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Influence of excited states of Mg acceptors on hole concentration in GaN

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The influence of the excited states of the acceptors on the hole concentration in p-type GaN is investigated theoretically and experimentally. Using the temperature dependence of the hole concentration $p(T)$ in Mg-doped GaN epilayers, a distribution function suitable for Mg acceptors is examined. It is found that the influence of their excited states on $p(T)$ as well as the temperature dependence of the average acceptor level cannot be ignored, when the acceptor level is deep ($\geq$150 meV). Moreover, it is elucidated that due to their excited states the ionization efficiency of acceptors is higher at elevated temperatures than the ionization efficiency expected from the Fermi–Dirac distribution function.

1 Introduction The excited states of the substitutional dopants in a semiconductor have been theoretically discussed using the hydrogenic model [1], and the existence of their excited states in Si has been experimentally confirmed using infrared absorption measurements [1]. However, the influence of their excited states on the majority-carrier concentration has not been experimentally confirmed because their excited state levels in Si are too shallow. On the other hand, an acceptor level (ΔE_A) in GaN or SiC, measured from the valence band maximum (E_V), was reported to be deeper than 150 meV [2, 3]. Moreover, according to the hydrogenic model, their first excited state level (ΔE_2) is nearly equal to ΔE_A of B in Si.

The Fermi-Dirac distribution function $f_{FD}(\Delta E_A)$, which does not consider the influence of the excited states of the acceptors, is given by

$$f_{FD}\left(\Delta E_A\right) = \frac{1}{1+4\exp\left(\dfrac{\Delta E_A - \Delta E_F}{kT}\right)}\ , \tag{1}$$

where ΔE_F is the Fermi level measured from E_V, k is the Boltzmann constant, and T is the absolute temperature. Using $f_{FD}(\Delta E_A)$, the values of ΔE_A, the acceptor density (N_A) and the compensating density (N_{comp}) were determined by a least-squares fit of the charge-neutrality equation to $p(T)$ in heavily Mg-doped GaN or Al-doped SiC. However, the obtained N_A was much higher than the Mg or Al concentration (C_{Mg} or C_{Al}) determined by secondary ion mass spectroscopy (SIMS) [4, 5], suggesting that this N_A should not be reliable. Therefore, it is necessary to newly introduce a distribution function $f(\Delta E_A)$ considering the influence of their excited states, which makes the obtained N_A reasonable. In heavily Al-doped SiC, $f(\Delta E_A)$ has been reported to be appropriate for the Al acceptors [6, 7].

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We have developed a graphical peak analysis method for determining the densities and energy levels of several dopant species without any assumptions regarding dopant species, called Free Carrier Concentration Spectroscopy (FCCS) [6–10]. In this article, the experimental data obtained by Hall-effect measurements are analyzed by FCCS using $f(\Delta E_{\mathrm{A}})$ or $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$.

2 Distribution function including excited states of acceptors The distribution function including the influence of the excited states of the acceptors is given by [6]

$$f(\Delta E_{\mathrm{A}}) = \frac{1}{1+4\exp\left(-\dfrac{\overline{E_{\mathrm{ex}}}}{kT}\right)\cdot\left[\exp\left(\dfrac{\Delta E_{\mathrm{A}}-\Delta E_{\mathrm{F}}}{kT}\right)+\displaystyle\sum_{r=2} g_r \exp\left(\dfrac{\Delta E_r-\Delta E_{\mathrm{F}}}{kT}\right)\right]}\,, \tag{2}$$

where ΔE_r is the difference in energy between the $(r-1)$th excited state level and E_{V}, and g_r is the $(r-1)$ th excited state degeneracy factor. An ensemble average E_{ex} of their ground and excited state levels is given by [6, 7, 11]

$$\overline{E_{\mathrm{ex}}} = \frac{\displaystyle\sum_{r=2}\left(\Delta E_{\mathrm{A}}-\Delta E_r\right) g_r \exp\left(-\dfrac{\Delta E_{\mathrm{A}}-\Delta E_r}{kT}\right)}{1+\displaystyle\sum_{r=2} g_r \exp\left(-\dfrac{\Delta E_{\mathrm{A}}-\Delta E_r}{kT}\right)}, \tag{3}$$

and then an average energy level $\overline{\Delta E_{\mathrm{A}}}$ of the acceptors, measured from E_{V}, is expressed as [6, 7]

$$\overline{\Delta E_{\mathrm{A}}} = \Delta E_{\mathrm{A}} - \overline{E_{\mathrm{ex}}}\,. \tag{4}$$

When their excited states are neglected (i.e., $r=1$ and $\overline{E_{\mathrm{ex}}}=0$), Eq. (2) coincides with $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$.

3 Free carrier concentration spectroscopy[1] Using an experimental $p(T)$, the FCCS signal is defined by [6–10]

$$H(T, E_{\mathrm{ref}}) \equiv \frac{p(T)^2}{(kT)^{5/2}} \exp\left(\frac{E_{\mathrm{ref}}}{kT}\right) \tag{5}$$

and has a peak at the temperature corresponding to each acceptor level, where E_{ref} is the parameter which can shift its peak temperature within the measurement temperature range.

From the charge-neutrality condition, in p-type semiconductors, $p(T)$ is described as

$$p(T) = \sum_i N_{\mathrm{A}i} F(\Delta E_{\mathrm{A}i}) - N_{\mathrm{comp}}\,, \tag{6}$$

where $N_{\mathrm{A}i}$ and $\Delta E_{\mathrm{A}i}$ are the density and energy level of the i th acceptor species, and $F(\Delta E_{\mathrm{A}i})$ represents $f(\Delta E_{\mathrm{A}i})$ or $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}i})$. On the other hand, using the effective density of states $N_{\mathrm{V}}(T)$ in the valence band, $p(T)$ is expressed as

$$p(T) = N_{\mathrm{V}}(T)\exp\left(-\frac{\Delta E_{\mathrm{F}}}{kT}\right), \tag{7}$$

where

$$N_{\mathrm{V}}(T) = N_{\mathrm{V0}} k^{3/2} T^{3/2} \quad \text{and} \quad N_{\mathrm{V0}} = 2\left(\frac{2\pi m^*}{h^2}\right)^{3/2},$$

[1] The Windows application software for FCCS can be downloaded at our web site (http://www.osakac.ac.jp/labs/matsuura/).

m^* is the hole effective mass, and h is the Planck's constant. Substituting Eq. (6) for one of the two $p(T)$ in Eq. (5) and substituting Eq. (7) for the other $p(T)$ in Eq. (5) yield

$$H\left(T, E_{\mathrm{ref}}\right) = \sum_i \frac{N_{\mathrm{A}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{A}i} - E_{\mathrm{ref}}}{kT}\right) I\left(\Delta E_{\mathrm{A}i}\right) - \frac{N_{\mathrm{comp}} N_{\mathrm{V0}}}{kT} \exp\left(\frac{E_{\mathrm{ref}} - \Delta E_{\mathrm{F}}}{kT}\right), \tag{8}$$

where

$$I\left(\Delta E_{\mathrm{A}i}\right) = N_{\mathrm{V0}} \exp\left(\frac{\Delta E_{\mathrm{A}i} - \Delta E_{\mathrm{F}}}{kT}\right) F\left(\Delta E_{\mathrm{A}i}\right). \tag{9}$$

The function

$$\frac{N_{\mathrm{A}i}}{kT} \exp\left(-\frac{\Delta E_{\mathrm{A}i} - E_{\mathrm{ref}}}{kT}\right) \tag{10}$$

in Eq. (8) has a peak value of $N_{\mathrm{A}i} \exp(-1)/kT_{\mathrm{peak}i}$ at the peak temperature

$$T_{\mathrm{peak}i} = \frac{\Delta E_{\mathrm{A}i} - E_{\mathrm{ref}}}{k}. \tag{11}$$

As is clear from Eq. (11), E_{ref} can shift $T_{\mathrm{peak}i}$. Although the actual $T_{\mathrm{peak}i}$ is slightly different from $T_{\mathrm{peak}i}$ calculated by Eq. (11) due to the temperature dependence of $I(\Delta E_{\mathrm{A}i})$, we can determine $N_{\mathrm{A}i}$ and $\Delta E_{\mathrm{A}i}$ from the peak of the experimental FCCS signal easily and accurately, using a personal computer.

4 Experimental 2 μm-thick Mg-doped p-type GaN epilayers were grown at 1025 °C by metalorganic chemical vapor deposition on undoped GaN/sapphire, and annealed at 800 °C in N_2 for 20 min. The C_{Mg} in the epilayers was 2×10^{19} cm^{-3}. The $p(T)$ was obtained by Hall-effect measurements in a magnetic field of 1.4 T.

5 Results and discussion The open circles and open triangles in Fig. 1 represent the experimental $p(T)$ and ΔE_{F}. The FCCS signal (solid line in Fig. 2) is calculated by interpolating $p(T)$ with a cubic smoothing natural spline function at intervals of 0.1 K. Since there is only one peak, this epilayer includes only one species of acceptor. From the peak, the values of N_{A}, ΔE_{A} and N_{comp} are determined to be 8.9×10^{18} cm^{-3}, 149 meV and 1.5×10^{17} cm^{-3} for $f(\Delta E_{\mathrm{A}})$, and 2.1×10^{20} cm^{-3}, 154 meV and 2.2×10^{18} cm^{-3} for $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$. Because N_{A} is the concentration of Mg atoms located at the substitutional sites in GaN, N_{A} should be less than or equal to C_{Mg}, indicating that $f(\Delta E_{\mathrm{A}})$ is appropriate in this Mg-doped GaN epilayer. Therefore, it is found that ~45 % of Mg atoms in this epilayer act as an acceptor.

The broken and dotted lines in Fig. 2 represent the FCCS signals simulated using N_{A}, ΔE_{A}, and N_{comp} for $f(\Delta E_{\mathrm{A}})$ and $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, respectively. Only the broken line is in agreement with the solid line, suggesting that $f(\Delta E_{\mathrm{A}})$ is appropriate for Mg acceptors in GaN.

The open circles, and the solid and broken lines in Fig. 3 represent the experimental $p(T)$ and two $p(T)$ simulations using the values determined by $f(\Delta E_{\mathrm{A}})$ and $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, respectively. Since both the simulated $p(T)$ coincide with the experimental $p(T)$, it is difficult to determine which distribution function is suitable for explaining the ionization efficiency of the Mg acceptors in GaN.

Although N_{A} for $f(\Delta E_{\mathrm{A}})$ is much lower than N_{A} for $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, the simulated $p(T)$ using this lower N_{A} coincides with the experimental $p(T)$, because according to Eq. (4) their excited states make ΔE_{A} shallow at elevated temperatures. According to Poisson's equation, N_{A} influences the shape of the

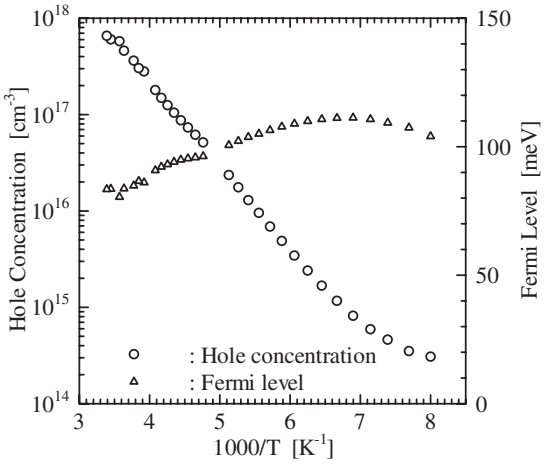

Fig. 1 Experimental $p(T)$ and ΔE_{F}.

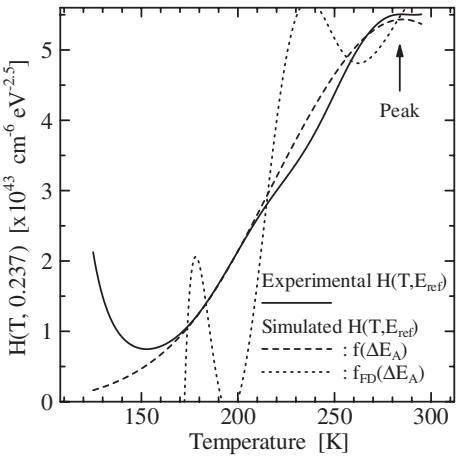

Fig. 2 FCCS signals with $E_{\mathrm{ref}} = 0.237$ eV.

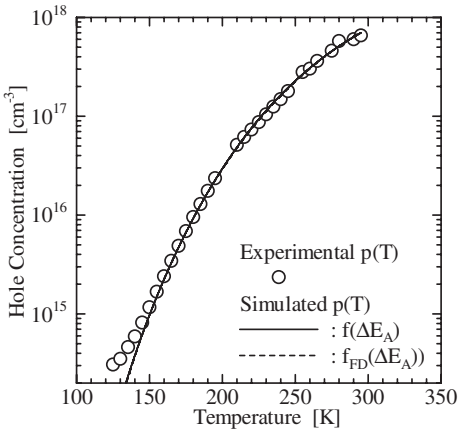

Fig. 3 Comparison between experimental $p(T)$ and two $p(T)$ simulations using $f(\Delta E_{\mathrm{A}})$ or $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$ with the values determined by the corresponding distribution function. Since the $p(T)$ simulation using $f(\Delta E_{\mathrm{A}})$ is very close to the $p(T)$ simulation using $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, the solid line overlaps with the broken line.

band bending in pn junctions, indicating that in GaN devices the electric characteristics obtained by device simulation should be affected by the Mg acceptor density. Therefore, it is essential to use $f(\Delta E_{\mathrm{A}})$ by which the accurate $p(T)$ is obtained using the actual value of N_{A}.

6 Conclusion The distribution function considering the influence of the excited states of the acceptors was proposed. In $f(\Delta E_{\mathrm{A}})$, an ensemble average of their ground and excited state levels was introduced. Using $f(\Delta E_{\mathrm{A}})$ or $f_{\mathrm{FD}}(\Delta E_{\mathrm{A}})$, the experimental $p(T)$ in p-type Mg-doped GaN was investigated. It is found that FCCS is more appropriate for investigating the influence of their excited states on $p(T)$ than the least-squares fit of the charge-neutrality equation to $p(T)$, and it is elucidated that $f(\Delta E_{\mathrm{A}})$ is appropriate for acceptors in GaN. Moreover, it is essential to use $f(\Delta E_{\mathrm{A}})$ in device simulations for GaN.

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