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Minority carrier transport in p -type $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ doped with phosphorus

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Minority carrier diffusion length and lifetime in p - $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ doped with phosphorus were obtained from local electron beam irradiation measurements. The irradiation resulted in an increase of up to 25% in minority electron diffusion length from the initial value of $\sim 2.12\ \mu\text{m}$ and in a simultaneous decrease of the peak near-bandedge cathodoluminescence intensity. The observed phenomena are attributed to charging of phosphorus-related deep acceptor level(s), which is consistent with the activation energy of $256 \pm 20\ \text{meV}$ found for the effect of electron injection in $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$. © 2005 American Institute of Physics. [DOI: 10.1063/1.1844037]

ZnO is a II–VI wide band gap semiconductor with properties similar to GaN. The band gap energy of ZnO is 3.3 eV at room temperature and it is an attractive material for the fabrication of blue and UV optoelectronic devices.¹ Short-wavelength laser diodes are a possible application, since the exciton binding energy of ZnO is 60 meV, which is 2.4 times that for GaN (25 meV).² Due to its unique piezoelectric properties, ZnO can also be used in electroacoustic applications such as SONAR emitters and detectors.

Until recently, p -type doping of ZnO has been a major challenge for the implementation of bipolar devices.^{3–15} Light-emitting diodes (LEDs) with ZnO active region have been successfully demonstrated, however, utilizing p -AlGaIn¹⁶ and p -AlGaIn/ p -GaIn heterostructure¹⁷ for hole emitters. Due to chemical and crystallographic differences between ZnO and AlGaIn, defects can form at the hetero-interface, which can negatively impact optical and electrical properties. Therefore, devices formed from the heterostructures are expected to be inferior to all MgZnO-based devices.

The problem with p -type doping of ZnO is similar to that in wide band gap GaN. The potential acceptors in ZnO, such as nitrogen, phosphorus, and arsenic, tend to be deep and thus have small fractional ionizations at room temperature. Moreover, lattice energetics tend to greatly favor formation of donors over acceptors.¹⁸ In ZnO, therefore, donors act as compensation centers if acceptors are deliberately added. N -type background concentration can be lowered by incorporating Mg in the lattice of ZnO to increase the band gap and then to dope the ZnMgO with P at high concentrations, followed by annealing, to obtain type conversion to p -type.¹⁹

With p -type doping of ZnO becoming more robust, it is very likely that minority carrier devices such as LEDs, laser diodes, and transparent p - n junctions can be achieved in the near future. This makes studies of minority carrier transport in ZnO-based material especially timely. In this letter, we report electron beam induced current (EBIC) and cathodoluminescence (CL) studies of minority electron transport in $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ subjected to electron beam irradiation, which mimics carrier injection in p - n junctions as shown previously for GaN.²⁰

In this work, pulsed-laser deposition was employed for growth of $\sim 1.4\text{-}\mu\text{m}$ -thick $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ films on (0001) undoped bulk ZnO single crystals. Phosphorus-doped ($\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$) targets were fabricated using high-purity ZnO (99.9995%) and MgO (99.998%), with P_2O_5 (99.998%) serving as doping agent.¹⁹ After growth, the samples were annealed at 600 °C in a 100 Torr O_2 ambient for 60 min to suppress possible donor defects. Capacitance–voltage profiling of similar films, grown using the same procedure, resulted in net acceptor concentration of $\sim 2 \times 10^{18}\ \text{cm}^{-3}$ after annealing. Pt/Au(200/800 Å) layers were deposited on phosphorus-doped $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ films by electron beam evaporation and patterned by lift-off with contact diameters ranging from 50 to 375 μm . Circular electrode pairs with significantly different surface areas were employed for the EBIC measurements. The electrodes create an asymmetric rectifying junction, based on back to back Schottky diodes, with the larger area electrode being pseudo-Ohmic.

The experiments were carried out *in situ* in a Philips XL30 scanning electron microscope (SEM) which is integrated with a Gatan MonoCL3 CL system allowing wavelength-dependent and temperature-dependent optical measurements. Sample temperature in the CL measurements was varied from 25 to 125 °C. For each temperature, CL measurements were carried out at a different location under continuous excitation (up to $\sim 2000\ \text{s}$). The CL measurements were conducted at an accelerating voltage of 12 kV, resulting in a current of up to several nanoamperes absorbed in the sample. The electron beam penetration depth in the material was estimated to be $\sim 0.8\ \mu\text{m}$. Excitation was combined with periodic acquisition of CL spectra taken under SEM magnification of 4000. CL results were compared with those obtained from the EBIC measurements carried out on the same sample by moving an electron beam of SEM from the edge of the Schottky barrier outwards (line-scan) and recording an exponential decay of induced current. Detailed description of EBIC experiments can be found elsewhere.²¹

EBIC measurements were performed at room temperature. After a single EBIC line-scan was completed (12 s), the excitation of the sample with the electron beam moving back and forth along the same line was continued for the total time of $\sim 1200\ \text{s}$. EBIC measurements were periodically repeated

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FIG. 1. Experimental dependence of minority electron diffusion length on duration of electron injection at 300 K. **Inset:** calculated minority electron lifetime dependence on duration of electron injection. For lifetime calculations, minority electron mobility in $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ was assumed to be $50 \text{ cm}^2/\text{V s}$.

to extract the minority carrier diffusion length,^{21,22} L , as a function of the duration of electron beam irradiation, t . As displayed in Fig. 1, a linear increase of L as a function of t was observed. Note that L tends to saturate at $t > 1200 \text{ s}$. We also note that the irradiation-induced increase of minority carrier diffusion length persists for at least 4 days at the same saturated level. We have reported a similar behavior in GaN doped with Mg or Mn.^{22,23} EBIC measurements carried out on undoped bulk ZnO substrates did not reveal any noticeable increase of L with t (up to 2000 s), suggesting that the presence of phosphorus is important for the observed behavior.

Similar to the case of p -GaN, the observed increase of L in ZnMgO is attributed to an increase of nonequilibrium minority electron lifetime, τ , in the conduction band. While the experimental evidence for this was obtained from CL measurements, the inset of Fig. 1 shows an increase of τ , calculated as explained in Ref. 22, based on experimentally measured L values.

CL experiments were started at room temperature with the acquisition of an initial spectrum [spectrum (1) in Fig. 2]. The edge of this spectrum at $\sim 355 \text{ nm}$ (see also the inset of

FIG. 2. Room temperature CL spectra measured in the same location at different times of electron injection. (1) is a preinjection spectrum; (2), (3), and (4) correspond to a duration of electron injection of 359, 793, and 1163 s, respectively. **Inset:** preinjection broad-range CL spectrum taken in a different location than spectra in Fig. 2.

FIG. 3. Variable temperature dependence for the square root of inverse normalized intensity on duration of electron injection. The rate at every temperature is obtained from the slope of a linear fit. **Inset:** temperature dependence for the rate of the square root of inverse normalized intensity (open circles) and the fit. The slope of the graph yields $\Delta E_A = 256 \pm 20 \text{ meV}$.

Fig. 2) is in agreement with 10% Mg content in ZnO lattice.²⁴ The observed CL spectrum is attributed to the band-to-band as well as band-to-impurity (P -acceptor) optical transitions. The inset of Fig. 2 shows a wider range spectrum featuring a broad band, which is likely defect related.²⁵

While no changes were observed in the broad band CL (cf. inset of Fig. 2), the near-band-edge luminescence in Fig. 2 exhibits a continuous decay with increasing duration of electron beam irradiation (injection). A similar decay in the CL intensity was observed for Mg doped (Al)GaN²⁶ and Mn doped GaN.²³ As L is proportional to the square root of lifetime and depends linearly on t ,^{22,23,26} the inverse CL intensity, $1/I$, which is also proportional to τ (larger τ determines longer nonequilibrium carrier stay in the band, and, as a result, lower rate of recombination), should depend on duration of electron injection quadratically. This is, indeed, observed in Fig. 3, where the square root of the inverse normalized (with respect to its initial maximum value) intensity, $I^{-1/2}$, is plotted versus t . The rate, R , for the linear increase of $I^{-1/2}$ with duration of electron beam injection depends on the sample's temperature, T , as

$$R = R_0 \exp\left(\frac{\Delta E_A}{2kT}\right), \quad (1)$$

where R_0 is the scaling constant, ΔE_A is the activation energy, and k is the Boltzmann's constant. Note that the factor of 2 before the thermal energy kT comes from the two competing factors: R dependence on duration of electron injection [$\sim \exp(\Delta E_A/kT)$] and on temperature [$\sim \exp(-\Delta E_A/2kT)$].²⁶ It is assumed that ΔE_A for both competing factors are close to each other.

Evidently, an increase in temperature results in a decrease of R , suggesting existence of a thermally activated process which counteracts the effect of electron irradiation, thereby leading to a decrease of τ . The activation energy of $256 \pm 20 \text{ meV}$ for this process was calculated from the Arrhenius plot shown in the inset of Fig. 3. This activation energy is in good agreement with that for a phosphorus acceptor obtained based on a simple hydrogenic model.²⁷

The proposed mechanism for the observed effects is as follows:

- (1) Electron beam irradiation leads to injected electron trapping on relatively deep P levels in the forbidden gap. As the fractional ionization of phosphorus is small, there is a sufficient number of neutral P atoms ready to capture an injected electron.
- (2) Capturing injected electron on P levels prevents recombination of the nonequilibrium conduction band electrons, generated by the electron beam, through these levels. As a result, the nonequilibrium electrons stay longer in the conduction band thereby increasing their lifetime and diffusion length. Longer lifetime is equivalent to a fewer number of recombination events and, thus, to a decrease of CL intensity with duration of electron injection.
- (3) As the temperature increases, there is a higher probability for the trapped electrons to escape from the meta-stable P levels (this is equivalent to a hole capture). Thus, these levels become available for band-to-impurity recombination, and the rate for CL decrease slows down.
- (4) Absence of the electron injection-induced effects in undoped ZnO crystals supports our hypothesis for phosphorus being involved in the phenomenon of interest.

In conclusion, minority carrier transport was studied in p -type $\text{Zn}_{0.9}\text{Mg}_{0.1}\text{O}$ under electron beam irradiation, which resulted in increased carrier lifetime and diffusion length. These effects were attributed to charging of meta-stable P -related levels. The experimentally obtained activation energy of 256 meV for the effect is in good agreement with the ionization energy for the P acceptor.

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