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Citation: [Applied Physics Letters](#) **85**, 4956 (2004); doi: 10.1063/1.1826223

View online: <http://dx.doi.org/10.1063/1.1826223>

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## Efficient *p*-type doping of GaN films by plasma-assisted molecular beam epitaxy

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(Received 18 February 2004; accepted 24 September 2004)

In this paper we report on the mechanism of efficient incorporation of Mg in GaN films during growth by plasma-assisted molecular beam epitaxy. It is found that Mg incorporates more efficiently during growth of GaN films at high temperatures (770 °C) under extreme Ga-rich conditions. We propose that this result is due to the dissolution of Mg in the excess Ga on the growth surface and its incorporation into the GaN film via liquid-phase processes. Transport measurements at 300 K together with secondary-ion-mass-spectroscopy indicate that the Mg-doping efficiency of GaN under these conditions of growth is 10%. Using this method of doping, *p*-type GaN films free of Ga droplets, with hole concentrations varying from  $2 \times 10^{17}$  to  $3 \times 10^{18}$  cm<sup>-3</sup> and corresponding mobilities varying from 30 to 2 cm<sup>2</sup>/V s, are obtained. The lowest resistivity achieved is 0.3 Ω cm. © 2004 American Institute of Physics. [DOI: 10.1063/1.1826223]

The *p*-type doping of GaN and its alloys with InN and AlN is still one of the most challenging problems in the development of efficient devices based on this class of materials. During growth by the metalorganic chemical vapor deposition (MOCVD) method, it was found that the incorporation of Mg in GaN was facilitated by simultaneous co-doping with hydrogen, which was subsequently removed from the sample by postgrowth annealing.<sup>1,2</sup> In plasma-assisted molecular beam epitaxy (MBE), it was reported early on<sup>3-5</sup> that *p*-type doping of GaN with Mg was accomplished without requiring any postgrowth annealing. Our group attributed this finding to co-doping of the GaN film with electrons arriving from the plasma source.<sup>6</sup> The growth of III-Nitrides by plasma-assisted MBE generally takes place under group III-rich conditions which lead to smooth surface. This is contrary to other III-V compounds (arsenides) where growth takes place under group V-rich conditions. The difference is attributed to the high reactivity of the nitrogen species, produced by the plasma sources, and thus the migration length of the Group-III adatoms is limited under excess nitrogen leading to rough and faceted surface. It has been reported that small doses of Mg act as a surfactant during growth of GaN (0001) under nitrogen-rich conditions.<sup>7</sup> It has also been reported that larger doses of Mg lead to polarity inversion from Ga-polar to N-polar GaN.<sup>7</sup> This polarity inversion was reported recently to be more prominent when growth takes place under nitrogen-rich conditions, while polarity inversion was inhibited in the presence of a Ga wetting layer.<sup>8</sup>

An additional problem in the incorporation of Mg during growth of GaN by plasma-assisted MBE is the high vapor pressure of Mg at the usual growth temperature of GaN.<sup>9,10</sup> To overcome this problem, the general practice is to grow the *p*-type films at relatively low substrate temperatures and relatively high Mg fluxes.<sup>9,11</sup> The finding that the Mg incorporation saturates with the Mg flux, at certain substrate temperature, suggests that incorporation takes place through surface phase accumulation or via the availability of specific sites on the surface.<sup>9</sup>

Reports in the literature indicate that incorporation of Mg in GaN in the range of  $2 \times 10^{19}$ – $1 \times 10^{20}$  cm<sup>-3</sup> leads to hole concentrations of  $p \sim 10^{17}$ – $10^{18}$  cm<sup>-3</sup>, i.e., a doping efficiency of 1% at 300 K.<sup>8</sup> This relatively low doping efficiency was accounted for by the high acceptor activation energy of Mg, which was reported by different authors to be 150–250 meV.<sup>12</sup> In this letter we report the efficient incorporation of Mg at relatively high growth temperatures (770 °C) with doping efficiency of 10%. Furthermore, a mechanism is proposed of Mg incorporation in GaN films by plasma-assisted MBE.

The GaN films were deposited by rf-plasma assisted-MBE in a Varian GenII system using an Applied Epi rf plasma source to activate the molecular nitrogen. Ga and Al were supplied from Applied Epi SUMO™ cells and Mg was supplied by a standard effusion cell. The substrates used were 2 in. *c*-plane sapphire wafers. All films were grown using a three-step method. First, the substrates were exposed to nitrogen plasma at 870 °C, for nitridation of the sapphire surface. Then, a 1000-Å-thick AlN buffer was grown at 870 °C. This step ensured that the films were grown in the [0001] Ga-polar direction.<sup>13,14</sup> The GaN films were deposited

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at 770 °C at a growth rate of about 400 nm/h. The GaN films were grown initially without Mg, and then the Mg shutter was opened without interrupting the growth. The growth was monitored during the various steps by reflection-high-energy electron diffraction (RHEED). The surface morphology of the films was examined by optical microscopy and scanning electron microscopy (SEM). The microstructure and film composition of the samples were determined by cross-section transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS) measurements. The transport constants at room temperature were obtained using the van der Pauw method.

Two series of GaN:Mg films, grown under different regimes of group III to group V ratio and variable Mg flux, were investigated. In both series, the rf power in the plasma source was kept at 450 W and the flow of nitrogen was kept at 3 sccm. In series A, the Ga beam equivalent pressure (BEP) was  $9.0 \times 10^{-7}$  Torr, while in series B the Ga BEP was 30% higher at  $1.3 \times 10^{-6}$  Torr. Under both of these growth conditions, a thin Ga film was present on the surface during growth, although the thickness of this Ga film was greater for the films of series B. Specifically, we observed that for series A, upon interrupting the Ga beam, it took about 10 s for the RHEED diffraction pattern to brighten, whereas it took about 2–3 min for films of series B. At the end of growth, the sample was kept at the growth temperature for about 10 min to clear the surface of excess Ga. The Mg cell temperature for both series of films was varied from 310 to 370 °C, corresponding to Mg BEP ranging from  $1.5 \times 10^{-8}$  Torr to  $1.5E^{-7}$  Torr. All investigated films showed streaky RHEED patterns with only the bulk (1 × 1) structure at growth temperature as well as upon cooling to low temperature (200 °C). This structure is consistent with films having Ga polarity. Postgrowth examination of the films by optical microscopy and SEM showed no evidence of Ga droplets although the growth took place under extreme Ga-rich conditions.

Figure 1(a) shows the resistivity of the Mg-doped GaN films from series A and series B as a function of Mg cell temperature. Note that the resistivity of series B films, which were grown with higher Ga flux, is reduced by more than an order of magnitude over the films grown with lower Ga flux. Thus, the excess Ga on the growing surface promotes Mg incorporation and doping, as discussed in the following. The lowest resistivity obtained in this study was  $0.3 \Omega \text{ cm}$ . Figure 1(b) presents the hole mobility versus carrier concentration for a number of films from series B. Some of these data points were taken from different parts of the same 2 in. wafers. The observed spread in the data can be accounted for by the fact that Ga accumulation during film growth was larger in the center of the wafer than at the edge of the wafer, which we attribute to small variations in the substrate temperature from the center to the edge. Thus, by varying the Mg-cell temperatures, films with carrier concentration varying from  $2 \times 10^{17}$  to  $3 \times 10^{18} / \text{cm}^3$  with corresponding mobilities varying from 30 to  $2 \text{ V/cm}^2 \text{ s}$  were obtained.

In order to understand the observed differences in the resistivity of films in series A and B, cross-sectional TEM and SIMS studies were conducted on two *p*-type GaN films, one from each series. The results are presented in Fig. 2. The Mg cell temperature for both samples was 370 °C, the highest Mg cell temperature employed in this work. It should again be stressed that there was no interruption between the

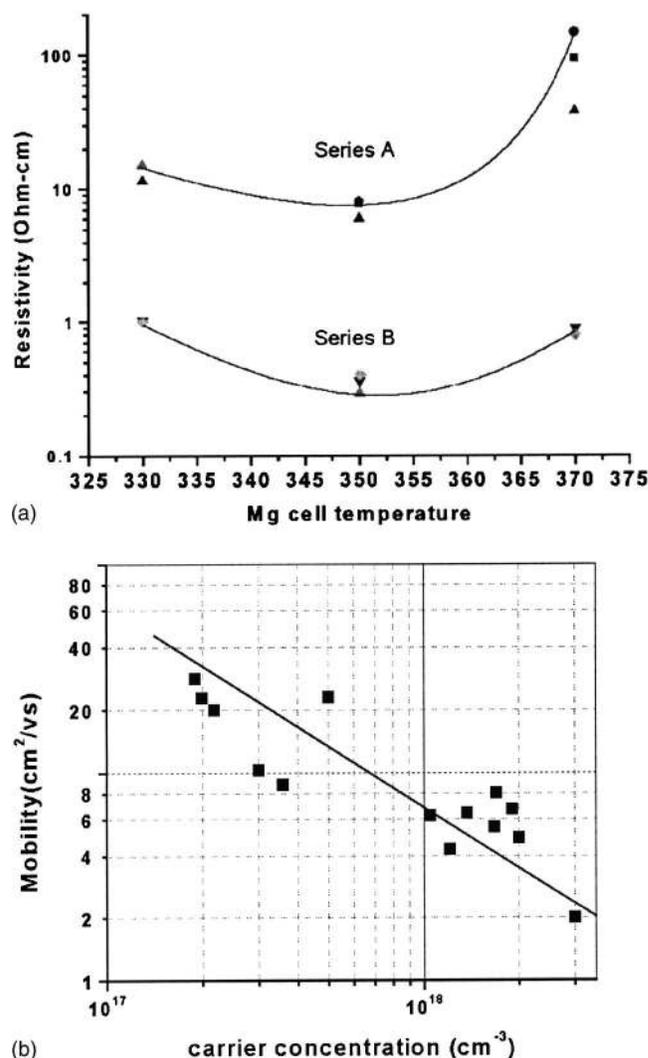


FIG. 1. Electrical characterization of Mg-doped GaN samples. (a) Resistivity of *p*-GaN films from series A and series B as a function of Mg cell temperatures. (b) Hole mobility vs hole concentration for GaN films of series B.

growth of undoped and doped layers The AlN buffer, the undoped GaN film, and the Mg-doped GaN layer are clearly visible in each TEM micrograph. The interface between the undoped and Mg-doped layers are of the most relevance here. For the sample from series A, shown in Fig. 2(a), the position of the interface was highly distinctive, being marked by a thin continuous region with lots of strain and closely spaced faceting. This appearance is similar to that reported by Romano *et al.*,<sup>15</sup> and was attributed to the inversion of film polarity due to excess Mg at the growth front. For the sample from series B, shown in Fig. 2(b), the position of the interface could again be readily identified, but the local appearance was quite different. Faceting on inclined planes as well as short horizontal stacking faults, possibly inversion domains, were visible. However, much of the film growth continued uninterrupted and defect-free across the interface region.

The corresponding SIMS results clearly indicate that the Mg in the film of series A incorporates preferentially at the interface between the undoped and doped film up to a level of  $10^{20} \text{ cm}^{-3}$  and then progressively drops off to a level of  $10^{18} \text{ cm}^{-3}$ . On the other hand the Mg concentration is slightly higher at the interface between undoped and doped

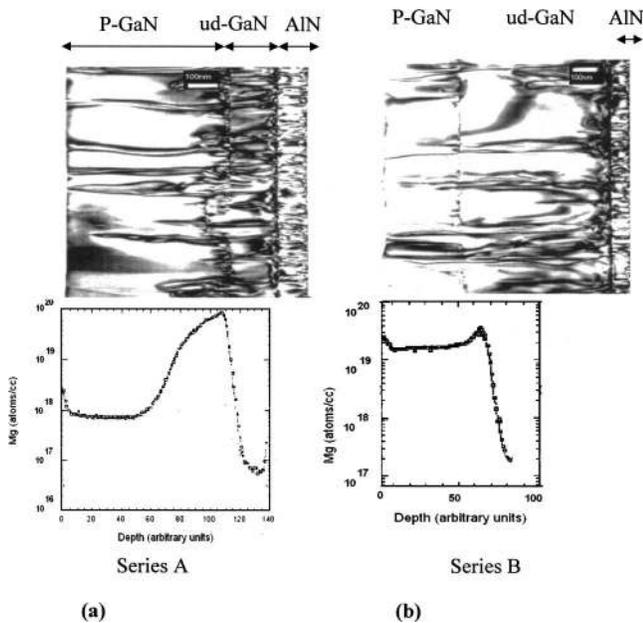


FIG. 2. Cross-sectional TEM micrographs and SIMS analysis of two Mg-doped GaN thin films grown with Mg cell at 370 °C and Ga beam equivalent pressure of: (a)  $9.0 \times 10^{-7}$  Torr; (b)  $1.3 \times 10^{-6}$  Torr.

films for series B and then saturates at about  $2 \times 10^{19} \text{ cm}^{-3}$ . Thus, although the Mg flux was the same in both films, the incorporation of Mg in GaN was more than an order of magnitude higher in the film of series B. The sample discussed in Fig. 2(b) was measured by the Hall-effect method to have a carrier concentration at 300 K of  $2 \times 10^{18} \text{ cm}^{-3}$ . Thus, the doping efficiency for the films grown under excessive Ga is 10%. This value should be contrasted with reports in the literature that films produced either by the MOCVD or MBE method generally have doping efficiency at 300 K of about 1%.

Based on these results we propose that the more efficient incorporation of Mg during growth of the *p*-type GaN films in the presence of excess Ga must be due to the dissolution of Mg in the metallic Ga on the surface of the growing GaN film. This process increases the sticking coefficient of the arriving Mg atoms, which otherwise would have re-evaporated at the high growth temperature employed (770 °C), since the vapor pressure of Mg is 10 Torr at this temperature.<sup>16</sup> We believe that the incorporation of Mg into the GaN from the solution of (Ga+Mg) proceeds via processes similar to liquid-phase epitaxy. Thus, thermodynamic rather than kinetic mechanisms become important in the efficient incorporation of Mg in the presence of excess Ga. Such mechanisms are likely to lead to the incorporation of Mg in the Ga sites, where they act as *p*-type dopants.

Recently, Neugebauer *et al.*<sup>17</sup> proposed that a thin metallic film on a semiconductor surface may open up an efficient diffusion channel for lateral adatom transport. This con-

cept was used to explain why In acted as a surfactant and Ga acted as an auto-surfactant on GaN surfaces during GaN growth. Whether this proposal is applicable to our findings in Mg incorporation needs to be investigated.

In conclusion, we have studied the role of group III to group V ratio in the incorporation of Mg during GaN growth by MBE at relatively high growth temperatures (770 °C). We found that Mg incorporated more effectively during growth at extreme Ga-rich conditions. We attribute these findings to the dissolution of Mg in the Ga film which increases its sticking coefficient. Transport coefficients and SIMS measurements of films grown under these conditions show that the doping efficiency is  $\sim 10\%$ . Using this method of doping, *p*-type GaN films were obtained, free of Ga droplets with hole concentration up to  $3 \times 10^{18} \text{ cm}^{-3}$  and lowest resistivity of 0.3  $\Omega \text{ cm}$ .

The work at Boston University was supported partially by DARPA (monitored by Dr. J. Carrano and Dr. J. Lorenzo), AFOSR (MURI, monitored by Dr. T. Steiner), and ONR (monitored by Dr. C. Wood). The authors acknowledge the use of facilities of the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

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