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Low energy electron beam induced vacancy activation in GaN

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Experimental evidence on low energy electron beam induced point defect activation in GaN grown by metal-organic vapor phase epitaxy (MOVPE) is presented. The GaN samples are irradiated with a 5–20 keV electron beam of a scanning electron microscope and investigated by photoluminescence and positron annihilation spectroscopy measurements. The degradation of the band-to-band luminescence of the irradiated GaN films is associated with the activation of point defects. The activated defects were identified as in-grown Ga-vacancies. We propose that MOVPE-GaN contains a significant concentration of passive V_{Ga}-H_n complexes that can be activated by H removal during low energy electron irradiation. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3696047]

Gallium nitride and its alloys are important materials for applications in blue and ultraviolet optoelectronics and in electronic devices operating at high temperatures and voltages. III-N materials are generally considered as chemically hard and well resistant to radiation making them suitable materials for devices in rough environments.[1]

Irradiation with MeV-scale electrons is known to generate Ga and N vacancies in GaN, causing degradation of electrical and optical properties.[2,3] Irradiation damage has also been observed after electron irradiation with significantly lower energies in the 5–35 keV range,[4–7] well below the Frenkel pair generation thresholds of 150 and 500 keV for the N and Ga sublattices, respectively. This includes low energy e-beam irradiation (LEEBI), which was widely used to activate Mg acceptors in p-doped GaN.[7] The damage is thought to be due to activation of vacancies, defect migration or clustering of point defects. However, due to the indirect nature of low energy irradiation induced damage formation the exact mechanisms are not clear.

In this letter, the optical degradation of GaN films, grown by metal-organic vapor phase epitaxy (MOVPE), during LEEBI is associated with the activation of point defects, more specifically in-grown Ga-vacancies. The GaN films were irradiated with 5–20 keV e-beam with total doses up to 500 μC/cm^2 (3×10^{15} cm^{-2}). Ga vacancies became detectable in significant concentrations in positron annihilation experiments, suggesting that this activation process is the cause of the observed degradation of band-to-band luminescence intensity.

The thin-film GaN samples were grown on c-plane sapphire (Al_2O_3) by MOVPE. The precursors for N and Ga were ammonia and trimethylgallium, respectively. In all the samples, a 3-μm-thick undoped c-plane GaN layer was grown on sapphire with the two-step method.[8]

The samples were exposed to an e-beam using a Zeiss Supra 40 scanning electron microscope (SEM). The exposure was performed by rapidly sweeping the e-beam on a specific area of the sample surface. The e-beam energy was varied between 5 and 20 keV and the dose in the range of 0–508 μC/cm^2 (0–3×10^{15} cm^{-2}) by controlling the exposure time and the beam current. The e-beam spot size was approximately 2 nm in diameter and the corresponding momentary current density 0–130 kA/cm^2. An unexposed area was preserved on each sample to have an unaltered reference point. The photoluminescence (PL) spectra of the designated sample areas were measured at room temperature before and after the e-beam exposure using a monochromatic He-Cd laser (lambda = 325 nm, P = 80 W/cm^2) as an excitation source. The penetration depth of the laser beam is approximately 100 nm in GaN.

We studied the presence of cation vacancy defects in the samples with a variable energy positron beam (E = 0–38 keV). The trapping of positrons at vacancy defects can be observed as the narrowing of the Doppler-broadened 511 keV annihilation line, recorded with a Ge detector. The measured spectra were characterized by the conventional line shape parameters S and W, determined as fractions of positrons annihilating with low ($|p_L| < 0.4$ a.u.) and high momentum electrons (1.5 a.u. $< |p_L| <$ 3.9 a.u.), respectively.[9]

The integrated band-to-band emission PL intensities of irradiated GaN films are plotted in Fig. 1 as a function of the exposure dose for e-beam kinetic energies of 5, 10, 15, and 20 keV. The PL results agree well with our previous work on LEEBI damage on InGaN/GaN single quantum wells (SQWs) and GaN films.[6,10] The behavior of the PL degradation with varying e-beam energies can be explained if we consider the e-beam energy dissipation profile and the absorption depth of the excitation laser. As can be seen from Fig. 2, approximately half of the energy of a 5 keV e-beam is dissipated within the laser absorption depth of 100 nm. The electron dissipation profiles were calculated with a cubic polynomial approximation[11] of the Bethe-Bloch method.[12] The energy dissipated within the laser absorption depth decreases with increasing e-beam energy, so the effect on the PL intensity is weaker with higher electron energy. No change was observed in the emission peak position or the full width at half maximum.

The possible contribution of e-beam induced surface hydrocarbon contamination[13] to PL intensity was excluded by post-exposure acid treatments. Aqua Regia and Piranha

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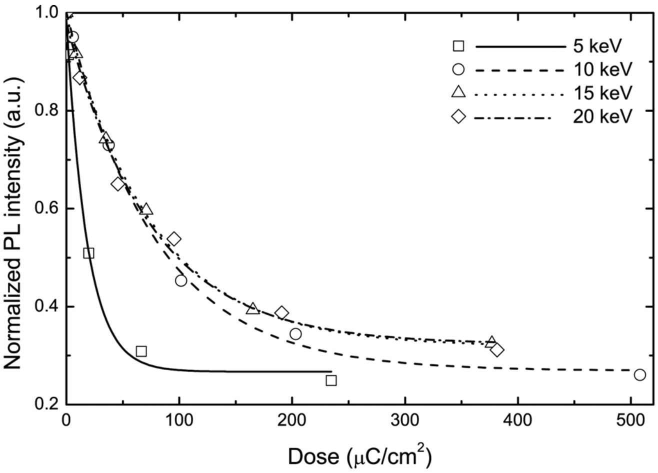

FIG. 1. Normalized GaN band-to-band PL intensities as a function of 5–20 keV e-beam irradiation dose. Exponential curves serve as a guide to the eye.

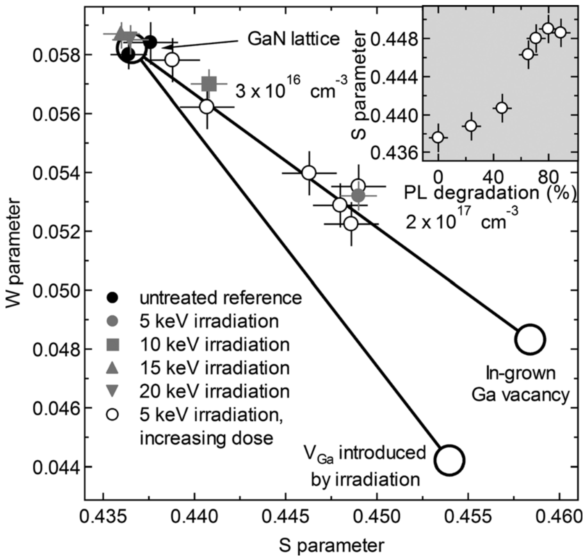

FIG. 3. The *S* and *W* parameters measured from the irradiated samples with selected positron implantation energies. Values characteristic of the GaN lattice and the in-grown Ga vacancy-related defects are also shown. The open circles show the parameters for 5 keV e-beam with dose increasing from 5 to 160 μC/cm^2. The inset shows the increase of the *S* parameter as a function of percentual decrease of the PL intensity with increasing 5 keV dose.

solutions (HCl:HNO$_3$ 3:1 and H$_2$SO$_4$:H$_2$O$_2$ 3:1, respectively, 12 min both) were used to remove organic and metallic contamination from the sample surface. No measurable effect on the PL intensity was observed.

With the aim of investigating possible vacancy-related effects correlated with the loss of PL intensity in the e-beam treatments, we performed positron annihilation spectroscopy on the samples. We used a slow positron beam and chose the positron acceleration energies to match the positron implantation profiles[14] and the e-beam energy dissipation profiles. As can be seen from Fig. 2, in practice it was sufficient to choose the same energy for the positron beam as for the e-beam in order to maximize the possible irradiation effect detectable by positrons.

Fig. 3 shows the S and W parameters measured from the e-beam irradiated (dose constant 40 μC/cm^2 (2.4×10^{14} cm^{-2})) samples with positron implantation energies matching the e-beam energies and additionally the S and W parameters for samples irradiated with constant e-beam energy (5 keV) and increasing dose (5–160 μC/cm^2 (0.3–9.6×10^{14} cm^{-2})). The values obtained from an untreated sample as well as those characteristic of the GaN lattice (obtained from a reference sample where no positron trapping at defects is observed[3]), isolated Ga vacancies (introduced in high-energy electron or ion irradiation) and typical in-grown Ga vacancy-related defects[9] are also shown. The identity of dominant positron traps can be evaluated from the position in the (*S*, *W*) plot. From Fig. 3, it is evident that the untreated samples and the samples irradiated with 15 keV and 20 keV electrons cannot be distinguished from each other, and the concentrations of positron-trapping vacancy defects are below the room-temperature detection limit of about 10^{16} cm^{-3}. This is typical of MOVPE GaN.[15] The samples irradiated with 5 keV and 10 keV electrons show clearly different behavior: their *S* and *W* parameters are on the line connecting the GaN lattice and in-grown Ga vacancy parameters, indicating that Ga vacancy-related defects become detectable in the lowest-energy irradiations. The increase of the 5 keV dose correlates with the change in the (*S*, *W*) parameters and the decrease of PL intensity (shown in the inset of Fig. 3). The peak concentrations of the observed Ga vacancies can be estimated[9] from the position of the (*S*, *W*) parameters on the lattice-defect line, using a typical room-temperature positron trapping coefficient of $\mu_V = 3 \times 10^{15}$ s^{-1} for the Ga vacancy and assuming that the vacancy profile is given by the electron energy dissipation profile. The estimated values are around 3×10^{16} cm^{-3} for the 10 keV sample and 2×10^{17} cm^{-3} for the 5 keV sample. Furthermore, as shown by the inset in Fig. 3, the positron S parameter clearly increases (i.e., the concentration of observed Ga-vacancy defects increases) with stronger reduction of the PL intensity (increasing dose).

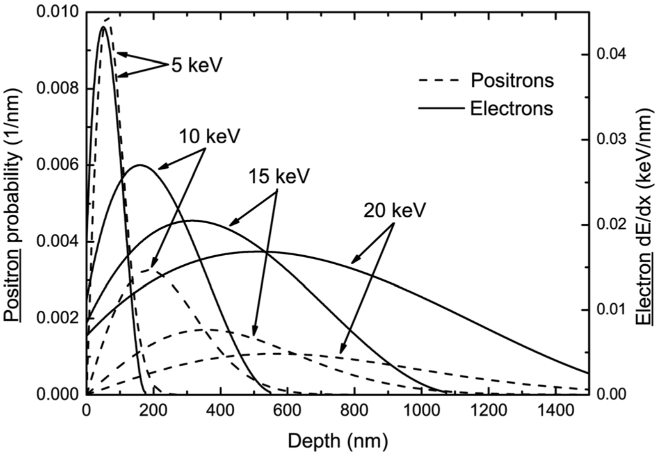

FIG. 2. Positron stopping profile and electron energy dissipation profile plotted as a function of depth in GaN.

The observation of relatively high concentrations of Ga vacancies after 5–10 keV e-beam irradiation is unexpected, as the displacement energies of the N and Ga atoms in GaN are such[3,16] that electrons with energies below 500 keV should not produce Ga vacancies, while N vacancies should not be produced below 150 keV. Hence our low energy e-beam treatments should not create Ga vacancy defects, but rather activate existing ones both from the electro-optical and positron trapping point of view. This is also evident from the data in Fig. 3: isolated Ga vacancies actually produced by electron irradiation have a different signature in positron experiments—the Ga vacancy related defects observed here are similar to typical in-grow Ga vacancy defects (complexed with impurities such as O and/or H) (Ref. 17) observed in GaN.

LEEBI treatments have been used to activate Mg acceptors in GaN,[7] and since the dominant passivation of Mg is through Mg-H complexes,[18] it is likely that these treatments can strip H from Mg. The mechanism can be direct energy transfer during electron stopping, or current density-activated diffusion (high current densities are typical of LEEBI treatments). It is possible that a similar effect is present here: the Ga vacancies may be complexed with H (this is, in fact, rather likely in MOVPE GaN (Ref. 17)). However, V_{Ga}-H and V_{Ga}-H_2 are not good candidates, as both are readily detectable with positrons, while complexes with more hydrogen do not trap positrons.[17] Hence we propose that MOVPE GaN contains a significant concentration ($>10^{17}\,cm^{-3}$) of V_{Ga}-H_n complexes where $n > 2$, while the concentrations of V_{Ga} with less or no hydrogen are below $10^{16}\,cm^{-3}$. Theoretical calculations suggest that for a typical room-temperature Fermi level of $E_F = E_C$ - 0.5 eV (corresponding to electron concentration $n_e = 10^{17}\,cm^{-3}$), the V_{Ga}-H_4 complex is unstable, while the energy required to remove one hydrogen atom from the V_{Ga}-H_3 complex is roughly 1 eV, enough to make it stable. This complex should be neutral throughout the band gap.[19] The LEEBI treatment with sufficient current density and dose could then efficiently remove hydrogen from the complexes, creating deep acceptor levels in the gap that can act as a non-radiative recombination centers, while making the complex detectable by positrons.

It should be noted that with the present data it is not completely clear whether it is the electron energy transfer during the stopping process or the current density that activates the vacancy defects. However, if it is the latter, our results provide one possible explanation for the degradation process of nitride-based laser diodes, where current densities are similar[20] to the ones used in our e-beam treatment. The effect of local heating of the sample is insignificant since the temperature rise is known to be at most few tens of degrees.[21]

In summary, we associate the optical degradation of MOVPE grown GaN films during LEEBI with the activation of in-grown vacancies. We suggest that the in-grown Ga-vacancies are initially complexed with 3 or more hydrogen atoms and neutral. The LEEBI treatment with sufficient current density and dose could then remove hydrogen from the vacancy complex resulting in a deep acceptor level in the band-gap.

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