, resulting in low 10^{18} cm^{-3} hole concentration. The MME approach at the low growth temperatures is the only approach reported to enhance hole concentration over 10^{19} cm^{-3}.

To better understand the role of the buildup and depletion process in Mg-doped MME growth, while maintaining a

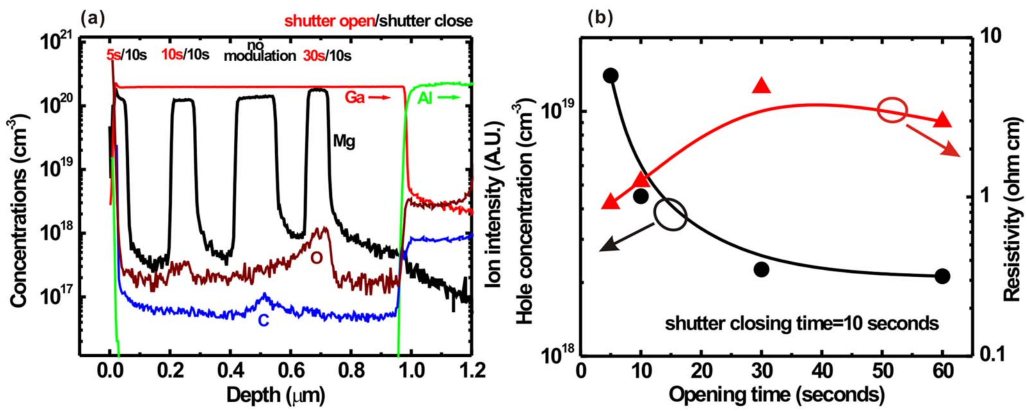

FIG. 2. (Color online) (a) SIMS profile of alternating Mg-doped/undoped GaN with different periodic (open/close) duty cyclings with constant Ga flux $=6.5\times 10^{-7}$ Torr, and (b) individual hole concentrations and resistivities grown under different periodic duty cyclings.

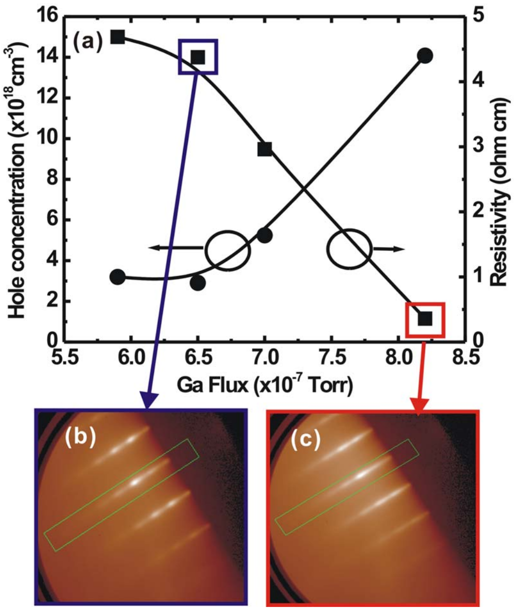

FIG. 3. (Color online) (a) Hall-effect data for Mg-doped GaN with different Ga fluxes with a duty cycle (5/10 s); (b) RHEED images recorded for Mg-doped GaN with a Ga flux of 6.5×10^{-7} Torr; and (c) with a Ga flux of 8.2×10^{-7} Torr.

constant duty cycle of shutter opening (5 s) and closing (10 s) the Ga fluxes were increased from 5.2 to 8.2 $\times10^{-7}$ Torr BEP. The resultant hole concentrations are shown in Fig. 3(a) and it is seen that in this BEP range, the highest hole concentrations are obtained with the lowest Ga fluxes (most N-rich average conditions). It is also found that the reflection high-energy electron diffraction (RHEED) images depend strongly on Ga fluxes and are closely correlated to the resulting hole concentration. As shown in Fig. 3(b), a sample with high hole concentration $>10^{19}$ cm^{-3} shows the spotty patterns with streaky lines, indicating progressive N-rich growth. In contrast, as seen in Fig. 3(c), a GaN sample with a hole concentration of 10^{18} cm^{-3} shows a more streaky RHEED pattern. Further study on RHEED intensity on this sample indicates that modulation growth under higher Ga flux (8.2×10^{-7} Torr) occurs in the Ga-rich region, indicated in Fig. 1(b). More detail studies on RHEED intensity will be presented later.

Based on these observations, the extremely high hole concentrations over 10^{19} cm^{-3} can be obtained only when the surface depletion process occurs during the transitions between Ga-rich and N-rich regions.

Preliminary analysis of temperature-dependent Hall-effect measurements has been performed on Mg-doped GaN samples grown with different shutter duty cycles. It is found that the donor/acceptor compensation ratio is about 0.3 for a sample with a high hole concentration of 1.45×10^{19} cm^{-3}. An accurate acceptor activation energy cannot be measured because the Mg ions are not isolated, as would be the case at lower concentrations. At a concentration of (1–2) $\times10^{20}$ cm^{-3}, the average Mg separation is about 1.1 nm, which is close to the expected Bohr radius of Mg (about 0.8 nm for a 200 meV acceptor in GaN). Therefore, there will be considerable wavefunction overlap, and the conduction will be highly dependent on interimpurity tunneling, a process not describable by the usual thermal activation energy. A detailed discussion of these results, including identification of the compensating donors and temperature-dependent Hall effect, will be presented separately.

In summary, a doping growth technique has been developed by effectively establishing the periodic buildup and depletion process to facilitate the incorporation of Mg dopants into Ga substitutional sites while suppressing the formation of compensating defects. The highest hole concentrations obtained with MME doping are $\sim1.5\times10^{19}$ cm^{-3} at room temperature, with a resistivity of 0.9 Ω cm and mobility of 0.5 cm^2/V s. RHEED characteristics needed to reproduce these results have been described. The demonstrated capability of high hole concentrations in *p*-type GaN will expedite the development of future nitride based electronic and optical devices.

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