Non-Equilibrium Acceptor Concentration in GaN:Mg Grown by Metalorganic Chemical Vapor Deposition

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ABSTRACT

It is shown that the high p-type conductivity in GaN:Mg, grown by metal-organic chemical vapor deposition followed by post-growth annealing, is due to non-equilibrium acceptor concentrations. A series of samples cut from a single GaN:Mg wafer, which initially had undergone rapid thermal annealing (RTA) after growth, has been investigated. The samples were annealed at various temperatures in nitrogen ambient for over 12 hours, and temperature-dependent Hall effect measurements were performed. For samples annealed at temperatures higher than 850 °C, the hole concentrations decrease by at least an order of magnitude, compared with the original sample. This behavior is explained by an Mg acceptor concentration in excess of its equilibrium solubility limit in the original sample; thus, at high enough temperatures, in the absence of hydrogen, Mg acceptors diffuse either to form electrically inactive precipitates or are eliminated. It is worth noting that the acceptor activation energy remains the same for all samples.

INTRODUCTION

GaN and its alloys have great potential for various electronic and optoelectronic applications [1-3]. Often good bipolar doping is an essential requirement for optimal device performance; however, it is difficult to obtain highly p-type GaN and many related alloys. Although rapid progress has been made and hole concentrations of $\sim 10^{18}$ cm^{-3} have been achieved by both molecular beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD) (for review see e.g. Ref. [4]), some further investigations on the basic mechanism of p-type doping of GaN appear useful.

Regarding MOCVD, it is well known that as-grown p-type (e.g. Mg doped) GaN is highly resistive and post-growth treatments such as low-energy electron-beam irradiation [5] or thermal annealing in non-hydrogen containing atmospheres (e.g. N_2) at temperatures above 700°C [6] are required to "activate" acceptors. It is widely accepted (see e.g. Ref 7-9) that for MOCVD-grown GaN:Mg atomic hydrogen acts as a compensating donor, leading to the highly resistive as-grown material. The acceptors, however, are activated (as mentioned above) when the hydrogen is removed.

Theoretical studies [10] have shown that, neglecting compensation aspects, the limiting factor in controlling doping in wide bandgap semiconductors, like GaN, is the solubility limit of dopants. To overcome this problem, one has to use growth techniques that result in non-equilibrium dopant concentrations. For MBE the non-equilibrium doping has been discussed previously [11]**.** As to MOCVD, we present here experimental evidence that proves that the concentration of Mg acceptors in MOCVD grown and activated GaN:Mg is also above its equilibrium value.

For these studies we have used a series of GaN:Mg samples grown by MOCVD, which were activated by RTA and then further annealed in N_2 at various temperatures for up to 12 hours. Temperature-dependant Hall effect measurements were carried out on all samples with Ni/Au Ohmic contacts [12, 13]. We have found that hole concentrations decrease by an order of magnitude or more, compared with the "baseline" sample (see below), when annealed at 850 °C or higher temperatures. This behavior is explained by Mg acceptor concentrations in excess of the equilibrium solubility limit; thus, at high enough temperatures and long annealing times Mg acceptors, in the absence of hydrogen, diffuse either to form electrically inactive precipitates or are eliminated from the sample. It is of interest that in this treatment the acceptor activation energy remained almost the same for all samples.

EXPERIMENT

The series of samples investigated in our studies has been prepared from a single GaN:Mg wafer grown by MOCVD on sapphire substrate with GaN buffer layer. The epitaxial GaN:Mg film is 1μm thick. First, the wafer was subject to rapid thermal annealing (RTA) at 950 °C in N_2 ambient for 8sec, and then it was cut into several pieces. One piece has been left as the "baseline" sample. The rest were further annealed at various temperatures from 750 °C to 930 °C in N_2 ambient for over 12h. To avoid GaN exposure to O_2 at high temperature, the furnace tube was purged by N_2 flow for at least 30min before increasing temperature; the N_2 flow was not turned off until the system returned to room temperature. The resistivity and Hall-effect measurements with Ni/Au Ohmic contacts in Van der Pauw geometry have been performed on all samples. The annealing conditions as well as resistivity (ρ), hole concentration (p), and mobility (μ) at room temperature are listed in Table I.

Due to its convenience, Van der Pauw method is frequently used. In our work, as also done previously [14, 15], the contact configuration for Hall-effect measurements using this technique consists of four very small contacts in the corners of a square sample. However, errors will be

Table I Annealing conditions, resistivity, hole concentration, and mobility at room temperature, also activation energy (E_{A0}), acceptor concentration, and compensating donor concentration obtained by fitting to Eq. (1).

Temp. Time	**ρ (Ω·cm)**	**p (10^{16} cm^{-3})**	**μ (cm^2/V·s)**	**E_{A0} (meV)**	**N_A (10^{17} cm^{-3})**	**N_D (10^{17} cm^{-3})**
950°C 8s, RTA	10.6	14.0	4.3	198	53.0	3.50
930°C 12hrs	89.1	0.48	15.0	196	1.10	0.55
850°C 14hrs	31.5	0.83	24.0	192	0.82	0.22
750°C 12hrs	2.00	49.0	6.6	189	120	1.70
750°C 20min	2.60	24.0	10.0	191	74.0	4.90

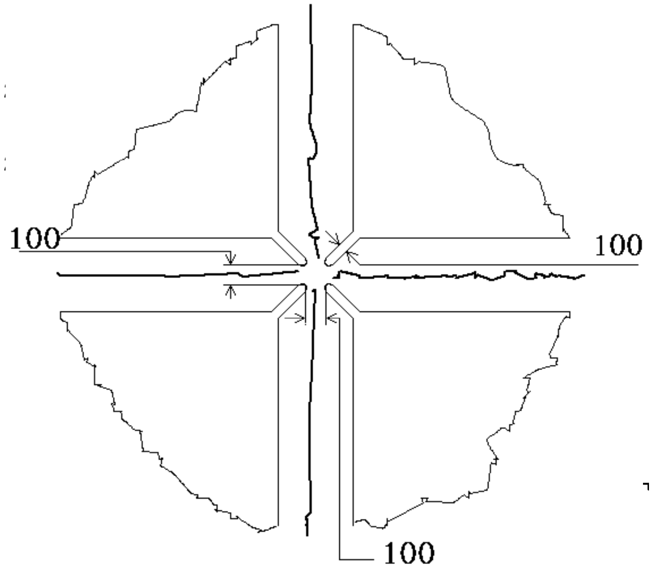

Figure 1 Contact pattern for Hall-effect measurement. Dimension is in microns. All areas exposed between metal pads are deliberately scratched, as depicted schematically by wavy lines.

introduced if contacts are not sufficiently small (the error relates to the ratio of contact diameter to sample dimension) [15] and/or if contacts are not placed on the periphery of the sample [14, 15]. Furthermore, because of the large activation energy of Mg in GaN and low hole mobility [16, 17], even activated GaN:Mg samples are still relatively resistive; thus to improve accuracy it is beneficial to restrict current flow to a relatively small area.

Based on the above considerations, a modified clover-leaf contact pattern (see figure 1) was employed [18]**.** The use of such a configuration results in the formation of four large contact pads with narrow (100μm in our case) tips extending toward the sample center. Photolithography was used to delineate the contact pattern on degreased sample surfaces. These cleaned surfaces were obtained by ultrasonic cleaning in acetone for 5 min, washing by isopropanol, rinsing in deionized water, and finally drying by N_2 flow. Prior to metal deposition, samples were etched with HCl (36.5%) for 2 min to remove the native oxide, and then were swiftly loaded into a thermal evaporator chamber. Ni/Au metal layers were deposited on GaN in vacuum with pressures lower than 1.5×10^{-7} Torr. After metal deposition, samples were rinsed in acetone, methanol, and isoproponal in sequence to strip off the photoresist, and then annealed at 500 $^{\circ}$C in air for 10 min in order to obtain Ohmic contacts [12, 13]. These contacts have shown Ohmic behavior in all temperature ranges used in our measurements. Finally, deliberate scratches were introduced between the metal pads to restrict current flow only to the limited central area of the sample, which in our case is approximately 100μm×100μm. The Hall-effect measurements were carried out with a magnetic field of 5000 Gauss on all samples.

RESULTS

Results of the Hall measurements are shown in figures 2 and 3, and table I [19]. Our experimental results show that the highest carrier concentration of ~4.9×10^{17} cm^{-3} was obtained in the sample annealed at 750 °C for 12h. Figure 2 shows the room temperature hole concentration (p) and resistivity (ρ) as a function of the annealing temperature (T_a) for samples annealed over 12h, and the inset is the room temperature Hall mobility (μ) as a function of the annealing temperature. The measured hole concentrations decrease by more than an order of

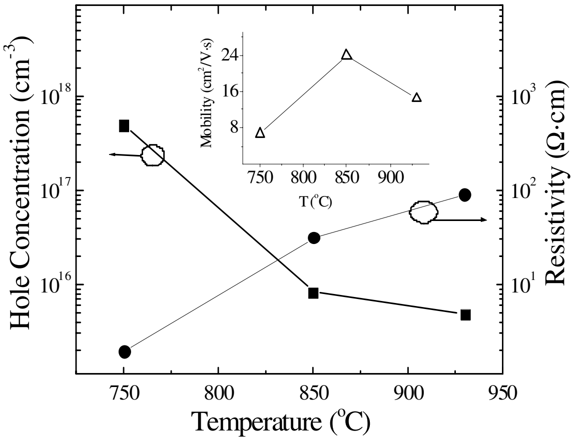

Figure2 Room temperature hole concentration, resistivity, and mobility as a function of annealing temperatures.

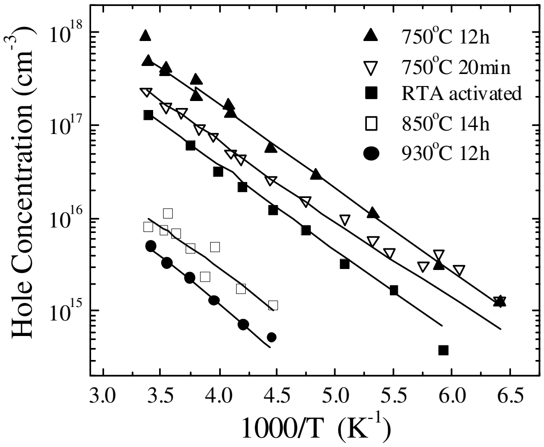

Figure 3 Hole concentration vs. reciprocal of temperature. Solid lines are from fitting.

magnitude for samples annealed at 850 °C or higher temperatures. The mobility does not change greatly and shows a maximum value of ~24.0 cm^2/V·s in the sample annealed at T_a = 850 °C. Figure 3 shows the temperature dependence of *p*, obtained from Hall measurements, for all five samples. Compared with the RTA sample, carrier concentrations increase for samples annealed at 750 °C after RTA, while for the samples annealed at $T_a \geq 850$ °C, carrier concentrations decrease with an increase in T_a.

DISCUSSION

To analyze results of the temperature-dependent Hall measurements, we have fitted the measured hole concentrations to eq. (1):

$$\frac{p(p+N_D)}{N_A - N_D - p} = \frac{N_V}{g}\exp\left(-\frac{E_A(T)}{k_B T}\right) \tag{1}$$

with

$$N_V = 2\left(\frac{2\pi m_{hh}^{*} k_B T}{h^2}\right)^{3/2} \tag{2}$$

and [20]

$$E_A(T) = E_{A0} - \frac{e^2}{\varepsilon} q(T). \tag{3}$$

Here, N_A is the acceptor concentration, N_D is the donor concentration, m_{hh}^{*} (= $0.8m_e$ [21]) is the heavy hole effective mass, *g* (=2 [21]) is the degeneracy factor, k_B is Boltzmann's constant, *T* is the absolute temperature, *h* is Planck's constant, *e* is the electron charge, *ε* is the dielectric constant, *q*(*T*) is the inverse screening radius, and E_{A0} is the Mg acceptor activation energy at *T* = 0 in lightly doped material. The expression for *q*(*T*) is taken from Ref. [22,23] and will be discussed in detail elsewhere. The results of fitting are shown as solid lines in figure 3, and the values of E_{A0}, N_A, and N_D are listed in Table I.

The acceptor and donor concentrations for the sample annealed at T_a = 750°C for 12h (it has the highest hole concentration) are 1.2×10^{19} cm^{-3} and 1.7×10^{17} cm^{-3}, respectively. As the annealing temperature T_a increases to $T_a \geq 850$ °C, p drops over an order of magnitude, N_A decreases nearly two orders of magnitude, and N_D decreases slightly. E_{A0} is similar in all the five samples (between 189meV and 198meV, see table I) and close to the Mg activation energies (208±4meV [24] and 203±10meV [24]) obtained from optical measurements. Thus we can assume that Mg_{Ga} is the only (or at least the main) acceptor contributing to the p-type conductivity in all five samples.

The dramatic decrease in carrier concentration observed at high annealing temperatures is of high interest. This observation, together with the corresponding decrease in acceptor concentration[1] [26], offers very convincing proof that Mg is indeed present, in the original RTA-annealed sample, in excess of its equilibrium solubility limit. Thus, once H, the compensating donor, is removed form the as-grown sample, the solubility of Mg acceptors decreases, and the Mg acceptor concentration thus presents in a super-saturated state and in excess of its equilibrium solubility limit in the absence of compensating donors [10]. Prolonged high-temperature annealing will then drive the system towards equilibrium and thus, in the absence of H, Mg_{Ga} diffuses either to form electrically inactive precipitates or is eliminated. We note that the existence of Mg precipitates in GaN:Mg annealed at high temperatures have been previously observed [27, 28]. For instance, Nakano and Jimbo [27] showed that Mg diffuses and segregates near the surface when GaN:Mg is annealed at temperatures above 800°C, while McCluskey *et al.* [28] observed, by transmission electron microscopy, pyramidal defects with Mg-rich inclusions in annealed GaN:Mg.

CONCLUSIONS

Temperature-dependent Hall effect measurements have been performed on a series of GaN:Mg samples grown by MOCVD, activated by RTA, and then annealed at temperatures varying from 750 °C to 930 °C in an N_2 atmosphere for up to 12h. In samples annealed above 850 °C for more than 12h, the carrier concentrations decreased by one order of magnitude or more compared with the “baseline” sample. Activation energies extracted by fitting to p as a function of temperauture are in the range 189~198meV for all samples. Acceptor concentrations obtained from fitting to the results for p show a decrease similar to that in carrier concentration, while the concentration of compensating donors decreases rather less. The plausible explanation for the drop in carrier and acceptor concentrations after annealing is that the Mg concentration in the RTA sample is well above its equilibrium solubility, and given a prolonged annealing at high enough temperatures in the absence of H, Mg will either precipitate or be eliminated from the sample.

ACKNOWLEDGMENTS

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[1] We note that Youn et al. [26] observed a decrease in carrier concentration for samples annealed at high temperatures and suggested that this was due to generation of compensating donors, like nitrogen vacancies, our fitting results show that the samples annealed at $T_a \geq 850$ °C have lower donor concentrations than the others, and thus, the decrease in p obviously cannot be explained by generation of nitrogen vacancies during high temperature annealing.

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