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### Low Temperature Electrical Transport Properties of MBE-grown Mg-doped GaN Subjected to a High Temperature Annealing Process

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In the case of molecular beam epitaxy, the Mg acceptors are electrically active in the asgrown material and a priori no additional annealing procedure is necessary. However, there are still some peculiarities in the electrical properties of ammonia-MBE grown GaN:Mg and some annealing effect can be observed. Additionally, the character of weak temperature dependence in the vicinity of room temperature suggests that to describe the conduction process an additional conduction channel not related to the free carriers in the valence band must be taken into account. For these reasons this paper presents the results of low temperature resistivity and Hall Effect studies of Mg-doped, ammonia-MBE grown GaN. The studied samples were grown on low temperature buffers of GaN deposited on sapphire substrate. High temperature annealing process (around 800 K) was carried out for all of them. The temperature dependences of the electrical transport properties before and after annealing procedure were especially investigated at temperatures ranging from 10 up to 300 K. It was found that the low temperatures transport properties are sensible to the annealing procedure and to describe the observed effects the hopping phenomena must be taken into account.

#### **1. Introduction**

The p-type doping of nitrides is the key for optical [1, 2, 3] and electronic [4, 5, 6, 7] devices. Understanding and explaining the properties of point defects in p-type material is crucial for improving the efficiency and longevity of light-emitting and/or power devices based on GaN. So far, magnesium (Mg) is the only acceptor dopant that generates sufficient p-type conductivity in a reproducible manner. Despite the technological maturity of GaN devices, there are still some basic properties related to the Mg doping mechanism and the p-type material behaviors, which are poorly understood, involving many questions. In the case of metal-organic vapor phase epitaxy (MOVPE), Mg acceptors are electrically inactive in asgrown material. An additional post-growth treatment is necessary to activate the dopant atoms. <sup>8</sup>] This technological step is systematically implemented in MOVPE samples with differences between the annealing conditions (temperature, atmosphere). It is usually accepted that this Mg activation consists in the dissociation of Mg-H complexes [<sup>9</sup>]. In the case of MBE, for which the hydrogen incorporation is much smaller than in MOVPE and the samples are grown at low temperature which decrease the density of donor like defects [<sup>10</sup>]. Mg acceptors are electrically active in the as-grown material and no additional annealing procedure is necessary. It was pointed out that annealing in an ambient nitrogen environment between 870 K and 1120 K for one hour led to no change in the electrical properties of the material grown by reactive MBE with ammonia  $[^{11}]$ . However in our previous work,  $[^{12}]$  from the electrical transport measurements carried out in the temperature range from 300 K up to 1000 K, we showed that for temperatures T exceeding some critical value  $T_C \ge 800$  K, the resistivity  $\rho$  and Hall concentration  $p_H$  became time-dependent. After the annealing process, a more than  $\sim 60\%$  irreversible decrease of the sample resistivity as well as an increase of the free hole concentration has occurred. The observed annealing effects are most likely related to a decrease in compensation, i.e., a decrease in the donor concentration, specifically hydrogen ions. At temperatures higher than 800 K, due to the creation of Ga vacancies, an efficient process of hydrogen-ion neutralization takes place. Moreover the observed, near room temperature, saturation of both  $p_H(T)$  and  $\rho(T)$  leads to the supposition that in this temperature range a conduction mechanism in the impurity band may be competitive to the conduction process in the valence band. The published results on resistivity vs temperature measurements in p-type GaN [<sup>13</sup>,<sup>14</sup>] indicate that the phenomenon of hopping may dominate the conductivity process up to room temperature and even to temperatures much higher. In this paper, we will verify the hypothesis of the influence of the two-path system of thermally activated band and hopping conduction on both, the Hall effect and conductivity. For this purpose, the electrical transport properties in the same type of samples were studied, before and after annealing, as a function of temperature in the low temperature range from room temperature to 10 K.

#### 2. Experimental methods

The crystal growth procedure was the same than the one applied for the samples in the previous study.[<sup>12</sup>] The materials under study were grown on 2-inch c-plane (0001) sapphire substrates by MBE in a "Riber 32P" reactor. Effusion cells were used for Ga and Al elements, the Mg dopant was supplied by a RIBER VCOR110 valved cell and ammonia (NH<sub>3</sub>) was used as the nitrogen source. Initially, the substrate surface was nitrided with ammonia at ~ 950 °C for 10 min. Then a GaN nucleation layer (30 nm) was grown at low temperature (~ 450 °C), followed by a 150 nm-thick AlN layer grown at 950 °C, with a growth rate of 0.1 µm/h. This AlN layer was inserted in order to get a compressive strain when growing the p-type GaN layer and avoid the formation of cracks. Finally, the Mg-doped GaN layers were grown at 770 °C, at a growth rate of 0.8 µm/h with a Mg cell temperature of 270 °C, corresponding to a Mg atom concentration in the crystals of about  $5 \times 10^{19}$  cm<sup>-3</sup>.

The samples were cut into  $5\times5 \text{ mm}^2$  squares with electrical contacts in van der Pauw configuration at the corners of the sample. The ohmic contacts were formed by the evaporation of Ni(20 nm)/Au(200 nm) electrodes and subsequent annealing in N<sub>2</sub> ambient at 400 °C. The samples were bonded with gold-wires to a ceramic support. For high temperature measurements and in-situ electrical characterization during annealing, the ceramic support was installed in a quartz tube inside a furnace. The temperature was measured with a platinum (Pt) resistor and stabilized with a precision better than 1 K. For low-temperature measurements the ceramic support was installed in a He-free cryostat enabling measurements at temperatures ranging from 10 K to 400 K.

During all electrical measurements, the current through the sample  $I_s$  was kept adequately low to ensure ohmic conditions. The resistivity measurements were performed using the van der Pauw method taking the average of all current configurations. Concerning Hall effect measurements, because of high carrier concentrations and low mobilities, to improve the Hall voltage  $V_H$  measurements, we used the van der Pauw approach [<sup>15</sup>] combined with the measurements as a function of the magnetic field *B* varying between ±1 Tesla. Then, the Hall carrier concentration  $p_H$  was deduced from the slope  $\beta$  of the Hall resistance  $\rho_{Hall}=V_H/I_s$ versus  $B: \beta = d\rho_{Hall}/dB$ . [<sup>12</sup>]

#### 3. Results

The electrical characteristics of the samples under study are presented in Table 1.

**Table 1:** Sample characteristics before annealing: resistivity  $\rho$ , Hall concentration  $p_H$  and Hall mobility  $\mu_H$  measured at 300 K. For comparison the sample E from paper [<sup>12</sup>] is shown.

| $\rho(T)$<br>[ $\Omega$ cm] | <i>р<sub>Н</sub>(T)</i><br>[ст <sup>-3</sup> ] | $\mu(T)$<br>[cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ]  |
|-----------------------------|--|---|
| 4.1                         | 7.0×10 <sup>17</sup>                           | 2.1   |
| 1.2                         | 2.1×10 <sup>18</sup>                           | 2.7   |
| 1.2                         | 2.0×10 <sup>18</sup>                           | 2.7   |
| 7.7                         | 2.2×10 <sup>17</sup>                           | 3.7   |
|                             | ρ(T)<br>[Ω cm]<br>4.1<br>1.2<br>1.2<br>7.7     | $ \begin{array}{c} \rho(T) & p_{H}(T) \\ [\Omega cm] & [cm^{-3}] \\ \end{array} $ 4.1 7.0×10 <sup>17</sup> 1.2 2.1×10 <sup>18</sup> 1.2 2.0×10 <sup>18</sup> 7.7 2.2×10 <sup>17</sup> |

#### 3.1. Electrical transport properties vs temperature



Figure 1. Conductivity  $\sigma$  of sample 1 as a function of temperature in the wide temperature range from 10 K up to 880 K. Graph as a function of  $T^{1/4}$ . Solid line - the linear fit of variable range hopping mechanism.

The temperature dependence of resistivity  $\rho$  for sample 1 is presented in **Figure 1**. In the whole investigated temperature range the conductivity increases with increasing temperature. The graph is done as a function of temperature  $T^{1/4}$  and as it can be seen from the figure, in a large temperature domain from 10 K to 140 K it corresponds to a linear variation of the conductivity.

Such linear dependence of  $Ln(\sigma)$  as a function of  $T^{1/4}$  indicate that at temperatures below 140 K the conduction process obeys Mott's law [<sup>16</sup>] of variable range hopping (VRH) and the resistivity vs T could be described by [<sup>17</sup>]:

$$\sigma_{hop}(T) = \sigma_o \exp\left[-\left(\frac{T_o}{T}\right)^{1/4}\right] \tag{1}$$

The values of  $\sigma_o$  and  $T_o$  parameters of linear fit (**Figure 1**) are respectively:  $\sigma_o=41 \ \Omega^{-1} \ cm^{-1}$  and  $T_o=3.3\times10^5 \ K$ .



**Figure 2**. Hall concentration  $p_H$  of sample 1 as a function of temperature in the domain in vicinity of room temperature. Solid line – typical dependence expected in the case of ionization of Mg acceptor states (modeling of neutrality equation for  $N_A=1.3\times10^{19}$  cm<sup>-3</sup>;  $E_A=160$  meV)

The temperature dependence of Hall concentration  $p_H$  for the same sample 1 is presented in **Figure 2**. Two distinct regions of  $p_H(T)$  dependence can be distinguished.

For T > 270 K: the observed increase in hole concentration  $p_H$  tends, with increasing temperature to the typical one resulting from the ionization of impurity acceptor states. The solid line on the figure corresponding to the solution of neutrality equation for ionization of Mg acceptor states characterized by a concentration  $N_A=1.3\times10^{19}$  cm<sup>-3</sup> and an energy  $E_A=160$  meV.

For T < 270 K: an unexpected increase in the apparent  $p_H$  concentration is observed.

The increase of Hall carrier concentration with decreasing temperature can be explained with the assumption that more than one type of carrier is involved in the conduction process. [<sup>18</sup>] Taking into account the possible Hall effect in the case of hopping conductivity [<sup>19,20</sup>] the experimental  $p_H(T)$  dependency could be analyzed taking into consideration both, band and hopping conductivity processes. [<sup>21,22</sup>] In this case:

- the conductivity can be described as:  $\sigma = \sigma_b + \sigma_{hop}$  (2) where index *b* corresponds to the conductivity in valence band  $\sigma_b = ep_b\mu_b$  (3) and index *hop* to the hoping conductivity according to the **Equation 1**
- the Hall effect can be described based on a general formula for the Hall coefficient  $R_H$  in the case of two types of carriers done by:

$$R_{H} = \frac{1}{ep_{H}} = \frac{e_{1}\mu_{1}^{2}p_{1} + e_{2}\mu_{2}^{2}p_{2}}{e^{2}(\mu_{1}p_{1} + \mu_{2}p_{2})^{2}}$$
(4)

It means that in the case of simultaneous conduction processes by the carriers in the valence band and by the hopping process, the experimentally determined Hall carrier concentration  $p_H$  is described by:

$$p_{H} = \frac{1}{e} \cdot \frac{(e\mu_{b}p_{b} + e\mu_{hop}p_{hop})^{2}}{e\mu_{b}^{2}p_{b} + e\mu_{hop}^{2}p_{hop}} = \frac{1}{e} \cdot \frac{(\sigma_{b} + \sigma_{hop})^{2}}{\sigma_{b}\mu_{b} + \sigma_{hop}\mu_{hop}}$$
(5)

where e is the elementary charge,  $p_i$  the hole concentration and  $\mu_i$  the hole mobility (with index *i* respectively *b* and *hop*).

In the first approximation, the temperature dependence of the conductivity  $\sigma$  and Hall hole concentration  $p_H$  can be estimated from **Equation 2** to **5** taking into account:

- hopping conductivity  $\sigma_{hop}$  described by **Equation 1** with the parameters for sample 1 determined from it,
- valence band conductivity  $\sigma_b$  described by **Equation 3** and calculated taking into account the hole concentration in valence band  $p_b(T)$  according to the  $p_H(T)$  model presented by the solid line in **Figure 2** and the temperature independent valence band hole mobility corresponding to the experimental value  $\mu_b$  (400 K) = 3 cm<sup>2</sup>/Vs,
- temperature independent hopping mobility  $\mu_{hop}$  considered as a fitting parameter



**Figure 3**. Temperature variation of conductivity  $\sigma$  and Hall concentration  $p_H$  of sample 1; solid line modeling results taking into account the conducting mechanism both in the valence band and by the hopping process. The hopping mobility value  $\mu_{hop} = 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was used as a fitting parameter.

As can be seen from **Figure 3**, assuming hopping mobility  $\mu_{hop} = 0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , such a simple model allows to describe qualitatively the experimentally observed temperature dependences of  $\sigma$  and  $p_H$ . In particular, to explain the increase in holes Hall concentration with decreasing temperature in the range below the room temperature. It should be stressed that, following the observed dependences, the hopping phenomenon may affect the measurements of material parameters and significantly increase the value of hole concentration determined at room temperature.





**Figure 4.** Resistivity  $\rho$  as a function of reciprocal of temperature in the wide temperature range from 20 K up to 880 K: (a) for sample 2 and (b) for sample 3. Circles – the experimental data before annealing process, diamonds – the experimental data after high temperature annealing.

The temperature dependences of the resistivity  $\rho(T)$  for samples 2 and 3 before and after the high temperature annealing (HTA) are presented in **Figure 4**. The annealing process leads, for both samples, to a distinct but different decrease in resistivity  $\rho(T)$  vs temperature dependence. Assuming the participation of hopping phenomena in the conduction mechanism below room temperature, the HTA process leads to an marked decrease of the T<sub>o</sub> parameter for both samples.



**Figure 5**. Conductivity  $\sigma$  of sample 4 as a function of temperature in the range below room temperature. Graph as a function of  $T^{1/4}$ . Circles – the experimental data before annealing process, diamonds – the experimental data after HTA.

In **Figure 5**, the same effect is presented for sample 4. For this sample, the effect was more pronounced and the participation of hopping phenomena in the conduction process more visible. The variable range hopping process is well defined and allows to determine the hopping parameters:

| - | before annealing: | $\rho_0 = 1.1 \times 10^6 \Omega \mathrm{cm}$ | and $T_0 = 2.0 \times 10^7 \text{ K}$ |
|---|-------------------|---|---------------------------------------|
| - | after annealing:  | $\rho_0 = 23 \Omega \text{ cm}$               | and $T_0 = 1.5 \times 10^5 \text{ K}$ |

The fitting  $T_o$  value before annealing is in good agreement with the results reported for similar samples in paper [<sup>14</sup>] ( $T_o = 2.3 \times 10^7$  K). Following the analysis from paper [<sup>17</sup>], the  $T_o$  parameter can be written as:

$$T_o \approx \frac{21.3}{k_B g(E_F) a_d^3} \tag{6}$$

where  $k_B$  is the Boltzmann constant,  $g(E_F)$  is the density of states at the Fermi level and  $a_d$  the extent of the defect wave function.

Subsequently applied approximations allow to write, in the case of p-type conduction, the relations:

$$T_o \propto \frac{N_A^{1/3}}{N_D} \tag{7}$$

Consequently, in order to describe the experimentally observed decrease of  $T_o$  as a result of HTA, it could be assumed that the annealing process leads to a decrease of the active acceptors or to an increase of the compensating donors. Both of these possibilities are unacceptable due to the fact that the HTA process leads to an experimentally observed increase of free holes concentration in the sample. The only possible solution is to assume a complex mechanism of HTA, taking into account the increase of the concentration of both donors and acceptors. Such a qualitative explanation is confirmed by the results of the previous paper [<sup>12</sup>], where the fitting procedure of experimental dependences  $p_H(T)$  before and after HTA process (sample E in reference [<sup>12</sup>]) required the adoption of the donors  $N_D$  and acceptors  $N_A$  parameters which could lead to a reduction of the  $T_o$  value after the annealing process:

- sample E before annealing:

$$N_D = 3.0 \times 10^{18} \text{ cm}^{-3}$$
;  $N_A = 2.5 \times 10^{19} \text{ cm}^{-3}$  and that is  $\frac{N_A^{1/3}}{N_D} = 9.7 \times 10^{-13}$ 

- sample E after annealing:

$$N_D = 9.5 \times 10^{18} \text{ cm}^{-3}$$
;  $N_A = 7.0 \times 10^{19} \text{ cm}^{-3}$  and that is  $\frac{N_A^{1/3}}{N_D} = 4.3 \times 10^{-13}$ 

#### **3.** Conclusions

In this paper, the results of low temperature conductivity  $\sigma$  and Hall effect  $p_H$  measurements of Mg-doped GaN epilayers grown of ammonia-MBE and subjected to high-temperature annealing ( $T_c \sim 880$  K) have been presented. The HTA process leads to an irreversible decrease of the sample resistivity related to the increase of the free carrier concentration. We have demonstrated that in the investigated material, beside the free carriers in the valence band, an additional conduction channel by hopping process (VRH) must be taken into consideration in the conduction process. Neglecting it, the room temperature electrical parameters could be determined erroneously. The HTA process has a significant impact on this hopping conduction mechanism. To explain the observed effects it should be assumed that it leads to an increase in concentration of both donors and acceptors.

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