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Ga-vacancy activation under low energy electron irradiation in GaN-based materials

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ABSTRACT

We present results on optical degradation of gallium nitride based materials under low energy electron beam irradiation (LEEBI). GaN thin film and GaN/InGaN quantum well samples, grown by metal-organic vapor phase epitaxy (MOVPE), were exposed to a tightly focused (ø = 2 nm, J = 0-130 kA/cm²), rapidly scanning electron beam (e-beam) with energy of 5-20 keV and dose of 0-500 µC/cm². The irradiation severely reduced the band-to-band photoluminescence of the exposed sample areas. Performing positron annihilation spectroscopy measurements on the irradiated films revealed an important increase of Ga-vacancy concentration as a function of the irradiation dose. Based on the measurements we propose that in-grown passive V₆Ga-H₈ complexes are present in MOVPE grown GaN (and its alloys), and are activated by LEEBI.

INTRODUCTION

Gallium nitride is a widely used material for blue/UV LEDs and laser diodes. It is mechanically and chemically hard and considered as a suitable material for rough environments. Although GaN is in general well resistant to radiation, generation of Ga and N vacancies by MeV electron irradiation has been reported. [1, 2] Minimum electron beam energies for V₆N-N₆ and V₆Ga-Ga, Frenkel pair generation are estimated to be 0.42 MeV and 2 MeV, respectively. Defect formation has also been associated with low energy electron beam irradiation (LEEBI). [3, 4, 5, 6] In this case the defect formation is thought to involve activation of vacancies, defect migration and clustering of point defects.

In this paper, we present LEEBI induced optical degradation of GaN thin films and GaN/InGaN near surface single quantum wells (SQW), grown by metal-organic vapor phase epitaxy (MOVPE). The decrease of the band-to-band photoluminescence (PL) emission is associated with activation of in-grown Ga-vacancies during LEEBI. Based on the results we propose that in-grown passive V₆Ga-H₈ complexes are present in MOVPE grown GaN (and its alloys) and can be activated by the LEEBI treatment.
**EXPERIMENTAL**

All GaN-based samples were grown on c-plane sapphire (Al₂O₃) by MOVPE. The precursors for N, In and Ga were ammonia, trimethylindium and trimethylgallium, respectively. First, a 3-µm-thick undoped c-plane GaN layer was grown on sapphire, with the usual two-step method. [7] On two samples 3-nm-thick InₓGa₁₋ₓN SQWs were grown on the GaN buffer layer, together with an undoped 20 nm GaN capping layer. The emission wavelengths of the quantum wells were (x = 0.12) 470 nm and (x = 0.20) 525 nm.

A Zeiss Supra 40 scanning electron microscope (SEM) was used as a source of the e-beam irradiation. During the exposure, the tightly focused e-beam scanned rapidly the sample surface, resulting in an exposed area of 3 x 3 mm². The e-beam energy was E = 5-20 keV and dose D = 0-500 µC/cm². The beam diameter was roughly 2 nm in diameter corresponding to a momentary current density of 0-130 kA/cm². An unexposed reference area was preserved on each sample. The PL spectra of the samples were measured before and after the irradiation at room temperature. The excitation source was a He-Cd laser with λ = 325 nm and P = 80 W/cm² having approximately 100 nm penetration depth to GaN.

The irradiated samples were characterized with positron annihilation spectroscopy (PAS) measurements with varying positron beam energies (E = 0 – 38 keV). The conventional S and W line shape parameters (determined as |pL| < 0.4 a.u. and 1.5 a.u. < |pL| < 3.9 a.u.) were used to describe the measured spectra. [8]

**RESULTS AND DISCUSSION**

Fig. 1 shows the normalized PL intensities of GaN thin films irradiated with e-beam energies of 5 and 10 keV, together with GaN/InGaN near surface SQWs irradiated with e-beam energy of 10 keV, as a function of the irradiation dose. Exponential degradation of optical quality with increasing dose is seen in all samples. It can be observed that the optical degradation of the GaN/InGaN SQW samples is almost identical to the GaN film irradiated with 10 keV e-beam regardless of the In content. This suggests the optical degradation mechanism in the irradiated GaN/InGaN SQW samples to be the same as in the GaN film, even though the luminescence originates from the InGaN QWs.
Figure 1. Normalized PL intensity of 5 and 10 keV e-beam irradiated GaN thin film samples and 10 keV irradiated GaN/In$_{x}$Ga$_{1-x}$N (x=0.12; 0.20) SQWs as a function of the irradiation dose. The S-parameter of the positron annihilation measurement for the 5 keV GaN film is also shown.

It can also be seen from fig 1. that the PL intensity reduces faster with lower e-beam energy. This behavior can be explained with the energy dissipation profile of electrons in GaN, shown in fig. 2. The profiles were calculated by the Bethe-Bloch method. [5, 9] The energy dissipation of a 5 keV beam is tightly focused on the topmost 100 nm of the GaN film, which corresponds to the laser absorption depth. The energy dissipation profile broadens and the peak shifts deeper into the film with increasing e-beam energy. This suggests that the energy dissipation density of an e-beam is responsible for the optical degradation, regardless of the beam energy in the studied range.

No observable change was detected in the full width at half maximum or band-to-band emission peak position in the PL spectra [10] indicating no change in the film tension which could be related to generated dislocations. Furthermore, contribution of local heating can be neglected when using irradiation parameters of this experiment. Also the surface contamination effects during SEM have been ruled out. [5, 10]

PAS was used to determine the presence of cation vacancy defects and their density in the samples. Positron beam energy was used to match the positron implantation depth with the e-beam energy dissipation profiles. As shown in fig. 2, it was sufficient to utilize same energy for positrons as was used in the e-beam irradiation. The results for GaN films irradiated with an increasing 5 keV dose are included in fig. 1. The displayed increase of the PAS S-parameter corresponds with the increase in density of cation vacancies in the positron implantation depth in the material. As can be seen in fig 1, the point defect concentration increases with increasing dose indicating that defects are introduced in the material by the 5 keV e-beam. The correlation between the increase in point defect concentration and PL reduction suggests that these defects are responsible for the degradation of the material optical quality.
Figure 2. Electron energy dissipation profile and positron stopping profile as a function of the penetration depth for 5, 10, 15 and 20 keV electrons and positrons.

Fig. 3 shows the W- and S- parameters obtained with PAS measurements from GaN samples irradiated with 5 – 20 keV e-beam energies with a dose of 40 µC/cm² and 5 keV with increasing dose from 0 to 160 µC/cm². The W- and S-parameters of both in-grown vacancies and high-energy electron or ion induced vacancies are also shown. It can be seen that the vacancies generated by LEEBI match the in-grown Ga-vacancy profile. The vacancy density corresponds well with the dose of 5 keV beam and the energy dissipation density of 5 – 20 keV energy beam with constant dose. This supports our previous conclusion that the energy dissipation density is a key factor in Ga-vacancy formation and optical degradation of the material.

The observation of Ga vacancy formation by 5–20 keV e-beam irradiation is surprising, since the displacement energies of the N and Ga atoms in GaN are 150 keV and 500 keV, respectively. [11] Therefore, we propose that rather than generating new defects, the LEEBI
treatment activates existing passive in-grown Ga-vacancies in MOVPE grown GaN. The phenomenon is similar to the case of Mg-doped p-GaN, where H passivates the Mg-acceptors during growth. Low energy e-beam treatments have been used to break these complexes to activate Mg acceptors in GaN [12], by stripping H from the Mg-H complexes [13].

Ga-vacancies forming complexes with H is rather likely in MOVPE GaN. [12] In the case of MOVPE GaN V_{Ga-H}_n complex with n > 2 is most likely, since n = 1 or n = 2 complexes would be readily detectable with positrons. [14] Furthermore, the n = 4 complex is predicted to be unstable while n = 3 should be electrically neutral [15], and the energy required to remove one hydrogen atom from n = 3 complexes is approximately 1 eV. As the local current density during the LEEBI treatments was in a similar range than the operating current of GaN-based laser diodes, the activation of Ga-vacancies might be also behind the limited lifetime of these devices [16]. However more studies on the mechanisms of low energy electron beam and high current density on the in-grown defects in GaN are needed to clarify the phenomenon.

CONCLUSIONS

In this paper, the degradation of optical quality of MOVPE grown GaN-thin films by tightly focused LEEBI is associated with the activation of in-grown Ga-vacancies. The optical quality of GaN films was found to degrade with increasing energy dissipation density and dose of a low energy e-beam. Low e-beam energy of 5-20 keV, well below the defect generation energy threshold was sufficient to cause the degradation. The degradation was associated with the activation of in-grown Ga-vacancies in MOVPE grown material by positron annihilation spectroscopy. The Ga-vacancy concentration was found to correlate with optical degradation, and increase with both energy dissipation density and dose of a low energy e-beam. Based on the results we propose that in-grown passive V_{Ga-H}_n complexes are present in MOVPE grown GaN (and its alloys), and are activated by LEEBI.

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