Electron-beam-induced modifications of electronic properties in GaN-based quantum well structures

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ABSTRACT: The electronic properties of (In,Ga)N/GaN quantum wells fabricated by MOCVD vary significantly during investigations using low-energy electron beam irradiation (LEEBI) such as cathodoluminescence (CL) if a certain exposure dose is exceeded. For unintentionally doped structures, we observe a simultaneous LEEBI-induced activation of donors and acceptors. Thus, the resistivity of the layers is not varied, while the quantum efficiency and optical transition energy increases significantly by LEEBI. A *p-n* structure is turned towards flat band conditions during LEEBI indicating an electron beam induced passivation of acceptors in the *p*-type layer.

1. INTRODUCTION

Low-energy electron-beam irradiation (LEEBI) of Mg-doped GaN layers grown by metalorganic chemical vapor deposition (MOCVD) causes a substantial decrease and increase of the resistivity and luminescence efficiency (η) of those layers (Amano et al 1989). There are also indications for a LEEBI-induced variation of η in undoped MOCVD-grown GaN (Li et al 1996, Toth et al 1999, Dassonneville at al 2001). While the activation mechanism of acceptors in *p*-type GaN has been comprehensively investigated and accepted to be a minority-carrier-induced dissociation of a Mg-H-N complex (Nakamura et al 1992, Pearton et al 1996, Saeger et al 2002), a consistent picture about LEEBI effects in undoped and *n*-type GaN cannot been drawn yet. Moreover, there is a lack of systematic investigations of LEEBI-induced variations of the electronic properties of GaN-based quantum well (QW) structures. An activation of dopands is accompanied by an increase of the free carrier concentration, which can lead to a screening of the electric field within GaN-based QWs. As a result, a blue-shift of the CL spectrum and an increase of η of the QW is expected. Consequently, characterization and imaging of GaN-based QWs by electron beam methods such as cathodoluminescence (CL) and electron beam induced current (EBIC) are expected to be significantly influenced by the measurement itself.

We have investigated LEEBI effects in an undoped (In,Ga)N/GaN multiple QW fabricated by MOCVD as well as in a commercial light-emitting diode (LED: Nichia Chemical Industry Ltd.) containing a single QW in the active region. As references, an undoped (In,Ga)N/GaN MQW fabricated by plasma-assisted molecular-beam epitaxy (MBE) and a MBE-grown GaAs/(Al,Ga)As single QW were exposed by an electron beam under the same conditions. While η and the optical transition energy (E_t) of the GaAs/(Al,Ga)As and MBE-grown (In,Ga)N/GaN QW does not vary and vary little during LEEBI, respectively, for the MOCVD-grown (In,Ga)N/GaN MQW, both η and E_t increase significantly.

2. EXPERIMENTAL DETAILS

The growth conditions of the (In,Ga)N/GaN MQWs fabricated by MOCVD and plasma-assisted MBE are described in (Pecharroman-Gallego et al 2002) and (Waltereit et al 2001), respectively. The

MOCVD-grown MQW consists of 10 periods of a 2.6-nm-thick $In_{0.1}Ga_{0.9}N$ well and a 7.0-nm-thick GaN barrier layer deposited on a sapphire substrate with a 1.2-µm-thick GaN buffer. The MBE-grown MQW consists of 10 periods of a 3.1-nm-thick $In_{0.16}Ga_{0.84}N$ well and a 12.1-nm-thick GaN barrier layer deposited on a SiC substrate with a 1.0-µm-thick buffer. The GaAs/(Al,Ga)As reference sample consists of a 4.8-nm-thick single well embedded in two short-period AlAs/GaAs superlattices as barriers deposited on a (001)GaAs substrate. The light-emitting (In,Ga)N/GaN diode used in our experiments is described in (Nakamura et al 1995). It consists of a 3-nm-thick $In_{0.45}Ga_{0.55}N$ well layer embedded between a 4-µm-thick *n*-GaN layer at the bottom and a 100-nm-thick *p*-$Al_{0.2}Ga_{0.8}N$ as well as a 500-nm-thick *p*-GaN layer at the top of the *p-n* structure.

The samples were exposed by the electron beam of a scanning electron microscope (SEM) at 5 and 300 K. The beam energy and current amounted to 5 to 15 keV and 0.05 to 8 nA, respectively. The exposed area amounted to 29 µm^2. After distinct charge doses (D_c), CL spectra were acquired by a charged-coupled device detector. For the light-emitting diode, additionally the EBIC signal has been measured at the same time. Furthermore, Hall measurements were performed at 300 K using van der Pauw structures of the MOCVD-grown MQW.

2. RESULTS AND DISCUSSION

2.1 Unintentionally Doped QW Structures

A characterization of QWs by CL is usually done at low temperatures. Therefore, we firstly exposed the samples and acquired CL spectra at 5 K. Figure 1(a) and (b) depict the integrated CL intensities and the variation of the transition energies (ΔE_t) of the QWs as a function of D_c, respectively, for all three undoped samples. For the GaAs-based QW, both η and ΔE_t remain almost constant during the electron exposure. For the MBE-grown GaN MQW, only ΔE_t increases by about 10 meV after an exposure dose of 2 C cm^{-2}. The CL intensity and ΔE_t of the MOCVD-grown MQW, however, increase significantly during the electron exposure. Since non-radiative recombination centers are effectively suppressed at low temperatures, the observed increase of η accompanied by a blue-shift of E_t can be interpreted as a result of electric-field screening in the QWs. Similar results have been observed at 300 K, where η is even more enlarged by LEEBI compared with the low temperature exposure. Figure 1 (c) and (d) show the CL spectra of the MOCVD-grown MQW for an exposed (circles) and unexposed (squares) region at 5 and 300 K, respectively. The electron exposure has been performed at 5 K. The enhancement of the CL intensity by LEEBI is about 10 times higher in the room temperature spectrum compared with the one obtained at 5 K. The results of Fig. 1 show that one should pay

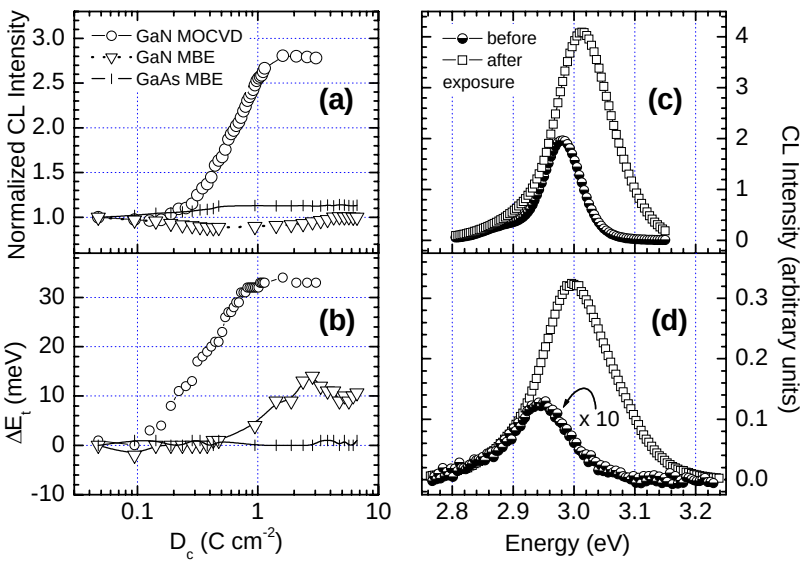

Fig. 1. Integrated CL intensities (a) and variation of the optical transition energy (b) of (In,Ga)N/GaN MQWs fabricated by MBE and MOCVD as well as of a GaAs/ (Al,Ga)As single QW as a function of the electron exposure dose (D_c) at 5 K. (c) and (d): CL spectra of the MOCVD-grown MQW at 5 and 300 K. Circles and squares represent spectra obtained from unexposed and exposed (D_c = 2 C cm^{-2}) regions, respectively. The exposure has been performed at 5 K and 5 keV.

attention to electron beam-induced variations of optical properties of QWs in the GaN system, in particular, in MOCVD-grown ones.

Besides a blue-shift and an increase of the QW CL of the MOCVD-grown sample, we observe at the same time an increase of the CL intensity of the GaN buffer layer as a function of D_c. Figure 2 depicts CL spectra before and after LEEBI at 15 keV and 5 K within the spectral range of the GaN excitons. The electron exposure causes an increase of the intensity by more than an order of magnitude, a red-shift, as well as a broadening towards lower energy values of the exciton line. The inset displays the respective integrated CL intensity as a function of D_c. Similar results regarding the increase of the intensity of the exciton CL in undoped bulk GaN grown by MOCVD during LEEBI have been reported by Toth et al (1999). The authors explain their data by electron beam-induced in-diffusion of oxygen. Figure 2 clearly reveal that free and bound exciton transitions dominate the CL spectra before and after LEEBI, respectively. Moreover, at least two distinct bound excitons evolve as a result of the electron exposure a neutral donor bound exciton (D^0,X) and the so-called I_x exciton. The latter has been identified by Chtchekine et al (1999) to be an exciton bound to a neutral acceptor. Consequently, it appears that rather an activation of both hydrogen-passivated acceptors and donors is responsible for the increase of the CL intensity by electron beam exposure of undoped GaN than an in-diffusion of impurities. This conclusion is confirmed by the distinctly different behavior of MOCVD- and MBE-grown MQWs.

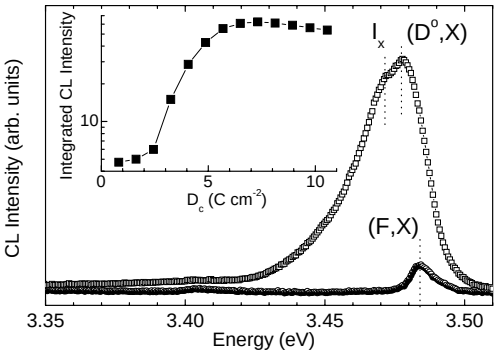

Fig. 2. CL spectra before (circles) and after (squares) LEEBI at 5 K. I_x, (D^0,X), and (F,X) mark an acceptor bound, donor bound, and free exciton. Inset: Integrated CL intensity of the exciton lines as a function of the exposure dose.

However, in contrary to *p*-type GaN, the increase of η of the QWs and GaN buffer layer is not accompanied by a decrease of the resistivity after electron exposure. Hall measurements did not show any variation of the sheet resistivity before and after LEEBI at 300 K. Consequently, LEEBI results not in a significant increase of the net free carrier concentration. This result is consistent with the observation of a simultaneous LEEBI-induced activation of acceptors and donors preserving the compensating state of the material, while the probability for optical transitions and thus η increases significantly.

We are, however, still left with the question: Why is a dopand activation without a measurable increase of the net free carrier concentration accompanied by a blue-shift of the QW CL? This question can be qualitatively understood if we take into account that the QWs are situated near the surface (20-nm-thick cap layer), where the electric field of the QWs can interact with the electric field, which is caused by surface polarization. If donors are activated by LEEBI, the surface depletion region becomes narrower and the corresponding electric field increases. Since the surface polarization field and the internal electric field of the QWs act in opposite directions, the QW field is screened with increasing field of the depletion region. As a result, we obtain a blue-shift of the QW CL. The much more pronounced LEEBI-induced enlargement of η observed at 300 K compared with the one of 5 K [Fig. 1 (c) and (d)] is due to a larger capture probability of carriers within the QW at higher temperatures, where localization of carriers excited within the barrier material is suppressed.

2.2 Quantum well within a *p-n* junction

The CL intensity (I_{CL}) and E_t of a QW situated within a *p-n* junction of a light-emitting diode as well as the corresponding EBIC signal vary strongly under the electron beam if the exposure dose exceeds 0.1 C cm^{-2}. Moreover, whether the CL spectrum is red- or blue-shifted and I_{CL} increase or decrease depend strongly on the applied bias voltage. As an example, Fig. 3 (a) displays the normalized values of the intensity of the QW CL and of the EBIC signal as well as E_t as a function of D_c at 5 K for zero bias voltage. With increasing exposure dose, I_{CL} firstly increases accompanied by a red-shift and at the same time, the EBIC signal decreases. For $D_c > 0.7$ C cm^{-2}, I_{CL} decrease gradually, E_t

increases while the EBIC signal remains almost constant. Spatially resolved electroluminescence (EL) measurements revealed that the EL intensity is reduced by a factor of two within the exposed region. This LEEBI-induced damage is almost completely annealed after 4 hours operation of the diode at 10 mA (self-annealing).

For a tentative interpretation of these findings, we compare the dose dependence of I_{CL}, E_t, and of the EBIC signal [Fig. 3 (a)] with the dependence of the respective values on the bias voltage (U_{bias}) [Fig. 3 (b)]. The exposure dose used to acquire the whole data set of Fig. 3 (b) amounted to less than 5 mC cm^{-2}. Thus, exposure effects can be neglected in this case. Approaching flat band conditions by increasing U_{bias}, the EBIC signal and E_t are reduced, while I_{CL} firstly increases and than gradually decreases (for U_{bias} > 2 V). This bias dependence can be understood in terms of the interaction of the internal electric field of the QW with the external electric field of the depletion region of the *p-n* junction and a decreasing probability of carrier tunneling out of the QW with increasing bias voltage as follows: For zero bias voltage, the external electric field compensates the field of the QW resulting in a blue-shift of E_t compared with flat band conditions. With increasing values of U_{bias}, the compensating field is reduced resulting in a red-shift of the QW CL. Since for zero bias, the QW barriers are triangular shaped due to a large external field, the probability of carrier tunneling out of the QW is high at low values of U_{bias}. Thus, the tunneling barrier increases with increasing forward bias (decreasing external electric field) resulting in an increase of I_{CL}. The EBIC signal shows an opposite behavior as expected.

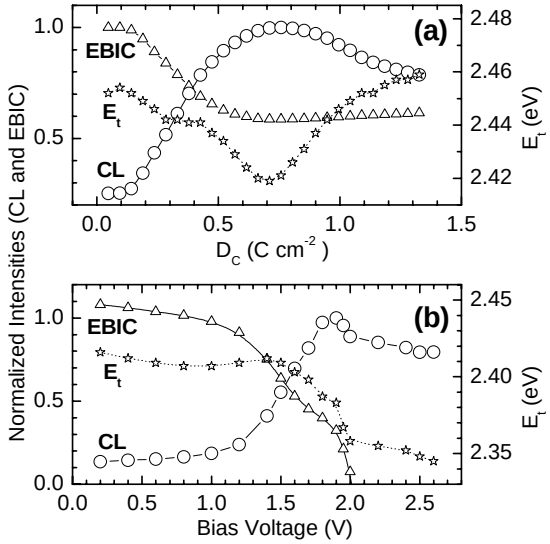

Fig. 3. Integrated CL intensity (CL), optical transition energy (E_t), and EBIC signal as a function of the exposure dose (a) and forward bias voltage (b) of a light-emitting diode at 5 K.

The bias dependence of I_{CL}, E_t, and of the EBIC signal shows – roughly speaking – the same behavior as observed for the respective dose dependence except for D_c > 0.7 C cm^{-2}, where E_t increases again. Consequently, we suggest that LEEBI of the light-emitting diode turns the system towards flat band conditions. A possible explanation for the evolution of flat band conditions during LEEBI is a passivation of acceptors of the *p*-type layer by electron beam-induced diffusion of hydrogen into the region of the *p-n* junction. The observed self-annealing of the LEEBI-related damage is consistent with the activation of hydrogen-passivated acceptors by electrical injection of minority carriers as reported by Miyachi et al (1998). The increase of E_t for D_c > 0.7 C cm^{-2}, which is accompanied by a broadening of the CL, is not yet understood, but could indicate an occupation of higher energy states if the electric field of the QW exceeds a certain value.

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