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Hole conductivity and compensation in epitaxial GaN:Mg layers

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The concentration p and the mobility μ of holes in metal-organic chemical vapor deposition (MOCVD) GaN:Mg layers were studied by room temperature Hall-effect measurements as a function of the Mg concentration N_A in the range $3\times10^{18}\,\mathrm{cm}^{-3}\leqslant N_A\leqslant 1\times10^{20}\,\mathrm{cm}^{-3}$. The hole density first increases with increasing N_A, reaches a maximum value $p_{\max}\approx6\times10^{17}\,\mathrm{cm}^{-3}$ at $N_A\approx2\times10^{19}\,\mathrm{cm}^{-3}$, decreases for larger N_A values, and drops to very small values at $N_A\approx1\times10^{20}\,\mathrm{cm}^{-3}$. The hole mobility decreases monotonically with increasing N_A. The $p(N_A)$ data provide strong evidence for self-compensation, i.e., for a doping driven compensation of the Mg acceptor by intrinsic donor defects. This effect becomes significant when N_A exceeds a value of $2\times10^{19}\,\mathrm{cm}^{-3}$. A semiquantitative self-compensation model involving nitrogen vacancies is developed. It accounts satisfactorily for the measured $p(N_A)$ dependence and suggests that self-compensation limits the hole conductivity in bulklike MOCVD GaN:Mg layers grown near 1300 K to about 1.2 $(\Omega\,\mathrm{cm})^{-1}$.

I. INTRODUCTION

The discovery of *p*-type conductivity in magnesium-doped GaN grown by metal-organic chemical vapor deposition (MOCVD) following low energy electron irradiation[1] or thermal annealing[2] marks the beginning of GaN-based optoelectronics. Hydrogen depassivation of the Mg acceptor has been recognized as the essential process to convert as-grown high-resistivity GaN:Mg into *p*-conducting material.[3] Today high brightness yellow, green, blue GaN-based light emitting diodes (LED's), and UV-LED's as well as violet laser diodes are commercially available.[4] Despite these breakthroughs the hole conductivity in GaN:Mg has remained low, two orders of magnitude below that of say GaAs:Be at a doping level of $2\times10^{18}\,\mathrm{cm}^{-3}$, one reason being the large Mg-acceptor ionization energy. This limited *p*-type conductivity is one of the major reasons that hampers further rapid development of nitride-based laser diodes as well as bipolar electronics. After acceptor depassivation (thermal annealing), the typical hole concentrations at room temperature (RT) of MOCVD-grown GaN:Mg, as reported by several groups, are $(2-5)\times10^{17}\,\mathrm{cm}^{-3}$ for doping levels in the mid $10^{19}\,\mathrm{cm}^{-3}$ range. The corresponding RT hole mobilities are around 10 cm^2/Vs. Thus, the typical hole conductivities σ are less than 1 $(\Omega\,\mathrm{cm})^{-1}$. This is sufficient for LED's, just sufficient for laser diodes but critical for electronic bipolar device applications.

This paper addresses the question whether the limited hole conductivity in properly annealed MOCVD GaN:Mg is due to donor *impurity* background *compensation* or whether it has more fundamental character, namely *self-compensation* (SC) by intrinsic lattice defects such as vacancies or interstitial host atoms. In binary compounds with a high band gap energy the latter type of compensation has been known to be important for a long time.[5] Energetically SC is favored if the formation energy of a compensating lattice defect is smaller than the trapping energy of a free carrier at this defect. A well established example is donor- (say Cl) doped ZnS. In this case, the compensating acceptor centers are nearest neighbor associates of a zinc vacancy and Cl on a sulphur site as has been demonstrated by electron spin resonance.[6] Corresponding compensating defects can be expected in GaN:Mg since GaN and ZnS have similar band gap energies and other similar physical properties. Actually, it is known from photoluminescence studies that Mg doping of GaN leads to the formation of a deep donor in addition to the shallow Mg acceptor.[7,8]

In the experimental part of this work the measured hole density p as a function of the Mg concentration N_A is presented over the doping range $3\times10^{18}-1\times10^{20}\,\mathrm{cm}^{-3}$. The hole density is found to be peaked at $N_A\approx2\times10^{19}\,\mathrm{cm}^{-3}$ and drops to very small values when N_A approaches $1\times10^{20}\,\mathrm{cm}^{-3}$. This dependence is shown to be incompatible with an impurity compensation model. Since the nitrogen vacancy V_N, a triple donor, has a particularly low formation energy in p-GaN (Refs. 9 and 10) two idealized SC models involving V_N are treated semiquantitatively: first, SC only by *isolated* V_N and second, SC only by the nearest neighbor *pair* $\mathrm{Mg_{Ga}}V_\mathrm{N}$, a double donor. These model calculations predict that SC limits the maximum hole density in GaN:Mg grown near 1300 K to about $5\times10^{17}\,\mathrm{cm}^{-3}$ corresponding to a maximum conductivity σ of ≈1 $(\Omega\,\mathrm{cm})^{-1}$, given a mobility near 13 cm^2/Vs. They provide a satisfactory explanation for the drop in hole density at the highest doping levels, and they suggest that a significantly improved hole conductivity can be achieved only if partial suppression of SC becomes possible.

II. EXPERIMENTAL DETAILS

The samples studied were prepared over a period of about two and a half years. X-ray studies have confirmed that all layers have wurtzite structure. They were grown by low pressure metal-organic chemical vapor deposition on 2 in. sapphire substrates using a 30-nm-thin GaN nucleation layer. The subsequent layer sequence consists of 1.5-μm-thick undoped GaN and a (0.5–0.8)-μm-thick GaN:Mg layer with a doping level ranging from 1×10^{19} to $1\times10^{20}\,\mathrm{cm}^{-3}$. For Mg concentrations below $1\times10^{19}\,\mathrm{cm}^{-3}$ the realization of good ohmic contacts to p-GaN:Mg, required for reliable electrical

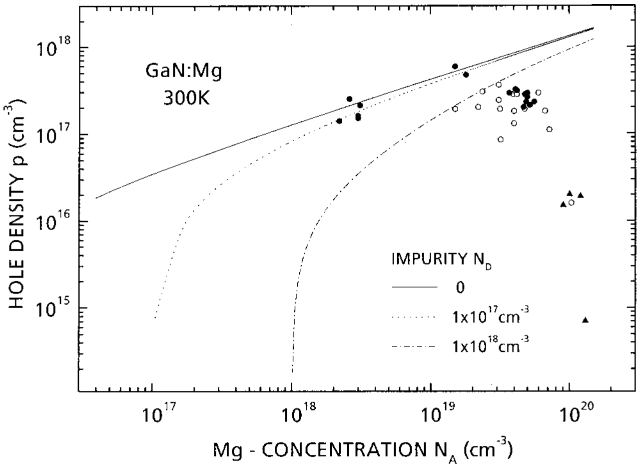

FIG. 1. Hole concentrations in GaN:Mg as measured by RT Hall effect (circles and triangles). Solid circles correspond to samples that were grown more recently. The triangular data points are from Ref. 11. The three curves correspond to the calculated hole densities in an impurity compensation model for three residual donor densities as shown in the legend.

measurements is difficult. Therefore, in this doping regime the layer sequence above the nucleation layer was modified and consists of 0.5 μm undoped GaN, 1.8 μm moderately doped GaN:Mg, and a GaN:Mg contact layer with a doping level of $3\times10^{19}\,\mathrm{cm}^{-3}$. The latter layer was removed by dry etching except at the points where the contact metal had been placed. All GaN:Mg films were grown near 1300 K with a V/III flow ratio of 4000. Following growth, the wafers were annealed in a nitrogen atmosphere typically at 600 °C for 10 min in order to depassivate the Mg acceptors. The chemical Mg concentrations of the samples were determined by secondary ion mass spectroscopy (SIMS) using Mg ion-implanted standards.

For Hall-effect measurements small ohmic contacts in van der Pauw geometry were evaporated through a mask at the corners of $5\times5\,\mathrm{mm}^2$ squares. The contacts are formed by a 10-nm-thick Ni and a 400-nm-thick Au layer. A thermal treatment of the contacts, similar to that used for acceptor activation, often improved their ohmic characteristics and decreased the contact resistance.

III. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 1 the measured RT hole densities p of the present GaN:Mg samples are plotted versus the Mg concentration N_A. Each data point (circle) corresponds to a separate wafer. For N_A values close to $1\times10^{20}\,\mathrm{cm}^{-3}$ four data points (triangles) obtained by another group[11] are also included. For a given N_A there is considerable scatter in the hole density of different samples. This is not due to the Hall measurements which are reproducible. Rather the scatter is the result of improvements in growth procedure, postgrowth annealing conditions, and contact technology during the course of this investigation. The solid circle data points were obtained from samples grown more recently. The three curves correspond to the expected p vs N_A relation for three residual donor concentrations N_D in an impurity compensation model. They were calculated at RT with the expression appropriate in the case of incomplete ionization[12]

$$p=-\frac{N_D+K}{2}+\sqrt{\left(\frac{N_D+K}{2}\right)^2+K(N_A-N_D)}, \qquad (1)$$

where N_D is the donor impurity density, N_A the Mg doping concentration, and K is given by $K=1/\beta N_{val}\exp(-E_A/kT)$. Here β is the valence band (vb) degeneracy factor, N_{val} the temperature dependent vb density of states (DOS), E_A is the thermal Mg-acceptor ionization energy, k is the Boltzmann constant, and T is the temperature. The evaluation of β and N_{val} must include all three, slightly split valence bands A, B, and C of the wurtzite structure since they all are partially occupied at RT. Therefore β is obtained by summing over the degeneracy factors (each being 2) of the individual bands weighted with the appropriate Boltzmann factors giving $\beta(\mathrm{RT})=3.6$ for GaN on $\mathrm{Al_2O_3}$ and a typical strain situation. The value of N_{val} at RT is obtained accordingly using the familiar expression for the DOS.[12] The individual calculated DOS masses (in units of the free electron mass) of the A, B, and C valence bands are $m_i\approx0.6\,(i=A,B,C)$.[13] Experimentally, these masses are larger[13] which is why $m_i\approx0.8$ is used here. This results in $N_{val}=3.2\times10^{19}\,\mathrm{cm}^{-3}$, a value which is about a factor of 2 larger than the one quoted previously.[14] Strictly speaking, the activation energy E_A depends on N_A.[15,16] For simplicity, a constant value, $E_A=160\,\mathrm{meV}$, appropriate for $N_A\approx4\times10^{19}\,\mathrm{cm}^{-3}$ is used here, at the cost that this value is somewhat too large (small) for N_A above (below) $4\times10^{19}\,\mathrm{cm}^{-3}$. Finally, K at RT is obtained as $K=1.8\times10^{16}\,\mathrm{cm}^{-3}$.

Returning to Fig. 1 it is noted first, that up to about $N_A\approx2\times10^{19}\,\mathrm{cm}^{-3}$ the full circle data points are close to the theoretical $N_D=0$ and the $N_D=1\times10^{17}\,\mathrm{cm}^{-3}$ curve. This indicates that in the moderate doping range, $3\times10^{18}\,\mathrm{cm}^{-3}\leqslant N_A\leqslant2\times10^{19}\,\mathrm{cm}^{-3}$, hydrogen depassivation is very effective and impurity compensation as well as self-compensation play a minor role. When N_A becomes larger than $2\times10^{19}\,\mathrm{cm}^{-3}$, the measured hole concentrations fall progressively lower below the $N_D=0$ curve. The decrease in p becomes especially pronounced for $N_A>5\times10^{19}\,\mathrm{cm}^{-3}$ until practically complete compensation is reached near $N_A=1\times10^{20}\,\mathrm{cm}^{-3}$. Actually, a comparison of the data points with the $N_D=0$ curve indicates that the degree of compensation increases with increasing Mg-acceptor density for $N_A>2\times10^{19}\,\mathrm{cm}^{-3}$. It is evident that such a behavior at the highest doping levels is incompatible with impurity compensation, whatever the donor concentration N_D is.

Previously, the decrease in hole concentration for $N_A>5\times10^{19}\,\mathrm{cm}^{-3}$ has been attributed to the solubility limit of $\mathrm{Mg_{Ga}}$ and the formation of a second phase, $\mathrm{Mg_3N_2}$.[11] However, in this case one would expect an increasing hole density with increasing N_A which saturates at a maximum p value but does not decrease again at still higher N_A values. In order to clarify experimentally the role of a second phase, two GaN:Mg samples with N_A close to $1\times10^{20}\,\mathrm{cm}^{-3}$ have been examined by x-ray diffraction. Using a Guinier-type focusing x-ray diffractometer with the sample rotating around its surface normal symmetrical $\theta/2\theta$ scans yielded peaks attributable to GaN-0002 and sapphire-0002 reflections. Two spurious peaks with intensities more than a factor of 10^{-4} below that of the GaN-0002 peak could not be as-

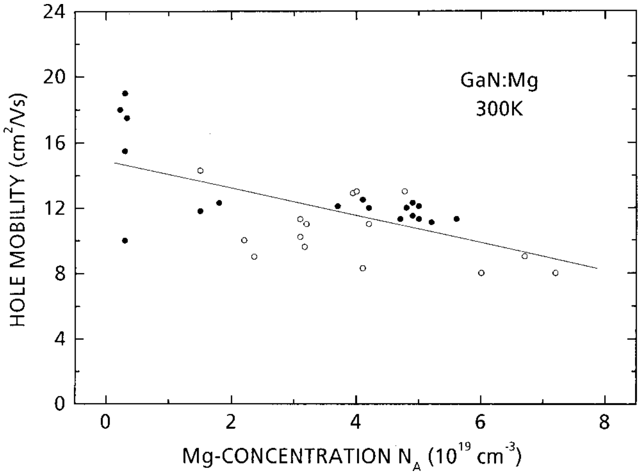

FIG. 2. Room temperature Hall mobility of holes in GaN:Mg as a function of the Mg doping concentration. Solid circles correspond to samples that were grown more recently. The straight line is a linear fit to all data points.

signed. Thus, if a second ordered phase were present its volume fraction should be much less than 1% and its effect on the hole density should be negligible even for $N_A = 1 \times 10^{20}\,\mathrm{cm}^{-3}$.

Part of the decrease in hole concentration above $N_A = 2 \times 10^{19}\,\mathrm{cm}^{-3}$ could also arise from a deterioration of the layer crystallinity at very high doping levels. However, as Fig. 2 shows, there is no dramatic change in hole mobility over the N_A range 3×10^{18}–$7 \times 10^{19}\,\mathrm{cm}^{-3}$.[17] Since the mobility reacts more sensitively to a dopant induced degradation of crystalline quality than the carrier concentration, a degraded crystallinity is unlikely the cause for the drop in hole density at very high Mg doping levels. It is therefore concluded that neither impurity compensation nor the solubility limit of $\mathrm{Mg}_{\mathrm{Ga}}$ nor the degradation of crystallinity limit the maximum hole density in MOCVD GaN:Mg at Mg doping levels above $\approx 2 \times 10^{19}\,\mathrm{cm}^{-3}$.

The remaining possibility to explain the electrical data in Fig. 1 is self-compensation (SC), i.e., the formation of intrinsic compensating donors or complexes of such donors with dopant atoms in concentrations comparable with those of the acceptor dopant at high doping levels. There is strong previous evidence for SC in GaN:Mg. First, different groups have inferred a compensation ratio $N_D/N_A \sim 0.1$ at a Mg doping level N_A of $2-5 \times 10^{19}\,\mathrm{cm}^{-3}$ from temperature dependent Hall measurements.[14,18] Thus, $N_D \sim 2-5 \times 10^{18}\,\mathrm{cm}^{-3}$, which is at least an order of magnitude larger than the residual donor impurity content in state of the art undoped MOCVD GaN. This indicates that the majority of compensating donors must arise from SC. Second, for Mg concentrations above $2 \times 10^{19}\,\mathrm{cm}^{-3}$ GaN:Mg reveals an intense blue photo luminescence band peaked near 2.8 eV at RT.[7,8] This blue band has donor-acceptor pair character. The natural acceptor candidate is isolated $\mathrm{Mg}_{\mathrm{Ga}}$ while a likely candidate for the deep donor is the nearest neighbor pair $\mathrm{Mg}V_{\mathrm{N}}$.[7] Thus, together with the data in Fig. 1, the evidence for SC in GaN:Mg for doping levels above $2 \times 10^{19}\,\mathrm{cm}^{-3}$ is compelling. In the following the effect of SC as a function of the doping level is treated semiquantitatively.

IV. MODELING OF SELF-COMPENSATION

In *p*-type GaN, the intrinsic defect with the lowest formation energy, 0.3–0.5 eV depending on the position of the Fermi level E_F, is the nitrogen vacancy V_{N}.[9,10] Consequently, it dominates in concentration at the typical MOCVD growth temperatures, $T \approx 1300\,\mathrm{K}$. In addition, it is a triple donor.[9,10] Therefore, in GaN:Mg compensation of Mg acceptors by isolated V_{N} or V_{N} complexed with the dopant is very likely. Two idealized cases of SC in GaN:Mg are now considered. In case 1 ($l=1$) the compensating donor $D^{(1)}$ is the isolated nitrogen vacancy V_{N} which, as a triple donor, has a multiplicity $m_1 = 3$. In case 2 ($l=2$) the donor $D^{(2)}$ is the nearest neighbor complex $\mathrm{Mg}V_{\mathrm{N}}$ which is a double donor with a multiplicity $m_2 = 2$. The former case is considered to be less realistic but is included for comparative purposes. The latter case is considered important since large fractions of the dopant and the vacancies are ionized at $T \approx 1300\,\mathrm{K}$ and the latter are mobile. Thus they tend to form near neighbor pairs, in particular when the doping concentration is high (upper $10^{19}\,\mathrm{cm}^{-3}$ range), and the mean separations are of the order of a few nanometers only. In fact, such nearest and next nearest neighbor dopant vacancy pairs have been detected in the high gap semiconductor ZnS by electron-spin resonance.[6,19]

In analogy to the definition of the compensation ratio in the case of impurity compensation, the self-compensation coefficient c_l is now defined by $c_l = N_D^{(l)}/N_A$ where $N_D^{(l)}$ and N_A are the donor and the Mg doping concentration, respectively. It should be noted that the c_l in the present cases do not directly correspond to the SC *ratios* r_l. These are given by $r_1 = 3c_1$ and $r_2 = 2c_2/(1-c_2)$. Complete compensation, $r_l = 1$ in both cases, is reached for $c_l = \frac{1}{3}$. With the above definition for the coefficients c_l Eq. (1) for the impurity compensation case can be rewritten for the two special cases of SC considered here,

$$p = -\frac{m_l c_l N_A + K}{2} + \sqrt{\frac{(m_l c_l N_A + K)^2}{4} + K N_A (1 - 3c_l)}, \tag{2}$$

where all symbols have been defined above. The task now is the calculation of the c_l as a function of N_A.

In case 1, $N_D^{(1)} = N_V$ where N_V is the concentration of nitrogen vacancies V_{N}. In thermal equilibrium at the growth temperature T it is given by $N_V = (N_S/2)\exp(S/k)$ $\exp(-H_V/kT)$ where $N_S = 8.8 \times 10^{22}\,\mathrm{cm}^{-3}$ is the number of sites per cubic centimeter GaN, and S and H_V are the V_{N} vacancy formation entropy and energy, respectively. The latter is a piecewise linear function of the Fermi level E_F and can be written[9,20] as $H_V = H_V^q + qE_F$ where q denotes the charge state of V_{N}, i.e., 0 to 3+, and H_V^q is the value of H_V in charge state q for $E_F = 0$, i.e., when E_F lies on the vb edge. The vacancy concentration can then be written in the following form:

$$N_V = (N_S/2) C_q \exp(-qE_F/kT), \tag{3}$$

with $C_q = \exp(S/k)\exp(-H_V^q/kT)$. Thus, for each charge state $q \neq 0$, N_V increases exponentially with decreasing E_F, i.e., when E_F approaches the valence band. Of course, the position of the Fermi level E_F relative to the vb edge is related to the acceptor concentration N_A. If residual donor impurities can be neglected the appropriate expression to be used here is that of the compensation free case which reads[12]

$$E_F = kT \ln\left\{ \frac{N_{val}}{2N_A}\left[1+\sqrt{1+\alpha\frac{N_A}{N_{val}}}\right]\right\}, \tag{4}$$

with $\alpha = 4\beta \exp(E_A/kT)$. At the growth temperature (1300 K), $\beta = 5.1$, $\alpha \approx 85$, and $N_{val} = 2.9\times 10^{20}\,\mathrm{cm}^{-3}$. Inserting Eq. (4) into Eq. (3) and using the definition for c_1 one finds in case 1

$$c_1 = C_q \frac{N_S}{N_{val}}\left(\frac{2N_A}{N_{val}}\right)^{q-1}\left(1+\sqrt{1+\alpha\frac{N_A}{N_{val}}}\right)^{-q}. \tag{5}$$

This form of $c_1(N_A)$ is not yet useful for comparison with experiment since the quantity C_q is unknown. Elimination of C_q and replacement by a parameter more readily inferred from experiment is deferred for the moment.

In case 2, the compensating donor concentration $N_D^{(2)}$ is proportional to both N_V and N_A. Thus $N_D^{(2)} = M^{-1}N_A N_V$ where M^{-1} is a temperature dependent proportionality constant. The SC coefficient c_2 can now be calculated along the lines exemplified above for c_1 and is obtained as

$$c_2 = C_q \frac{N_S}{2M}\left(\frac{2N_A}{N_{val}}\right)^{q}\left(1+\sqrt{1+\alpha\frac{N_A}{N_{val}}}\right)^{-q}, \tag{6}$$

where $q = 1, 2, 3$ corresponds to the positive charge states of V_{N} as in case 1. In the doping range of interest, say $5\times 10^{18}\,\mathrm{cm}^{-3} \leqslant N_A \leqslant 1\times 10^{20}\,\mathrm{cm}^{-3}$, the separation of E_F from the vb at the growth temperature, as obtained from Eq. (4) is less than 480 meV. For simplicity of discussion it is assumed that the separation of the $V_{\mathrm{N}}^{2+}/V_{\mathrm{N}}^{3+}$ donor level from the vb is larger than this value. In this case V_{N}^{3+} is the stable charge state of V_{N} even for moderate Mg doping levels in the mid $10^{18}\,\mathrm{cm}^{-3}$ range, and q in Eqs. (5) and (6) can be restricted to $q = 3$.

If now for case 2 and case 1 a fit parameter N_{CC} is introduced, defined as the doping concentration N_A for which complete compensation occurs, i.e., $c_l(N_{CC}) = \frac{1}{3}$, Eqs. (5) and (6) can be renormalized and compactly rewritten in the form

$$c_l = \frac{1}{3}\left(\frac{N_A}{N_{CC}}\right)^{l+1}\left(\frac{1+\sqrt{1+\alpha N_{CC}/N_{val}}}{1+\sqrt{1+\alpha N_A/N_{val}}}\right)^3, \tag{7}$$

where $l = 1$ and $l = 2$ corresponds to case 1 and case 2, respectively for $q = 3$. It should be noted that the parameters α and N_{val} in Eq. (7) are not independent. Rather, $\alpha/N_{val} \equiv 4/K$ the expression for K being given in Sec. III. Thus, when calculating $p(N_A)$ from Eqs. (2) and (7) only two parameters are required as in the impurity compensation case (K, N_D), namely K and the fit parameter N_{CC} which depends on unknown properties of the vacancy V_{N}.

Since the V_{N} donors are generated at the growth temperature T, the values of α and N_{val} in Eq. (7) are those at $T \approx 1300$ K as quoted in connection with Eq. (4). During cooling of the crystal to RT the equilibrium vacancy concentration may change since these defects can migrate and may be annihilated. As is usually done, it is assumed that the equilibrium V_{N} concentration is frozen which is justified if cooling is sufficiently rapid. Under this premise Eq. (7) can be used for a comparison with RT data. Now the desired $p(N_A)$ dependence at RT can be calculated from Eqs. (2) and (7) using the well established input parameters of the Mg acceptor (E_A), the vb (β, N_{val}), as well as the fit parameter N_{CC}, which can be inferred from the present experiment. If N_A is small compared to N_{CC} it follows from Eq. (7) that the SC coefficients c_l are very small. In the present cases this requirement is satisfied for $N_A < 1\times 10^{19}\,\mathrm{cm}^{-3}$ since N_{CC} turns out to be larger than $1\times 10^{20}\,\mathrm{cm}^{-3}$. This means that SC in GaN:Mg is very small or negligible for $N_A < 1\times 10^{19}\,\mathrm{cm}^{-3}$ but becomes progressively more significant when N_A approaches N_{CC}. This behavior is fundamentally different from impurity compensation which is most pronounced at low or moderate doping levels, compare Fig. 1.

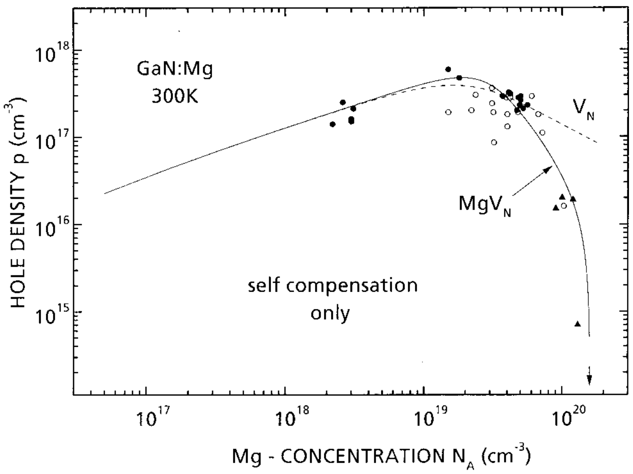

FIG. 3. Hole concentrations in GaN:Mg as in Fig. 1. The dashed and the full curve are fits based on the self-compensation models 1 and 2, respectively. The arrow above the abscissa marks the fit parameter N_{CC} for model 2.

V. COMPARISON WITH SELF-COMPENSATION MODELS

In Fig. 3 the experimental p vs N_A data are replotted and compared with the calculated $p(N_A)$ curves for case 1 ($D^{(1)} = V_{\mathrm{N}}$, dashed line) and case 2 ($D^{(2)} = \mathrm{Mg}V_{\mathrm{N}}$, full line). A comparison of these curves with the compensation free case, curve $N_D = 0$ in Fig. 1, once more demonstrates that SC effects for $N_A < 1\times 10^{19}\,\mathrm{cm}^{-3}$ are negligible for practical purposes. The fitting parameters N_{CC} for the two curves in Fig. 3 were obtained by a least square procedure. In this way $N_{CC} \approx 1.6\times 10^{20}\,\mathrm{cm}^{-3}$ and $N_{CC} \approx 3\times 10^{21}\,\mathrm{cm}^{-3}$ were determined for case 2 and case 1, respectively. In both cases the calculated hole density p reaches a maximum near $N_A = 2\times 10^{19}\,\mathrm{cm}^{-3}$ and decreases at higher Mg concentrations, thus strongly supporting that SC is the cause for the reduction in p at very high doping levels and for the concomitant limitation of p. The fit is less convincing for case 1 which supports the view that *isolated* V_{N} vacancies are unlikely the major compensators in heavily doped material. For case 2 where $\mathrm{Mg}V_{\mathrm{N}}$ pairs are the compensating donors the fit is satisfactory and the maximum RT hole density predicted is $p_{\max} = 4.7\times 10^{17}\,\mathrm{cm}^{-3}$ at $N_A = 2.0\times 10^{19}\,\mathrm{cm}^{-3}$. It is noted in passing that this N_A value coincides with the Mg concentration at which the Mg-related blue donor-acceptor pair photoluminescence band appears in MOCVD GaN:Mg.[7] The values used here for the parameters β, N_{val}, E_A, and N_{CC} which enter into the calculation of $p_{\max}$ are believed to be quite reliable. Therefore, significantly larger hole densities cannot be expected upon justifiable changes in parameters. Even if the hole DOS masses m_i entering N_{val} were 25% larger than used ($m_i = 1$ instead of 0.8) $p_{\max}$ would not exceed $6 \times 10^{17}\,\mathrm{cm}^{-3}$. Using this value and $\mu \approx 13\,\mathrm{cm}^2/\mathrm{Vs}$ at $N_A = 2 \times 10^{19}\,\mathrm{cm}^{-3}$, compare Fig. 2, gives an upper limit for the hole conductivity, $\sigma \leqslant 1.2\ (\Omega\,\mathrm{cm})^{-1}$ under the present growth conditions. The best σ value measured directly is 1.1 $(\Omega\,\mathrm{cm})^{-1}$ for one sample with $N_A = 1.5 \times 10^{19}\,\mathrm{cm}^{-3}$ in Figs. 1–3. Distinctly higher conductivities in MOCVD material appear to be possible only if the effect of SC can be suppressed, at least partially.

GaN:Mg layers grown by molecular beam epitaxy (MBE) should suffer much less from SC than MOCVD layers because of the 200–300 K lower growth temperature in MBE and the concomitant reduction in V_{N} concentration which reduces SC effects. In fact, a recent report on MBE GaN:Mg layers grown at 650 °C (Ref. 21) quotes $p = 1.4 \times 10^{18}\,\mathrm{cm}^{-3}$ and $\mu = 7.5\,\mathrm{cm}^2/\mathrm{Vs}$ at a Mg concentration of $7 \times 10^{19}\,\mathrm{cm}^{-3}$ corresponding to $\sigma = 1.7\ (\Omega\,\mathrm{cm})^{-1}$. In MOCVD material the hole concentration at this Mg level is about an order of magnitude lower, compare Fig. 3. On the other hand, the conductivity σ of the above MBE material is only about 55% higher than the maximum σ value obtained in this work for MOCVD GaN:Mg.

Self-compensation limited hole conductivity as discussed here for GaN occurs for other high-gap semiconductors as well. In p-type ZnSe:N the dopant N not only creates the shallow acceptor level but also two N-related compensating donor levels[22] which limit the hole concentration to $p \approx 1 \times 10^{18}\,\mathrm{cm}^{-3}$, the similarity with p-type GaN:Mg being obvious. Even in more conventional compound semiconductors SC can limit the conductivity but the effect is less severe since it occurs at a much higher carrier density level. For instance, in n-GaAs:Si the maximum electron concentration is limited to around $1 \times 10^{19}\,\mathrm{cm}^{-3}$ depending on the growth temperature.[23] Of course, in this case the amphoteric nature of the Si dopant, leading also to $\mathrm{Si}_{\mathrm{As}}$ acceptors at high doping levels, accounts for about one half of the compensating acceptors. However, there is also strong evidence that a comparable portion of acceptors is due to a deep defect complex involving $\mathrm{Si}_{\mathrm{Ga}}$ and a Ga vacancy.[24]

VI. SUMMARY

The RT hole density and mobility in MOCVD GaN:Mg layers, as obtained from Hall-effect measurements, were presented over a wide doping range, $3 \times 10^{18}\,\mathrm{cm}^{-3} \leqslant N_A \leqslant 1 \times 10^{20}\,\mathrm{cm}^{-3}$. It was shown that the experimental $p(N_A)$ dependence reaches a maximum at $N_A \approx 2 \times 10^{19}\,\mathrm{cm}^{-3}$ with $p_{\max} \approx 6 \times 10^{17}\,\mathrm{cm}^{-3}$ indicating an increasing degree of compensation with increasing N_A. These data cannot be explained by a compensation model involving residual donor *impurities* only. Based on suggestions that nitrogen vacancies V_{N} are the dominant defects in p-type GaN:Mg two semiquantitative SC models with either isolated V_{N} or MgV_{N} pairs acting as deep donors, respectively, were elaborated. A fit to the data points in both cases predicts that p reaches a maximum near $N_A = 2 \times 10^{19}\,\mathrm{cm}^{-3}$ with $p_{\max} \approx 5 \times 10^{17}\,\mathrm{cm}^{-3}$ in close agreement with the experimental findings. However, the results are in favor of the MgV_{N} pair model which for heavily doped material is reasonable for principal reasons. Based on the upper limit of the hole density and a mobility of 13 $\mathrm{cm}^2/\mathrm{Vs}$ at $N_A \approx 2 \times 10^{19}\,\mathrm{cm}^{-3}$ one can predict an upper limit for the hole conductivity in bulklike MOCVD layers grown near 1300 K, $\sigma \leqslant 1.2\ (\Omega\,\mathrm{cm})^{-1}$.

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