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Influence of oxygen on luminescence and vibrational spectra of Mg-doped GaN

Yasuo Koide[*, 1, 2], **D. E. Walker, Jr.**[1], **B. D. White**[1], **L. J. Brillson**[1], **T. Itoh**[3], **R. L. McCreery**[3], **Masanori Murakami**[2], **S. Kamiyama**[4], **H. Amano**[4], and **I. Akasaki**[4]

[1] Department of Electrical Engineering, The Ohio State University, Columbus, Ohio 43210, USA
[2] Department of Materials Science and Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
[3] Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA
[4] Department of Materials Science and Engineering, Meijo University, Tempaku-ku, Nagoya, 468-8502, Japan

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Mg-doped GaN epilayers are analyzed by Raman and low-energy electron-excited nanoluminescence (LEEN) spectroscopies before and after oxygen ambient annealing at temperatures from 450 to 550 °C. Annealing as low as 450 °C shows the appearance of a local vibrational mode of the Mg_{Ga} acceptor. Correspondingly, LEEN emission at 2.8 eV increases and that at 3.27 eV decreases after annealing in oxygen ambient. On the other hand, electron beam treatment decreases 2.8 eV emission and increases 3.27 eV emission. These luminescence properties are explained by a donor-acceptor pairs transition model due to hydrogen-related deep and shallow donors and Mg_{Ga} acceptor.

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1 Introduction A hydrogen atom plays an important role in controlling the electrical conductivity of Mg-doped GaN epilayer grown by metalorganic vapor phase epitaxy (MOVPE). Most researchers agree that hydrogen passivation of Mg acceptors occurs through the formation of an electrically neutral Mg–H complex. Thermal annealing in a nitrogen ambient has been used to obtain *p*-type epilayers by breaking the Mg–H complex and electrically activating Mg acceptors [1]. A few groups confirmed the existence of the Mg–H complex by detecting a local vibrational mode (LVM) of Mg–N–H complex with wavenumber of 3125 cm^{-1} using infrared spectroscopy [2] or Raman spectroscopy [3]. Also, LVMs of the Mg_{Ga} acceptor were detected by Raman spectroscopy at 136, 262, and 656 cm^{-1} for heavily doped *p*-GaN epilayers after being activated by annealing [4], close to theoretical predictions of Mg LVMs using a cluster approximation [5]. In these experiments, annealing temperatures as high as 800 °C were required to obtain the *p*-type epilayer with hole concentrations higher than mid-10^{17} cm^{-3}. This activation was explained by the surface barrier limiting the release of hydrogen [6] and precipitation of hydrogen around dislocations [7]. On the other hand, Amano et al. [8] demonstrated that electron beam irradiation at room temperature increased *p*-type conductivity and photoluminescence (PL) in a Mg-doped GaN epilayer. Pearton et al. [9] demonstrated *p*-type activation at 175 °C after injecting electrons from a n-type GaN epilayer. These results suggest the possibility of a low-temperature process of *p*-type activation.

Recently, many reports have shown that annealing in N_2/O_2 gas mixtures [10–12] or in air [13] increased hole concentrations significantly even at low temperatures (<600 °C). These results suggest that oxygen plays an important role in breaking the Mg–H complex at relatively low temperatures, however

* Corresponding author: Present address: National Institute of Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. e-mail: koide.yasuo@nims.go.jp, Phone: +81 29 860 4311, Fax: +81 29 851 4005

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the role of oxygen in this process is not yet understood. This paper reports measurements to explore the role of oxygen in dissociation reactions of the Mg–H complex in Mg-doped GaN using Raman and low-energy electron nanoluminescence (LEEN) spectroscopies [14]. This information will provide an impact on understanding the Mg–H complex dissociation due to oxygen at low temperatures.

2 Experimental The Mg-doped GaN epilayers were successively grown by MOVPE on *c*-face α-Al_2O_3(0001) wafers using a GaN buffer layer. One sample had a heavily-doped cap layer with thickness of 10 nm and a normally-doped epilayer with thickness of 1.0 μm. Another sample had a single Mg-doped epilayer with thickness of 1.0 μm. Both the as-grown epilayers had high resistivities. Since a thin heavily-doped GaN epilayer with Mg concentration higher than 10^{20} cm^{-3} was often used as an ohmic contact layer to reduce the contact resistance, we investigated difference in the luminescence properties between the heavily and normally Mg-doped epilayers. The hole concentration of the uncapped epilayer annealed in N_2 ambient at 800 °C was determined from Hall effect measurements to be 5.0×10^{17} cm^{-3}, and the Mg concentration was measured from secondary ion mass spectrometry (SIMS) to be 4×10^{19} cm^{-3}. Preliminary experiments showed that the same hole concentration was obtained after annealing in air at 575 °C, a significant reduction of the activation temperature. For the capped epilayers, the Mg concentration of cap layer was estimated to be higher than 10^{20} cm^{-3}. The samples were cleaned by immersion in buffered HF (NH_4OH : HF = 7 : 1) for 5 min, followed by a deionized water rinse for 5 min before both annealing and LEEN measurements. The samples were placed on a silica pedestal and annealed in an O_2 ambient at 450, 500, and 550 °C for times ranging from 16 to 400 min. The Raman spectroscopy was carried out by a Kaiser f/1.5 system equipped with a holographic monochromator [15], a 514.5 nm line of Ar ion laser, and a back thinned charge-coupled device (CCD) and backscattering collection optics. LEEN spectra were measured at room temperature by a modified ultra-high vacuum JEOL 7800F scanning electron microscope (SEM) Auger microprobe equipped with an Oxford Scientific MonoCL monochromator and a visible-UV sensitive photomultiplier tube [16]. The energy and current of incident electron beam were kept at 5.0 keV and 500 pA, respectively, over a 40×40 μm^2 raster square area, corresponding to a current density of 3.1×10^{-5} A/cm^2. The depth of excitation was evaluated to be 160 nm [16].

3 Results and discussion Figure 1 shows Raman spectra with wavenumber range from 300 to 900 cm^{-1} for the uncapped epilayer before and after annealing in an O_2 ambient at 450, 500, and 550 °C for various annealing times. Strong peaks are assigned to phonon modes of α-Al_2O_3 substrate (A_{1g} of 381, 417, and 448 cm^{-1}) [17], GaN (E_2 of 570 cm^{-1}), GaN [A_1(LO) of 738 cm^{-1}], and α-Al_2O_3 substrate (E_g of 749 cm^{-1}) features [18]. The Raman intensities are normalized to the 417 cm^{-1} sapphire peak. The E_2 and A_1(LO) peak energies of GaN were almost unchanged with annealing. A new peak indicated by "*" at 644–646 cm^{-1} is observed after isothermal annealing at 450 °C for longer than 256 min and at 500 and 550 °C for 16 min.

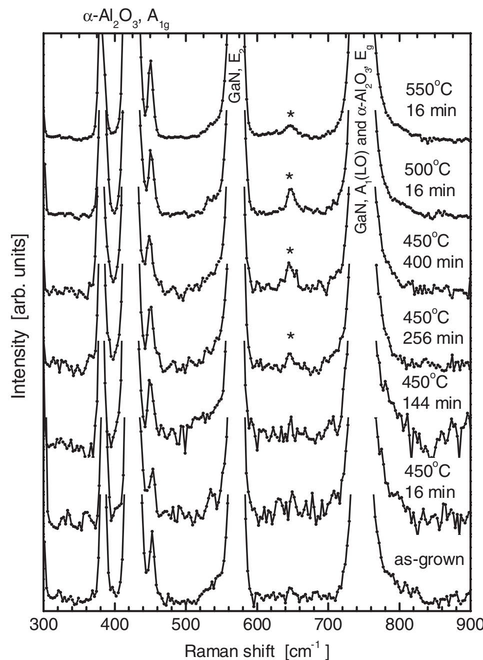

Fig. 1 Raman spectra of Mg-doped single GaN epilayer as a function of annealing temperature in O_2 ambient.

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This is assigned to be the LVM mode of Mg_{Ga} atoms, and the wavenumber is around 10 cm^{-1} smaller than the values reported by Kaschner et al. [4] and Harima et al. [3] Theoretical wavenumber of the Mg_{Ga} LVMs in GaN was calculated by Kaczmarczyk et al. [5], and they showed that the spring constant of Mg_{Ga} LVM was 15% smaller than that of GaN. The present small wavenumber values can be explained by the difference in spring constants of the LVMs. It was found from the result of Fig. 1 that annealing in O_2 ambient as low as 450 °C provided formation of the Mg_{Ga}–N bond, and that the Mg_{Ga} acceptor was formed as a result of dissociation of Mg–H complex. We also measured Raman spectroscopy of the highly doped capped epilayer. The LVM of Mg_{Ga}–N bond was detected at 645 cm^{-1} even in the as-grown state, which indicates less hydrogen passivation compared with that of the uncapped epilayer.

Luminescence features from LEEN spectra show how oxygen influences dissociation of the Mg–H complex. Figure 2 shows spectra from (a) uncapped and (b) capped samples before and after annealing (indicated by solid and dash lines, respectively) at 550 °C and 500 °C, respectively, for 16 min. Three LEEN peaks of near band edge (NBE) luminescence at 3.40 eV, ultraviolet luminescence (UVL) at 3.27 eV, and blue luminescence (BL) at around 2.8 eV are observed. The UVL and BL bands in PL are commonly observed. Note that BL intensity increases and UVL decreases after annealing. The UVL is believed to be due to transitions involving donor–acceptor pairs (DAP) of a shallow donor to the Mg_{Ga} acceptor or free-to-Mg_{Ga} acceptor transitions. The BL is believed to originate from DAP transitions of a deep donor to Mg_{Ga} acceptor [19, 20]. The BL increase with annealing as low as 500 °C in oxygen clearly indicates an increase in Mg_{Ga} acceptor levels in agreement with the Raman results.

Figure 3 shows successive changes of LEEN spectra for (a) uncapped and (b) capped samples indicated in Fig. 2 after annealing as a function of times indicated. Time $t = 0$ marks the end of the first

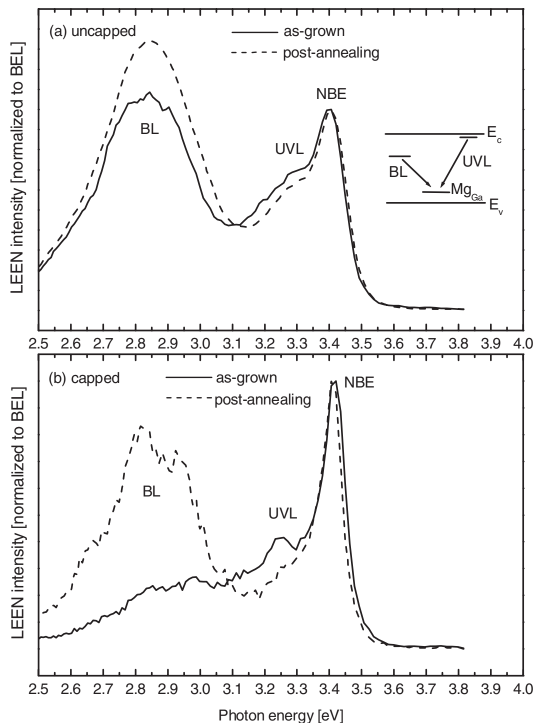

Fig. 2 LEEN spectra of a) uncapped and b) capped Mg-doped GaN epilayers before (solid) and after (dashed) annealing at 550 and 500 °C, respectively, for 16 min in O_2 ambient. Inset shows corresponding UVL and BL transitions.

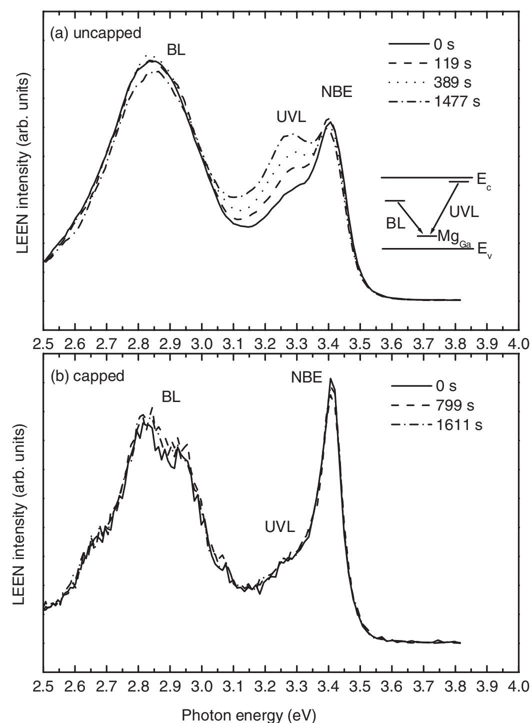

Fig. 3 LEEN spectra taken repeatedly from a) uncapped and b) capped Mg-doped GaN epilayers after annealing at 550 and 500 °C, respectively, for 16 min in O_2 ambient, where times are measured from the first measurement. Inset shows corresponding UVL and BL transitions.

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LEEN spectrum, and the LEEN measurement was carried out repeatedly by exposing the sample with the electron beam. For uncapped sample, intensities of the UVL increase with electron exposure, and, correspondingly, the BL is reduced. The UVL increase corresponds to additional increases in Mg_{Ga} acceptor states by dissociation of residual Mg–H complex. The BL decrease suggests the deep donor is a hydrogen-related complex (such as nitrogen vacancy-hydrogen, V_N–H) [20]. The small UVL decrease in Fig. 2 suggests that the annealing in oxygen reduced the density of the shallow donor, presumably hydrogen. On the other hand, for capped samples, the UVL and BL intensities are almost constant with electron exposure, which indicates that hydrogen is significantly removed from surface layer during annealing in oxygen.

4 Conclusion The Mg-doped GaN annealed in oxygen ambient showed the appearance of Mg_{Ga} LVM at temperatures as low as 450–500 °C. This annealing also increased (decreased) 2.8 eV BL (3.27 eV UVL) emission with increased Mg_{Ga} final states and decreased H-related shallow donor states. Electron beam treatment decreases (increases) 2.8 eV BL (3.27 eV UVL) emission due to reduced deep donor levels and further increases in Mg_{Ga}.

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