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Defect Complexes in Highly Mg-Doped GaN Studied by Raman Spectroscopy

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We report on local vibrational modes (LVMs) in highly Mg-doped GaN grown by molecular beam epitaxy. Two groups of LVMs in the region of GaN host phonons and in the vicinity of 2200 cm^{-1} are observed. We performed temperature-dependent Raman-scattering experiments and annealing experiments to investigate the defect complexes which are the origin of the high-energy LVMs. The temperature-dependent measurements show an unexpected hardening of the two most intense LVMs at 2166 and 2185 cm^{-1}. Furthermore, we found that all high-energy modes disappeared after annealing at 1065 °C. The experimental results are discussed in terms of existing theoretical models.

1. Introduction

The achievement of p-type conducting GaN by Mg doping [1] was one of the major breakthroughs for the application of the III–V nitrides in high-power optoelectronic devices in the ultraviolet and blue spectral range. Postgrowth treatment [2, 3] is necessary to obtain p-conductivity in GaN:Mg when grown under H-rich ambient conditions such as during metalorganic chemical vapor deposition (MOCVD). Hydrogen has been suggested to form a defect complex with Mg and therefore compensates the acceptor states. The Mg–H complex in MOCVD-grown GaN with a vibrational frequency of 3125 cm^{-1} was identified by Götz et al. [4] applying infrared absorption measurements. On the other hand, the vibrational modes around 2200 cm^{-1} in GaN:Mg grown by molecular beam epitaxy (MBE), which is p-type in the as-grown state [5], is still subject of scientific discussion [6, 7].

2. Experiment

The Raman-scattering experiments were carried out in backscattering geometry with a triple-grating spectrometer equipped with a cooled charge-coupled device detector. The line positions were determined with an accuracy better than 1 cm^{-1}. We used a micro-Raman set-up with a confocal optics and the line at 488 nm of an Ar^+/Kr^+ mixed-gas laser for excitation. The excitation power of 10 mW and a spot size of 1 μm result in a

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power density in the range of 1 MW/cm^2. The high power density was chosen to keep the integration time at a reasonable level, but no heating or nonlinear effects were observed. Temperature-dependent Raman-scattering experiments between 4 and 290 K and 290 and 590 K were performed using an Oxford microscope cryostat and a usual heater, respectively.

The samples under study were Mg-doped GaN films of about 1 μm thickness grown on sapphire (0001) substrates by MBE. Details are given elsewhere [8]. The samples are p-conductive at room temperature and have a magnesium concentration in the 10^{19} cm^{-3} range. Annealing experiments were performed at 580, 750 and 930 °C under N_2 atmosphere and at 1065 °C under $N_2 + NH_3$ atmosphere for 15 to 20 min, to avoid decomposition of the GaN.

3. Results

Fig. 1 shows Raman spectra of highly Mg-doped GaN in the region around 2200 cm^{-1}. The temperature was varied between 4 and 290 K for the spectra in Fig. 1a and between 340 and 590 K for Fig. 1b. The low-temperature spectra exhibit five modes at 2129, 2148 (2151), 2166 (2168) with a weak shoulder at 2159 cm^{-1}, 2185 (2185) and 2219 (2219 cm^{-1}) described in Ref. [7] (Ref. [6]). From 4 to 180 K a sixth mode at 2204 cm^{-1} is resolved but it is hardly observable at higher temperatures due to broadening. At temperatures higher than 340 K only the two most intense modes appear well resolved. At 590 K only one broad structure appears for the two modes and a further broad structure at 2230 cm^{-1} is observed. Notice that the modes do not disappear up to

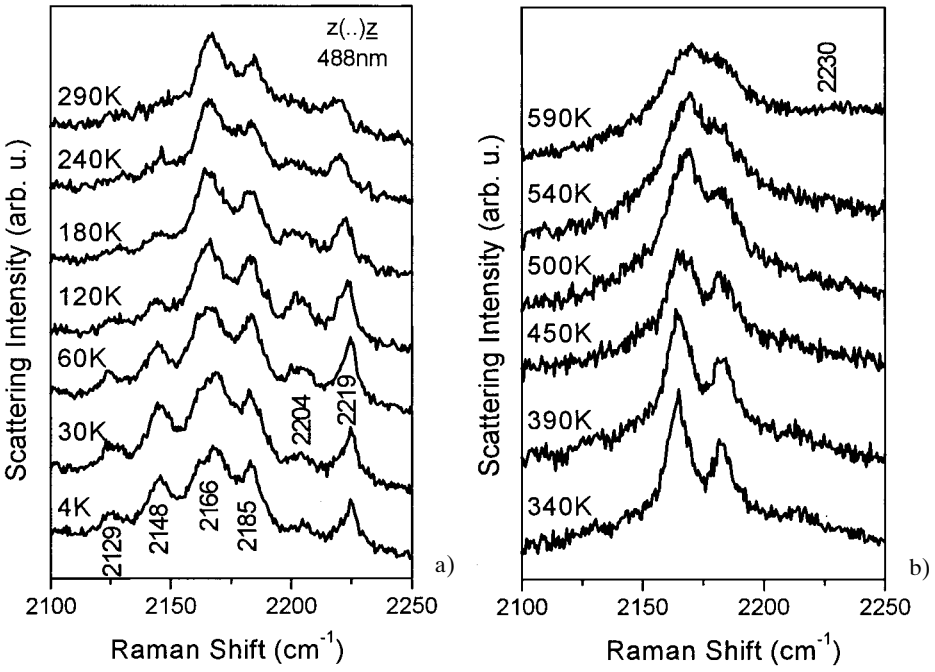

Fig. 1. Raman spectra of highly Mg-doped GaN around 2200 cm^{-1} at different temperatures between a) 4 and 290 K and b) 340 and 590 K

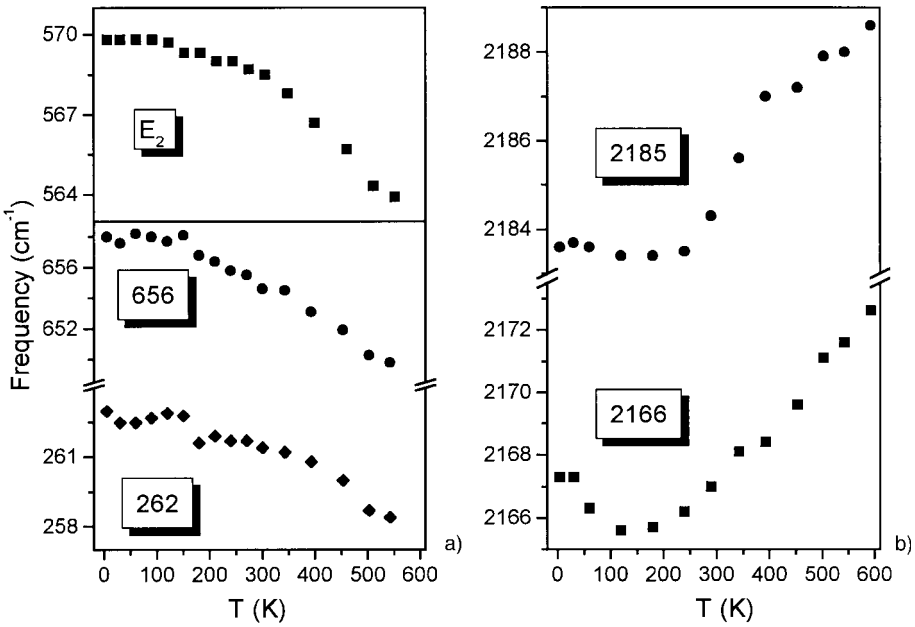

Fig. 2. Frequency of the LVMs as a function of the temperature in the a) low-energy range and b) high-energy range

temperatures as high as 590 K but are strongly broadened and shifted. The changes at these temperatures are reversible; all modes reappear after cooling down the sample to room temperature.

Fig. 2a and b show the frequencies of the low-energy modes reported in [7] and the two most intense high-energy modes as function of temperature. For comparison, the behavior of the E_2 host phonon is shown in the upper section of Fig. 1a. The low-energy modes exhibit a behavior similar to that of the host phonon, i.e. a softening of about 6 cm^{-1}. In contrast, the modes at 2185 and 2166 cm^{-1} unexpectedly shift to higher frequencies. Not all the high-energy modes have the same temperature dependence: the 2219 cm^{-1} and the 2204 cm^{-1} mode shift to lower frequencies between 4 and 290 K. At higher temperatures they cannot be reasonably analyzed for their line positions due to strong broadening.

Fig. 3 shows Raman spectra of different samples taken from the same wafer after annealing at various temperatures. Before annealing the spectra were similar. Annealing at 580 and 750 °C did not change significantly the discussed features in the spectra. The hole concentration determined by Hall measurements is about 1×10^{18} cm^{-3} at room temperature. Annealing at 930 °C causes drastic changes. The 2166 and the 2185 cm^{-1} mode change their relative intensities, the 2129 cm^{-1} mode becomes more pronounced and a weak, broad structure around 2230 cm^{-1} appears indicating a new formation of the involved defect complexes. At 1065 °C all modes vanished. Note that the modes also disappeared when the annealing was carried out in N_2 ambient only; this procedure, however, leads to a deterioration in surface morphology. Hall measurements showed that there is no improvement in p-conductivity when the modes disappeared.

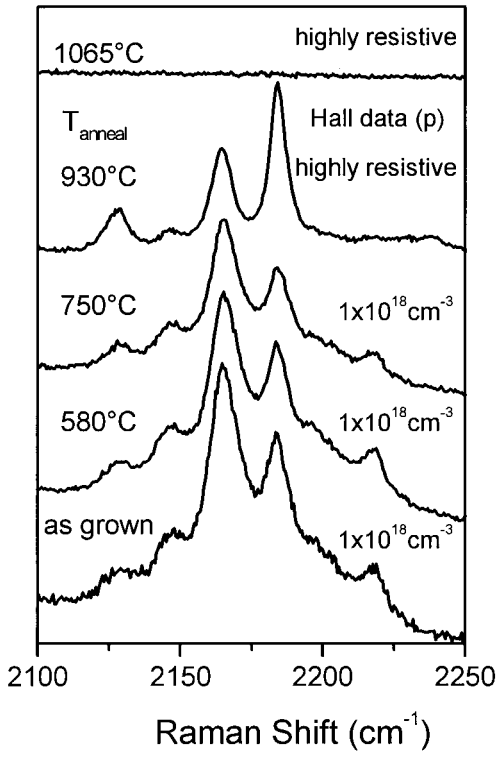

Fig. 3. Raman spectra of the high-energy LVMs in GaN:Mg after annealing at various temperatures. The two samples annealed at 930 and 1065 °C are highly resistive, whereas the others have a hole concentration of 1×10^{18} cm^{-3}

4. Discussion

Assigning all high-energy modes to different Mg–H complexes the disappearance of these modes can be explained by the removal of hydrogen from the crystal at 1065 °C. This explains why the modes around 2200 cm^{-1} are only reported for MBE-grown material and not for MOCVD material. The samples annealed at 930 and 1065 °C are highly resistive, which is surprising if we assume that compensating hydrogen was removed from the samples. In addition, this is contrary to the results for MOCVD-grown GaN:Mg reported in Ref. [2], where a lower resistivity for samples annealed at temperatures higher than 700 °C was found. Annealing at temperatures higher than 900 °C causes thermal damage [10] which most likely results in the formation of new defects and therefore could explain the inferior electrical properties of the material, but still the temperature of 1065 °C seems very high for the removal of hydrogen. Also the existence of the modes at temperatures as high as 590 K and the increasing frequency of the 2166 and the 2185 cm^{-1} modes with temperature are unexpected for H-related modes.

According to Ref. [9] it is not likely that hydrogen forms a bond with the Mg atom, therefore, the formation of Mg–H$_n$ complexes with n = 1,2,3 or Mg–H complexes with different Mg isotopes having a direct Mg–H bond seems unlikely unless it could explain the variety of modes. A more complex microscopic model was introduced by Reboredo and Pantelides [11], who suggested that hydrogen bound at substitutional/interstitial complexes gives rise to the high-energy modes in highly Mg-doped GaN. They calculated vibrational frequencies for different defect complexes and two of them agreed with the experiment within the uncertainty of 200 cm^{-1}. We could not confirm the predicted conversion of the 2200 cm^{-1} defect complexes into the 3125 cm^{-1} defect complex during annealing in a H- and N-rich atmosphere with our Raman-scattering experiments. However, magnesium and hydrogen forming a complex with an intrinsic defect, such as vacancies, interstitials or dislocations, could be the origin of LVMs with these high frequencies in the vicinity of 2200 cm^{-1}.

5. Conclusion

Temperature-dependent Raman-scattering experiments were performed to investigate the high-energy modes in Mg-doped GaN. We found an unexpected frequency shift of the two most intense modes to higher frequencies with increasing temperature, but no disappearance of these modes up to temperatures of 590 K indicating a certain thermal stability of the defect complex at this temperature. Annealing of the samples up to 750 °C does not change the Raman spectra significantly. After annealing at 930 °C the six observed high-energy modes change their relative intensities, and at 1065 °C all modes disappear. No improvement in p-conductivity for the latter two samples was observed, but an increase in resistivity. The reported results are not fully conclusive with the models discussed in literature. Further investigations are needed to completely exclude other than H-related defect complexes as the origin of the high-energy modes in GaN : Mg grown by MBE.

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