Influence Of Electron Trapping On Minority Carrier Transport Properties Of Wide Band Gap Semiconductors

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INFLUENCE OF ELECTRON TRAPPING ON MINORITY CARRIER TRANSPORT PROPERTIES OF WIDE BAND GAP SEMICONDUCTORS

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics in the College of Sciences at the University of Central Florida Orlando, Florida

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ABSTRACT

Minority carrier transport properties and the effects of electron irradiation/injection were studied in GaN and ZnO containing dopants known to form acceptor states deep within the materials’ bandgap. Minority carrier diffusion length and lifetime changes were investigated using Electron Beam Induced Current (EBIC) method, cathodoluminescence spectroscopy, spectral photoresponse and persistent photoconductivity measurements.

It is shown that electron irradiation by the beam of a scanning electron microscope results in a significant increase of minority carrier diffusion length. These findings are supported by the cathodoluminescence measurements that demonstrate the decay of near-band-edge intensity as a consequence of increasing carrier lifetime under continuous irradiation by the electron beam.

Temperature-dependent measurements were used to determine the activation energies for the electron irradiation-induced effects. The latter energies were found to be consistent with the involvement of deep acceptor states. Based on these findings, the effects of electron irradiation are explained via the mechanism involving carrier trapping on these levels.
Solid-state electron injection was also shown to result in a similar increase of minority carrier lifetime and diffusion length. Solid-state injection was carried out by applying the forward bias to a ZnO homojunction and resulted in a significant improvement of the peak photoresponse of the junction. This improvement was unambiguously correlated with the increase of the minority carrier diffusion length due to electron injection.
For my father, Sergey Lopatiuk (1955-1996), a man of great and unfulfilled potential,
with a sharp mind of a scientist and a gentle heart of an artist
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CHAPTER 1 - INTRODUCTION

1.1 Overview of Materials

Due to their intrinsic thermal and electronic stability, wide band gap semiconductors offer a significant advantage for high temperature, high power applications of both electronic and photonic devices. Gallium nitride (GaN) and zinc oxide (ZnO) compounds have been extensively investigated as good candidates for blue and UV opto-electronic devices, such as detectors and emitters, as well as high-power electronics. Additionally, high Curie temperatures and room-temperature ferromagnetism have been predicted in GaN and ZnO doped with transition-metal elements, such as Mn, Cr, and Fe, which in principle opens the door for room-temperature, semiconductor-based spintronic applications [1,2].

Recent developments in doping and growth of ZnO stimulated a particular renewal of interest in this material from the point of view of its applications in optoelectronic devices. As a direct wide bandgap semiconductor ($E_g \approx 3.35$ eV at room temperature) with high exciton binding energy (60 meV, compared to 25 meV in GaN), ZnO is a superior candidate for minority-carrier-based devices, such as light emitting diodes, laser diodes, and transparent p-n junctions. Moreover, it offers significant advantages over III-Nitride materials, which include availability of large area lattice-matched
substrates, lower materials costs, and use of wet chemical etching, as opposed to reactive ion etching employed in GaN technology.

The success of GaN and ZnO in the realm of bipolar devices hinges largely upon the achieving high, stable, and reproducible p-type doping in these materials. This is due to the fact that, while functional heterojunction devices have been produced with both GaN- and ZnO-based materials ([3-8]), crystallographic defects at the interface impede the optical and electrical properties, making these structures fundamentally inferior to homogeneous devices.

Even with the advent of new technology enabling the production of viable p-type materials, the performance of bipolar devices is fundamentally limited by the transport properties of minority carriers. In direct band gap semiconductors, which include ZnO and GaN, minority carrier diffusion length is generally several orders of magnitude lower than in indirect gap materials such as silicon or germanium. In order to noticeably increase minority carrier diffusion length by reducing scattering by the dislocation walls, the edge threading dislocation density must be reduced by at least two orders of magnitude from a typical value of about $10^9 \text{ cm}^{-2}$ in epitaxial layers [9-12].
1.2 Acceptor Levels in GaN and ZnO

In GaN, as well as ZnO, n-type doping never presented a problem, since even nominally undoped, as-grown specimens of both categories generally exhibit n-type conductivity. The origin of this behavior remains a widely debated subject. Intrinsic n-type conductivity has been attributed to native point defects (interstitials, antisites, and vacancies), as well as to contamination by ambient impurities, such as oxygen and hydrogen [13-16].

On the other hand, p-type conductivity with sufficiently high carrier concentrations appears to be much more elusive. Numerous studies have focused on attaining p-type conductivity in GaN by introducing group I and group II elements (Li, Na, Be, K, Ca), as well as other atoms (Zn, Cd, C, and Fe) [17-22]. At present, magnesium (Mg) has emerged as the most feasible acceptor dopant, albeit not without drawbacks due to its limited solubility, compensation issues, and high thermal activation energy. Since Mg acceptor level is located about 200 meV above the valence band, only about 1% of Mg atoms is ionized at room temperature [23].

Since its ionic radius is comparable to that of oxygen, nitrogen has long been considered the substitutional acceptor of choice for ZnO [24]. However, the attempts to obtain p-type ZnO through nitrogen doping appear to yield inconsistent results, which has been suggested to be a consequence of the transient nature of p-type conductivity in ZnO:N [25]. The possibility of p-type doping with larger radii group V atoms, such as
phosphorus [26-28], arsenic [29,30], and antimony [31,32], has also been explored. The studies demonstrated that despite the large size mismatch, which in principle should inhibit the substitution of these impurities, effective p-type doping with hole concentrations up to $10^{20} \text{cm}^{-3}$ can be achieved [31]. It is postulated that this phenomenon occurs due to the formation of acceptor complexes, rather than simple substitution of dopant on oxygen or zinc sites.

The following sections will focus on characteristics of additional acceptor-forming dopants which are pertinent to this study: carbon, iron, and manganese in GaN, and phosphorus, lithium, and antimony in ZnO.

### 1.2.1 Carbon, Iron, and Manganese as Acceptors in GaN

While magnesium remains the only feasible p-type dopant in GaN, numerous attempts have been made to introduce carbon as a shallow acceptor. These were motivated largely by the theoretical predictions that carbon, if substituted on nitrogen site, forms an acceptor level with ionization energy comparable to or lower than that of magnesium [21,33]. However, the same reports indicate that carbon is an amphoteric dopant, producing both donor and acceptor states in GaN. Evidently, relative concentrations and the stability of these states (and therefore, optical and transport properties of the resultant material) are strongly affected by the growth parameters: while some
researchers succeeded in achieving p-type conductivity [34,35], others obtained either insulating or n-type material [36,37].

Although Fe and Mn are also known to form acceptor states in GaN, their 3+/2+ charge transfer levels in GaN are located far from the edge of the valence band [1,38,39]. Therefore, studies of GaN:Fe and GaN:Mn are generally focused on goals other than obtaining a p-type material. Theoretical predictions have been made concerning the possibility of room temperature ferromagnetism in transition metal-doped GaN [40], and a number of researchers report apparent ferromagnetism attributable to Fe and Mn doping [41,42]. However, the success in this area is often limited by the insufficient carrier concentration arising from the deep nature of the acceptor states.

It should be mentioned that there is a fundamental difference between the character of the acceptor states formed by transition metals (TMs) and those created by electronically simpler, hydrogen-like impurities. Unlike the ionization levels of shallow hydrogenic donors and acceptors, which are defined relative to the extremum of the conduction or valence band, respectively, the charge transfer levels of different TMs are aligned with respect to an internal reference level, essentially independent of the host material. This property, called the internal reference rule, was postulated by Langer and Heinrich [43] and has been used to experimentally determine the band offsets in heterojunction structures [38,44].
1.2.2 Lithium, Phosphorus, and Antimony in ZnO

Lithium (Li) has been considered as a potential acceptor dopant in ZnO, since Li$_{Zn}$ (substitutional Li on Zn site) was predicted to form an acceptor level much shallower than those of group V elements – as shallow as 40 meV from the valence band maximum [45-47]. However, because of its small radius, incorporation of Li favors the formation of Li interstitials (Li$_i$), which act as shallow donors and greatly reduce the net hole concentrations. Lee et al. [45] suggested that the formation of compensating interstitials can be suppressed by co-doping with hydrogen to create more soluble Li$_{Zn}$-H$_i$ complex; hydrogen can subsequently be annealed out to activate the Li$_{Zn}$ acceptor.

Despite the encouraging theoretical predictions, the experimental reports on the energetic position of Li$_{Zn}$-acceptor suggest that its acceptor level is actually located somewhat deeper than expected. Several independent studies on Li-doped ZnO claim the detection of a Li-related acceptor with the activation energies ranging from 135 to over 500 meV [48-50]. Furthermore, Zeng et al. report observing two Li-related acceptors, one at about 150 meV and another, appearing at higher Li concentrations, at 250 meV [51].

Attempts to achieve p-type conductivity in ZnO using phosphorus (P) doping also show a discrepancy between theory and experimental results. Theoretical predictions place the P$_O$ acceptor level at about 0.5 eV above the valence band maximum [46,52,53], while experimental evidence suggests a much shallower P-related acceptor state with
the activation energy in the range of 130-180 meV [54,55]. Additionally, it has been demonstrated that phosphorus acts as an amphoteric dopant in ZnO [56]. Photoluminescence (PL) studies show the presence of both phosphorus-related donor and acceptor states, with their ratio (and hence the conductivity type of the films) strongly dependent on growth conditions.

The possibility of p-type doping with other group V elements, such as arsenic (As) and antimony (Sb), have also been suggested. Studies demonstrated that despite the large size mismatch, which in principle should inhibit the substitution of these impurities on the oxygen site, effective p-type doping with hole concentrations up to $10^{20}$ cm$^{-3}$ can be achieved [31]. These findings prompted the first-principles investigation by Limpijumpong et al., who suggested that the role of acceptors in size-mismatched impurity doped ZnO is performed by a complex of the impurity with two zinc vacancies ($X_{Zn}$-2$V_{Zn}$, where X denotes As or Sb), the ionization energy of which is several-fold lower than that of a substitutional configuration (around 160 meV for Sb) and is consistent with the independent experimental observations [57]. Despite the encouraging predictions, however, very few attempts at achieving p-type conductivity in antimony-doped ZnO have been effective. Aoki et al. reported surprisingly high hole concentrations of up to $5 \times 10^{20}$ cm$^{-3}$ in ZnO:Sb films prepared by excimer laser doping [31]. In a separate study, ZnO:Sb grown by molecular beam epitaxy (MBE) revealed p-type conductivity with carrier concentrations up to $10^{18}$ cm$^{-3}$ and thermal activation
energy of about 140 meV, as determined by temperature-dependent photoluminescence experiments [32].

1.3 Role of Minority Carrier Diffusion Length in Bipolar Device Performance

When non-equilibrium carriers are generated in a material due to external excitation in the absence of electric field, they diffuse over a certain distance before undergoing recombination. The average distance traveled in a particular direction between generation and recombination, is characterized by the diffusion length, L. The diffusion length is related to the carrier lifetime, \( \tau \), (i.e., the time between generation and recombination of non-equilibrium carriers) through carrier diffusivity, D:

\[
L = \sqrt{D \tau}
\]  

(1)

Diffusivity, or diffusion coefficient, is determined in turn by the mobility of the carriers, \( \mu \), according to the Einstein relation:

\[
D = \frac{kT}{q} \mu
\]  

(2)

where \( k \) is the Boltzmann’s constant, \( T \) is absolute temperature, and \( q \) is fundamental charge.
The diffusion process is driven by concentration gradients; since external excitation has a much larger impact on the concentration of minority carriers than that of majority ones (because generation density is usually much lower than the majority carrier density), it is the minority carriers that are more susceptible to diffusion.

Diffusion of minority carriers is a process that is fundamental to the operation of bipolar photovoltaic devices, with minority carrier diffusion length being the central parameter defining the device performance. In the presence of a p-n junction or a Schottky barrier, the non-equilibrium minority carriers generated by external excitation (e.g., light incident on a photodiode) within a few diffusion lengths of the space-charge region can be collected by the built-in field and thus contribute to the current flow across the device. The greater the diffusion length of the carriers, the more current can be collected, leading to the higher efficiency of the device. In photodiodes, it is usually only one side of the p-n junction that contributes to photocurrent. If the light is absorbed in the p-region of the junction, the quantum efficiency, $\eta$, can be represented as follows:

$$\eta = (1 - r) \left(1 - \frac{e^{-\omega W}}{1 + aL_n}\right) \tag{3}$$

where $r$ and $a$ are reflection and absorption coefficients, respectively, $W$ is the width of the space-charge region, and $L_n$ is the diffusion length of minority electrons.

Quantum efficiency is directly related to the spectral responsivity, $R$, of a photodiode:
where $I_{\text{ph}}$ is total photocurrent, $P_{\text{op}}$ is optical power incident on the device, $q$ is the fundamental charge, and $E$ is the energy of the incident photons. The relationship between minority carrier diffusion length and the responsivity of Schottky photodiodes has been examined in great detail in ref. [58].

Schottky photodiodes are among the simplest photovoltaic devices, where the non-equilibrium minority carriers generated in the bulk of the semiconductor due to light absorption are collected by the built-in field of the Schottky barrier deposited on the surface of the semiconductor. In order for the carriers to contribute to device current, they have to be generated within a few diffusion lengths of the collector.

For incident energies greater than the bandgap of the absorber material, non-equilibrium electron-hole pairs are generated only in the thin layer next to the surface of incidence, with the maximum depth of $1/a$. This value is on the order of 100 nm in ZnO and GaN [58-60] and is generally much smaller than the thickness of the absorber layer. Considering a front-illuminated configuration (in which the incident light passes through the semitransparent Schottky contact), if $L$ is greater than the generation depth, most of the non-equilibrium minority carriers can diffuse a sufficient distance to be collected by the built-in field of the space-charge region. In this case, the internal quantum efficiency of the device approaches 100%, and the responsivity is independent of the diffusion

\[
R(E) = \frac{I_{\text{ph}}}{P_{\text{op}}} = \frac{q \eta}{E}
\]
length value. Below this threshold, the responsivity decreases with L, provided that the width of the space-charge region is smaller than the generation depth.

If, on the other hand, the energy of incident light is below the bandgap, light penetration depth is large (on the order of several micrometers) [58-60], and a fair portion of the non-equilibrium carriers is generated in the neutral region of the semiconductor due to the ionization of the mid-gap levels. Since only the carriers within a few diffusion lengths of the space-charge region contribute to photocurrent, the responsivity at below-bandgap energies is limited by the diffusion length (unless the diffusion length exceeds the thickness of the absorber layer, in which case the latter is the limiting factor) [58].

1.4 Dissertation Scope and Layout

Based on the information presented in the previous sections, one may conclude that the GaN and ZnO-based technology is currently limited by two fundamental factors: first, the deep nature of acceptor species that impedes the availability of stable and reproducible p-type conductivity and second, the inherently short diffusion length of minority carriers. Earlier studies of Mg-doped GaN demonstrated that the latter parameter can be significantly increased by electron irradiation from a beam of a scanning electron microscope [61] or electron injection carried out by applying an external bias to a solid-state device, p-n junction, or a Schottky barrier [62-64]. This procedure resulted in a several-fold increase in minority electron diffusion length that
persisted for several days in ambient conditions. Temperature-dependent measurements revealed that the activation energy for this process was close the thermal ionization energy of Mg acceptor. Since no such effect was observed in n-GaN, it was attributed to charging of neutral Mg levels, which corresponds to the reduction in the number of recombination sites in the forbidden gap and therefore results in the increase of the carrier lifetime [65]. These findings effectively amount to using the drawback of deep-level acceptors (i.e., their low ionization fraction) to significantly improve and control the transport properties of p-GaN.

The present work demonstrates that the increase of the minority carrier diffusion length and lifetime in response to electron injection is not peculiar to GaN:Mg. The effects of electron irradiation, solid-state electron injection, and the properties of the electron traps responsible for the effect were investigated in a variety of GaN- and ZnO-based materials using EBIC and cathodoluminescence methods as well as photoresponse measurements. The kinetics of the injection-induced changes and the impact of doping levels were also studied. Furthermore, the practical implications of minority carrier diffusion length increase were demonstrated in a ZnO-based p-n junction photodiode.

1.4.1 Dissertation Layout

Chapter 2 covers the general description of techniques used in this study as well as a detailed account of experimental conditions for each experiment. The main
characterization and analysis techniques include electron beam induced current (EBIC) method for determining minority carrier diffusion length, cathodoluminescence (CL) spectroscopy to determine the relative changes in carrier lifetime, spectral photoresponse (PR) measurements to study the influence of electron injection on the device performance, and persistent photoconductivity (PPC) studies to probe carrier trapping.

Chapter 3 contains the description of the results obtained in this work and is organized by individual experiments. The general topics discussed in this chapter are temperature dependence of minority carrier transport properties in ZnO, the effects of electron irradiation on minority carrier diffusion length and lifetime in GaN and ZnO, and the influence of solid-state electron injection on device performance.

Chapter 4 summarizes the results obtained in this study and also discusses the impact of the findings on wide bandgap semiconductor device technology.
2.1.1.1 General Description of Experimental Methods

This section covers the characterization and measurement techniques common to all experiments described in this work. Experiment-specific details, such as measurement conditions and sample characteristics, will be described separately for each experiment in the Section 2.2.

2.1.2 Sample Characterization

Epitaxial GaN and ZnO samples used in this study were prepared by Molecular Beam Epitaxy (MBE), Metal-Organic Chemical Vapor Deposition (MOCVD), or Pulsed Laser Deposition (PLD) methods. The quality of the samples was assessed using X-ray diffraction, atomic force microscopy, and photo- and cathodoluminescence measurements. Concentrations of intentional and unintentional impurities were determined by Secondary Ion Mass Spectroscopy (SIMS).

Resistivity, carrier mobility, and carrier concentrations were determined by performing Hall effect measurements. For this, GaN- and ZnO-based samples were contacted with Ni/Au and Pt/Au, respectively. The contacts were deposited by thermal evaporation and
patterned by lift off. Indium solder and gold wire were used to connect the samples to the Hall effect setup.

![Sample wiring diagram for a hot probe setup.](image)

Figure 1. Sample wiring diagram for a hot probe setup. On the data acquisition (DAQ) board, channel 1 records thermocouple voltage, while channel 0 simultaneously reads the EMF induced between hot and cold probes.

Conductivity type was confirmed through Seebeck coefficient measurements using the Hot Probe technique. Experimental setup for hot probe measurements is shown in Figure 1. The measurement is performed by contacting the sample with a “hot” (heated) probe and a “cold” probe, both of which are connected to a voltmeter (Keithley KUSB-3108 digital data acquisition board was used). The temperature gradient results in the electro-motive force (EMF) between two probes due to the variation in the energy of valence and conduction bands relative to the Fermi energy. The value of the EMF is linearly related to the temperature difference, with the proportionality constant called
Seebeck coefficient. For the electrical connection shown in Figure 1, the positive values of Seebeck coefficient indicate p-type conductivity, while the negative ones correspond to n-type conductivity.

Schottky barriers were prepared by thermal or electron beam evaporation of metals to form rectifying and ohmic contacts. The rectifying characteristics of the barriers and p-n junctions were examined via current-voltage (I-V) measurements.

Figure 2. Instrumentation used for EBIC and cathodoluminescence studies.

2.1.3 Determination of Minority Carrier Diffusion Length

Due to a unique combination of convenience and reliability, Electron Beam Induced Current (EBIC) method is among the most popular techniques for minority carrier diffusion length measurements. It requires comparatively simple sample preparation
and is used in-situ in a scanning electron microscope (SEM). The photograph of the SEM and other laboratory equipment used electron microscopy-related experiments (EBIC and cathodoluminescence spectroscopy) is shown in Figure 2.

2.1.3.1 Overview of the Electron Beam Induced Current method

Figure 3 shows a typical measurement configuration known as planar-collector geometry. The use of this configuration was pioneered by Ioannou, Davidson, and Dimitriadis [66,67]. As a charge collection technique, EBIC method employs a Schottky barrier or a p-n junction to collect the current resulting from the non-equilibrium minority carriers generated by the beam of the SEM.

Figure 3. Experimental setup used for EBIC measurements in planar-collector configuration. The dashed ellipse represents the generation volume; $d$ is the variable distance between electron beam and the Schottky contact, represented by a solid rectangle.
As the beam is moved away from the barrier/junction in a line-scan mode, the current decays as fewer and fewer minority carriers are able to diffuse to the space-charge region.

The mathematical model for EBICurrent was further developed by Boersma et al. [68], who showed that the decay of current, $I_{EBIC}$, can be described by the following expression:

$$ I_{EBIC} = A d^\alpha \exp\left(-\frac{d}{L}\right) $$

(5)

where $A$ is a scaling constant, $d$ is beam-to-junction distance, and $\alpha$ is an exponent related to the surface recombination velocity, $v_s$. The diffusion length is usually extracted by rearranging the terms of Equation 5:

$$ \ln(I d^{-\alpha}) = -\frac{d}{L} + \ln(A) $$

(6)

which yields a linear relationship between $\ln(I d^{-\alpha})$ and $d$ with a slope equal to $-1/L$. This approach is taken to be accurate for $d > 2L$. It should be noted that in ref. [68], the authors analyzed only the two asymptotic cases, namely $v_s = 0$ and $v_s = \infty$, and found that $\alpha = -1/2$ for the former and $-3/2$ for the latter. Later, Chan et al. [69] demonstrated that this approach can be applied to materials with arbitrary surface recombination
velocity by selecting $\alpha$ such that a linear relationship between $\ln(Id^{\alpha})$ and $d$ is obtained. However, even if any value of $\alpha$ is used (such that $-3/2 \leq \alpha \leq -1/2$), the result for the diffusion length changes by less than 20% [63]; this is due to the fact that the exponential term dominating the value of $I_{EBIC}$ is independent of $\alpha$.

2.1.3.2 Minority carrier diffusion length measurements in GaN and ZnO

EBIC measurements were applied to study the temperature dependence of $L$ as well as its response to irradiation by the electrons from the SEM beam or, alternatively, to solid-state electron injection. EBIC data were acquired by scanning the beam of the SEM along a line perpendicular to the edge of a Schottky contact (or to the plane of the p-n junction interface) and recording the exponential decay of current. The recorded data were fitted with Equation 6 using $\alpha = -1/2$. This value corresponds to zero surface recombination velocity which, given the excellent luminescence properties of the samples and a good fit to the experimental results, is a reasonably good approximation.

To examine the influence of electron irradiation on the minority carrier diffusion length, the beam of the SEM was repeatedly moved along the same line, with EBIC data recorded intermittently.

For variable-temperature measurements, the samples were mounted on a hot/cold stage, the temperature of which was set by an external temperature controller (Gatan)
coupled to an *in-situ*, built-in heater and/or by circulating externally cooled nitrogen gas through the body of the stage. At each temperature, EBIC linescans were recorded at a new location in order to avoid the influence of electron irradiation.

EBIC measurements were also used to study the influence of solid-state electron injection on the diffusion length of minority carriers in a p-n junction. Electron injection was carried out by applying forward bias to the p-n junction using a Hewlett-Packard 4145A semiconductor parameter analyzer. Minority carrier diffusion length was measured after each application of bias. The electron beam was turned off during the bias application to exclude the effects of electron irradiation. Note that the duration of an EBIC scan (about 12 seconds) is small compared to the duration of each bias application interval (several hundred seconds); therefore, the influence of irradiation by the beam during a linescan can be assumed negligible.

### 2.1.4 Cathodoluminescence Measurements

Since minority carrier diffusion length is related to the lifetime of non-equilibrium carriers in the conduction band (cf. Equation (1)), cathodoluminescence measurements were used to monitor the changes in lifetime caused by electron irradiation as well as varying sample temperature. Radiative transitions in the near-band-edge (NBE) region of the spectrum of GaN and ZnO were recorded using a Gatan MonoCL cathodoluminescence system integrated with the SEM. The schematic representation of the system is shown
in Figure 4 (see also Figure 2). The emitted radiation was analyzed using a single grating (1200 lines/mm, blazed at 500 nm) and a Hamamatsu photomultiplier (PMT) tube with sensitivity in the 185-850 nm range. This setup allows combining periodic acquisition of CL spectra with continuous excitation of the samples by rastering the beam over the same location. As in EBIC measurements (Section 2.1.3.2), the temperature of the sample was varied in-situ by the external controller (Gatan).

Figure 4. Experimental setup used for in-situ cathodoluminescence measurements.
The effects of electron irradiation on non-equilibrium carrier lifetime were studied by performing CL measurements under concurrent exposure to the electron beam. A small (several square microns) rectangular section of the sample was continuously irradiated by rastering with the SEM beam, while the intensity of the NBE emission was monitored by recording the CL spectra intermittently. This process was repeated at several temperatures to study the variation of rate of lifetime change. At each temperature, the measurements were carried out on a previously unexposed area.

2.1.5 Photoresponse and Persistent Photoconductivity Measurements

Minority carrier diffusion length is one of the key parameters that determines the performance of a p-n junction in photodetector devices. Spectral photoresponse (PR) measurements were carried out in order to confirm that the electron irradiation-induced increase of L translates to an improvement in the collection efficiency of the photogenerated carriers. The photoresponse was induced by the light from a Xe-lamp that was spectrally resolved with a Jobin-Yvon Triax 320 monochromator. Photoresponse was measured using a Stanford Research Systems SR570 amplifier and a Keithley 2000 multimeter in the voltmeter mode. The schematic and the photograph of the experimental setup are shown in Figure 5. Specially written Labview-based software was used to record the spectral photoresponse data.
Figure 5. Photoresponse setup: a) schematic representation of the setup; the photogenerated carriers are collected by the built-in field at the Schottky contact, represented by the gray ellipse. The voltage between the Schottky contact and the ohmic contact (gray rectangle) is recorded as a function of the excitation wavelength by specially written software. b) Instruments and laboratory equipment used for photoresponse and persistent photoconductivity experiments. c) close-up view of the setup showing the illuminated sample (a photodiode array) on the sample stage.

Persistent photoconductivity (PPC) is a phenomenon associated with carrier trapping in wide bandgap semiconductors. PPC was studied by measuring the decay of photocurrent as a function of time after the photo-excitation was turned off. The same setup as that for PR experiments was used, with the excitation wavelength chosen to produce maximum photocurrent (i.e., the peak of the photoresponse spectrum). Thermal activation of PPC was investigated by performing temperature-dependent
measurements. The sample temperature was controlled by a calibrated hotplate coupled with an MMR Technologies temperature indicator/controller.

2.2 Materials and Experimental Conditions

This section contains detailed descriptions of experimental parameters, conditions, and materials used in this work as they pertain to the individual experiments.

2.2.1 Studies of Minority Carrier Transport in ZnO Compounds – Experimental Conditions

Minority carrier transport properties were studied over a range of temperatures in both n-type and p-type ZnO using EBIC method and CL spectroscopy. This section covers the materials and the conditions of experiments carried out on n-ZnO doped with Li and p-ZnO doped with Sb.

2.2.1.1 Temperature Dependence of Minority Carrier Diffusion Length and Lifetime in n-ZnO – Experimental Conditions

The samples under investigation were weakly n-type ZnO substrates with electron concentration of $\sim 10^{14}$ cm$^{-3}$ and mobility of $\sim 150$ cm$^2$/Vs. Secondary Ion Mass Spectroscopy (SIMS) measurements revealed the Li concentration of about $3\times10^{16}$ cm$^{-3}$.
The Schottky contacts for EBIC measurements were deposited on the non-polar a-plane of ZnO crystal by electron beam evaporation of 80 nm-thick Au layer and subsequent lift-off.

The studies of L as a function of temperature were carried out using EBIC method in a planar-collector configuration with a Schottky barrier (Section 2.1.3.1). At each temperature, five measurements were taken by scanning the beam of the SEM along a line perpendicular to the edge of the Schottky contact and recording the exponential decay of current. Each measurement was performed at a location that has not been previously irradiated by the beam. The average and standard deviation of L were determined.

In addition to diffusion length measurements, temperature-dependent changes in carrier lifetime were monitored by CL spectra in the near-band-edge NBE region (350-450 nm). The peak intensity of the NBE luminescence was monitored to assess variation in carrier lifetime with increasing temperature. Both EBIC and CL measurements were performed over the range of temperatures from 25 °C to 125 °C. Accelerating voltage of 20 kV was used, corresponding to the electron penetration depth of 1.5 μm. As for EBIC experiments, several spectra were recorded at every temperature, each at a new location, after which the mean value of the peak intensity was determined, along with the standard deviation.
2.2.1.2 Temperature Dependence of Minority Carrier Diffusion Length in p-Zn doped with Sb – Experimental Conditions

The experiments were performed on ZnO:Sb thin film grown on Si (100) substrate by an electron cyclotron resonance (ECR)-assisted MBE. Hall Effect measurements revealed strong p-type conductivity, with hole concentration of $1.3 \times 10^{17}$ cm$^{-3}$ and mobility of 28.0 cm$^2$/V s at room temperature.

Minority carrier diffusion length was determined using EBIC method. Schottky contacts for EBIC measurements were prepared by lift-off of e-beam evaporated Pt/Au (500Å/1000Å). All experiments were carried out using accelerating voltage of 5 kV. The diffusion length was measured at temperatures varied from 0 °C to 100 °C.

2.2.1.3 Carrier Concentration Dependence of Acceptor Activation Energy in p-ZnO doped with Sb – Experimental Conditions

The experiments were performed on ZnO:Sb layers grown on Si (100) substrates by an electron cyclotron resonance (ECR)-assisted MBE. Hall effect measurements revealed strong p-type conductivity, with hole concentrations up to $1.3 \times 10^{18}$ cm$^{-3}$ and mobility up to 28.0 cm$^2$/V·s at room temperature (Table 1).
Table 1. Room-temperature electronic properties of Sb-doped p-type ZnO films.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Hole Concentration (cm$^{-3}$)</th>
<th>Carrier Mobility (cm$^{2}$/V·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.3 \times 10^{17}$</td>
<td>28.0</td>
</tr>
<tr>
<td>2</td>
<td>$6.0 \times 10^{17}$</td>
<td>25.9</td>
</tr>
<tr>
<td>3</td>
<td>$8.2 \times 10^{17}$</td>
<td>23.3</td>
</tr>
<tr>
<td>4</td>
<td>$1.3 \times 10^{18}$</td>
<td>20.0</td>
</tr>
</tbody>
</table>

The decay of near-band-edge (NBE) cathodoluminescence intensity was monitored as a function of temperature in the range from 25 to 175 °C. Accelerating voltage of 10 kV was used. Note that each measurement was taken in a previously unexposed area to avoid the potential influence of electron irradiation.

2.2.2 Studies of the Effects of Electron Irradiation on Minority Carrier Transport in GaN and ZnO Compounds – Experimental Conditions

The influence of irradiation by the electron beam on the minority carrier diffusion length and lifetime were studied using EBIC and CL, respectively. The measurements were conducted over a range of temperatures in order to determine the activation energy of the irradiation-induced effects. This section contains the description of materials and methods used in the study of a variety of GaN and ZnO compounds.
2.2.2.1 Electron Irradiation-induced Effects in C-doped GaN – Experimental Conditions

Carbon-doped GaN was grown on sapphire substrates by MOCVD. The sample showed insulating characteristics. The thickness of the epitaxial layer was 3.4 μm.

EBIC measurements were performed at room temperature with electron beam accelerating voltage of 10 kV, corresponding to the electron penetration depth into the material of less than 1 μm. Total irradiation duration during EBIC measurements was about 500 s. Because of the highly compensated nature of GaN:C, the carrier diffusion length determined from EBIC most likely represents the effective diffusion length for the non-equilibrium electron-hole pairs.

Cathodoluminescence measurements were conducted over the range of temperatures from 55 °C to 200 °C in the spectral region of 350-390 nm. The total duration of irradiation was about 1000 s.

2.2.2.2 Electron Irradiation-induced Effects in Mn-doped GaN – Experimental Conditions

Doped and undoped GaN samples (1 μm thick) were grown by molecular beam epitaxy on sapphire. Doping resulted in Mn concentrations up to $10^{20}$ cm$^{-3}$ and almost intrinsic layers with resistivity $>10^6$ Ω cm. Platinum contacts (30 nm) were evaporated on the sample surface for EBIC measurements.
The increase of L under electron irradiation was monitored by EBIC at room temperature. The excitation was continued for a total of about 200 seconds. The results of EBIC measurements were correlated with lifetime changes using CL spectroscopy.

Cathodoluminescence measurements were performed in the spectral range of 350-385 nm. The temperature of the sample was varied from –50 °C to 80 °C. At each temperature, the sample was irradiated for a total of ~2000 s, with CL spectra recorded intermittently to monitor irradiation-induced decay peak intensity.

2.2.2.3 Electron Irradiation-induced Effects in Fe-doped (Al)GaN – Experimental Conditions

Highly resistive GaN:Fe and Al$_{0.2}$Ga$_{0.8}$N samples were grown by MBE. The thickness of the epitaxial layers was about 1.5 μm for both samples.

EBIC measurements were conducted at room temperature using the beam accelerating voltage of 10 kV for a total of 500 and 1300 s for GaN:Fe and AlGaN:Fe, respectively. As in GaN:C, it is likely that the carrier diffusion length measured by EBIC represents the diffusion length of non-equilibrium electron-hole pairs.

Temperature-depended CL spectroscopy was used to study the irradiation-induced lifetime changes. The intensity of the NBE transitions in the spectral regions of 350-390 nm for GaN:Fe and 300-340 nm for AlGaN:Fe was monitored as a function of
electron irradiation lasting for a total of about 1200 s for the former and 800 s for the latter.

2.2.2.4 Electron Irradiation-induced Effects in ZnMgO:P – Experimental Conditions

In this work, pulsed-laser deposition was employed for growth of 1.4-μm-thick Zn$_{0.9}$Mg$_{0.1}$O films on (0001) undoped bulk ZnO single crystals. Phosphorus-doped (Zn$_{0.9}$Mg$_{0.1}$)O targets were fabricated using high-purity ZnO (99.9995%) and MgO (99.998%), with P$_2$O$_5$ (99.998%) serving as doping agent [71]. 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 ~2x10$^{18}$ cm$^{-3}$ after annealing. Pt/Au (200/800 Å) layers were deposited on phosphorus-doped Zn$_{0.9}$Mg$_{0.1}$O films by electron beam evaporation and patterned by lift-off with contact diameters ranging from 50 to 375 μm.

EBIC linescan measurements were performed under continuous irradiation at room temperature for a total time of ~1200 s. The accelerating voltage was 12 kV, corresponding to the electron penetration depth of approximately 0.8 μm. CL measurements were performed under the same excitation conditions at temperatures
ranging from 25 to 125 °C. Total irradiation duration during CL experiments was about 2000 s.

2.2.2.5 Electron Irradiation-induced Effects in ZnO:Li – Experimental Conditions

The experiments were carried out on commercially available bulk ZnO (Tokyo Denpa Co.). The samples were weakly n-type, showing electron concentrations of ~ 10^{14} \text{ cm}^{-3} and mobility of ~ 150 \text{ cm}^2/\text{Vs} at room temperature. Secondary Ion Mass Spectroscopy (SIMS) measurements revealed the Li concentration of about 3\times10^{16} \text{ cm}^{-3} (Li is often added to ZnO to increase the resistivity of initially n-type samples). The Schottky contacts for EBIC measurements were deposited on the non-polar a-plane of ZnO crystal by electron beam evaporation of 80 nm-thick Au layer and subsequent lift-off.

Time-dependent cathodoluminescence measurements were conducted in-situ in the SEM under continuous excitation. For temperature-dependent CL measurements, the sample temperature was varied from 25 °C to 125 °C using specially designed hot stage and an external temperature controller (Gatan). The excitation for CL measurements was provided by a 20 kV electron beam, corresponding to electron penetration depth of about 1.5 \mu m. The effects of irradiation were monitored over a time period of about 2500 s.
To correlate the results of CL measurements to the increase in the minority carrier diffusion length, room-temperature EBIC measurements were also carried out. Additionally, persistent photoconductivity measurements were performed at temperatures ranging 34 °C to 93 °C. Excitation wavelength of 360 nm was used.

2.2.2.6 *Electron Irradiation-induced Effects in p-ZnO doped with Sb – Experimental Conditions*

The effects of exposure to the electron beam of the SEM were studied using EBIC on ZnO:Sb thin film grown on Si (100) substrate by an electron cyclotron resonance (ECR)-assisted MBE. Hole concentration of 1.3 × 10^{17} cm^{-3} and mobility of 28.0 cm^{2}/V\cdot s were obtained by performing Hall effect measurements at room temperature.

For EBIC experiments, the accelerating voltage of 5 kV was used. After initial acquisition (24 second scan), the irradiation was continued for a total of about 2000 s, with additional measurements taken intermittently. Further investigation of irradiation-induced effects was performed by varying sample temperature from 0 °C to 100 °C and repeating EBIC scans at a different location while continuously irradiating the location with electron beam.

2.2.2.7 *Carrier Concentration Dependence for the Electron Irradiation Effects in p-GaN – Experimental Conditions*
Experiments were conducted on four GaN commercially available 3-5 \( \mu \)m thick epitaxial films (TDI, Inc.) doped with different concentrations of Mg. The net hole concentrations were determined by Hall effect measurements and are \( 2 \times 10^{16} \), \( 9 \times 10^{16} \), \( 3 \times 10^{18} \), and \( 7 \times 10^{18} \) cm\(^{-3}\). The effects of electron irradiation were studied by CL with accelerating voltage of 20 kV. The decay of near-band-edge (NBE) luminescence intensity was monitored as a function of duration of irradiation by the electron beam. The rates of NBE intensity decay were measured at different temperatures ranging from 25 to 125 °C. At each temperature, the measurements were performed on a previously unexposed location.

2.2.3 Effects of Solid State Electron Injection on the Performance of ZnO Homojunction Diodes – Experimental Conditions

ZnO p-n junctions were grown by molecular-beam epitaxy (MBE). A ZnO:Sb layer was grown on \( p \)-Si substrate and was followed by a ZnO:Ga layer to form the p-n junction. Sb-doped ZnO layer had a hole concentration, mobility, and resistivity of \( 1 \times 10^{16} \) cm\(^{-3}\), \( 10 \) cm\(^2\) V\(^{-1}\)s\(^{-1}\), and \( 6 \) \( \Omega \cdot \) cm, respectively, while the Ga-doped layer had an electron concentration, mobility, and resistivity of \( 1 \times 10^{18} \) cm\(^{-3}\), \( 6 \) cm\(^2\) V\(^{-1}\)s\(^{-1}\), 0.9 \( \Omega \cdot \) cm, respectively. The schematic of the device is shown in the inset of Figure 6.
Figure 6. Cross-sectional view of the ZnO photodiode. Shaded rectangles represent Ti/Al contacts.

All experiments were carried out at room temperature. Solid-state electron injection into ZnO:Sb was achieved by applying forward bias (~ 5-10 V) to the p-n junction using a Hewlett-Packard 4145A semiconductor parameter analyzer. Forward bias resulted in currents ranging from 7 to 48 mA applied for the duration of about 1500 seconds, in 300 or 600 second increments, with total injected charge of approximately 25 C.

EBIC measurements and forward bias electron injection were carried out in-situ in the SEM using vacuum feed-through connectors incorporated in the microscope chamber. To expose the p-n junction, the wafer containing the devices was cleaved perpendicular to the plane of growth. Accelerating voltage of 30 kV was used, corresponding to electron penetration depth of about 3 μm. Following initial determination of $L$ from EBIC line-scan measurement, additional measurements of diffusion length were performed after each interval of forward bias electron injection. To avoid influence of electron irradiation on diffusion length, electron beam was turned off while external bias was applied. Note that although under EBIC line-scan measurement the sample is subjected
to a small amount of electron irradiation, the duration of the scan (~12 seconds) is negligible compared to about 1000 s necessary to induce a significant increase of $L$ at room temperature (cf. Chapter 3). To demonstrate the relationship between the minority carrier diffusion length and device performance, forward bias application was combined with periodic spectral photoresponse measurements. After each interval of injection, photocurrent was measured as a function of excitation wavelength (230-375 nm), as described in Section 2.1.5.
CHAPTER 3 - RESULTS AND DISCUSSION

3.1 Studies of Temperature Dependence of Minority Carrier Transport in ZnO Compounds

Because of its intrinsic thermal stability, ZnO is a good candidate for high-temperature optoelectronic devices. Therefore, the insight into the temperature dependence of minority carrier diffusion length and lifetime is of great value. However, the subject of the temperature dependence of minority carrier transport properties in ZnO has not yet been adequately addressed in the literature. This section presents the results obtained from variable-temperature studies of diffusion length and non-equilibrium carrier lifetime performed on bulk, n-type ZnO [72] and p-type ZnO doped with antimony [73, 74].

3.1.1 Temperature Dependence of Minority Carrier Diffusion Length and Lifetime in n-ZnO

Temperature-dependent EBIC measurements (Section 2.2.1.1) demonstrated that the diffusion length of minority holes in n-ZnO increases with increasing temperature, $T$. The results of the measurements are summarized in Table 1.
Table 2. Temperature dependence of minority carrier diffusion length and cathodoluminescence intensity of the near-band-edge peak in n-ZnO.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Diffusion Length (μm)</th>
<th>CL Intensity (10^3 counts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.438 ± 0.022</td>
<td>72.1 ± 3.7</td>
</tr>
<tr>
<td>50</td>
<td>0.472 ± 0.060</td>
<td>54.4 ± 3.8</td>
</tr>
<tr>
<td>75</td>
<td>0.493 ± 0.028</td>
<td>49.2 ± 2.4</td>
</tr>
<tr>
<td>100</td>
<td>0.520 ± 0.074</td>
<td>44.6 ± 4.7</td>
</tr>
<tr>
<td>125</td>
<td>0.547 ± 0.086</td>
<td>38.5 ± 6.8</td>
</tr>
</tbody>
</table>

\[ EA \text{ (eV)} \quad 0.045 ± 0.002 \quad 0.058 ± 0.007 \]

The increase of \( L \) with \( T \) in semiconductors is a common phenomenon. Similar trends were previously confirmed in GaAs [75] and later in GaN epitaxial layers [76]. In all cases this increase was exponential with temperature and was modeled with the following expression [75]:

\[
L = L_0 \exp\left(-\frac{E_A}{2kT}\right)
\]  

(7)

where \( L_0 \) is a scaling factor, \( E_A \) is activation energy, and \( k \) is Boltzmann constant. Figure 7 shows the experimental results for n-ZnO obtained in this work and the fit using Equation 7, which yields activation energy of 45 ± 2 meV. The latter parameter represents carrier delocalization energy, since it determines the increase of the diffusion
length due to reduction of recombination efficiency (see discussion below) [75]. The smaller is the activation energy, the more efficient is the thermally activated escape of captured carriers at any fixed temperature.

Figure 7. Experimental dependence of minority carrier diffusion length on temperature in n-ZnO (open circles). The line shows the fit (Equation 7) with activation energy of 45 ± 2 meV. (After reference [72]).

The temperature-induced increase of $L$ may be attributable to growing lifetime of non-equilibrium minority holes in the valence band, as illustrated by Equation 1. The role of increasing carrier lifetime is supported by the results of CL measurements (Section 2.2.1.1), which are presented in Figure 8. The inset of Figure 8 shows a cathodoluminescence spectrum in the vicinity of the NBE transition at 385 nm (3.22 eV).
It was observed that the peak intensity, $I$, of the NBE luminescence decays systematically with increasing temperature, providing direct evidence that the number of recombination events decreases. The decay proceeds exponentially according to the equation below [77]:

$$I = \frac{A}{(1 + B \exp(-\frac{E_A}{kT}))}$$  \hspace{1cm} (8)
where $A$ and $B$ are scaling factors, and $E_A$ is the activation energy, similar in nature to that in Equation 7. Based on the fit shown in Figure 8, the activation energy was determined to be $58 \pm 7$ meV. This energy is in reasonable agreement with that obtained by variable-temperature EBIC measurements, which suggests that the same underlying process is responsible for both the increase in the diffusion length and the CL intensity decay. This process is outlined below:

The increase in minority hole lifetime in the valence band is likely associated with a smaller recombination capture cross-section for this carrier at elevated temperatures. In GaAs, for example, detailed analysis for temperature dependence of capture cross-section indicates an order of magnitude decrease of recombination efficiency, measured in terms of an “effective capture radius”, in the temperature range from 100 to 300 K [75]. Non-equilibrium electron-hole pairs are generated by the beam of the SEM and subsequently annihilate by recombining with each other. Since the hole capture cross-section is inversely proportional to temperature [75,78], the frequency of the recombination events (and, hence, the CL intensity) decreases as the temperature is raised. This means that non-equilibrium holes exist in the valence band for longer periods of time and, consequently, diffuse longer distances before undergoing recombination.

Note that carrier diffusivity, $D$, is also a temperature-dependent quantity and, therefore, can affect the diffusion length. On the other hand, it has been demonstrated for n-ZnO
that the mobility, $\mu$, of majority carriers decreases in the temperature range of our experiments by about a factor of 2 [79]. Assuming that the mobility of the minority carriers exhibits the same behavior [76] and using the Einstein relation (Equation 2), it can be deduced from Equation 1 that the increase of the diffusion length is dominated by the growing lifetime of minority holes. From the Einstein relation, the above-referenced difference in mobility translates to about a 30% decrease in diffusivity at 125 °C as compared to 25 °C. Based on a 30% difference in diffusivity and using experimentally obtained values of diffusion length, we conclude that the lifetime of minority holes at 125 °C is nearly 2.5 times greater than at room temperature.

3.1.2 Temperature Dependence of Minority Carrier Diffusion Length in p-Zn doped with Sb

EBIC measurements performed on p-type ZnO:Sb samples (Section 2.2.1.2) also revealed that the value of $L$ increases exponentially as the temperature is raised, as is shown in Figure 9. This behavior is consistent with that observed in n-type ZnO (Section 3.1.1) and also can be described using Equation 7 [75].

Similar to n-ZnO, $E_A$ in Equation 7 likely represents carrier de-localization energy and determines the increase of the diffusion length due to the reduction in recombination efficiency [75]. Earlier photo- and cathodoluminescence studies on the similar samples had shown that the recombination route of non-equilibrium carriers involves transitions
to a deep, neutral acceptor level ($e, A^0$) [32,74]. An increase in the temperature of the sample leads to a higher ionization fraction of the acceptors, reducing the concentration of $A^0$ and thus inhibiting the recombination rate. Lower recombination rate translates directly to greater lifetime of minority electrons in the conduction band (cf. ref.[74]) and, consequently, to greater diffusion length, in agreement with Equation 1.

Figure 9. Diffusion length of minority electrons as a function of temperature in ZnO:Sb (open circles) and the fit with Equation 7 (solid line). Inset: Arrhenius plot of the same data yielding activation energy of 184 ± 10 meV. (After reference [73]).

From the Arrhenius plot shown in the inset of Figure 9, the value of $E_A$ was determined to be 184 ± 10 meV and is consistent with the reported activation energy for Sb-related
acceptor complex. This complex, $\text{Sb}_{\text{Zn}}\text{-2V}_{\text{Zn}}$, has been suggested to be the dominant acceptor species in Sb-doped ZnO [57].

3.1.3 Carrier Concentration Dependence of Acceptor Activation Energy in p-ZnO doped with Sb

The investigation of the luminescence properties of Sb-doped ZnO was started with the acquisition of room-temperature cathodoluminescence spectra shown in Figure 10. The inset of Figure 10 reveals that the CL spectra of all three samples are dominated by the NBE band, which generally contains the band-to-band transition as well as the transition from the conduction band to a deep, neutral acceptor level ($e, A^0$) [80,81]. Since acceptor levels form a band in the forbidden gap, the red shift of the NBE peak with increasing carrier concentration (i.e., higher doping levels) is consistent with the ($e, A^0$) emission and may indicate the broadening of the Sb-related acceptor band [82,83]. Another observation that can be made from Figure 10 is the systematic decay in intensity of the NBE luminescence with increasing doping level. This decrease may be attributed to the reduction in radiative recombination rates as more disorder is introduced into the ZnO lattice by large-radius Sb atoms. The increasing trend in the values of the full width at half-maximum (FWHM) of the NBE spectra provide further evidence for the impact of the size-mismatched dopant - FWHM values were determined to be about 16.1, 19.4, 23.5, and 21.7 nm (corresponding to 136, 163, 196, and 178 meV) for samples 1, 2, 3, and 4, respectively. Note that while FWHM of NBE
transitions in CL spectra tends to be greater than the width of photoluminescence (PL) peaks, the above values are comparable to those obtained for \((e, A^0)\) transitions in CL spectra of other ZnO and GaN materials [80,84,85].

Figure 10. NBE cathodoluminescence spectra of ZnO:Sb samples 1-4 taken at room temperature. The peaks are at 382, 384, 385, and 387 nm, respectively. Inset: broad-range CL spectra of the same samples. (After reference [74]).

The intensity of NBE luminescence was also monitored as a function of temperature. It was observed that the intensity decays with sample temperature, \(T\), in agreement with Equation 8. From this equation, it can be deduced that the inverse intensity, \(1/I\), should exhibit an exponential dependence on \(1/kT\). This is shown in the inset of Figure 11 on
the example of sample 1. Note that the intensity in this and subsequent figures was normalized with respect to its room-temperature value for each of the samples.

Figure 11. Arrhenius plot showing the decay of normalized NBE luminescence intensity with increasing temperature for ZnO:Sb sample 1 (open squares), sample 2 (open circles), sample 3 (open diamonds), and sample 4 (open triangles). The linear fits (solid lines) yielded activation energies of 212 ± 28, 175 ± 20, 158 ± 22 and 135 ± 15 meV for samples 1, 2, 3, and 4, respectively. The data were vertically offset for clarity. Inset: exponential decrease of CL intensity for sample 1 (open squares) and the fit (solid line). (After reference [74]).

The activation energies, $E_A$, were obtained from the slopes of Arrhenius plot shown in Figure 11. In case of a $(e, A^0)$ transition, $E_A$ is related to the ionization energy of
acceptors: the lower the value of the activation energy, the more likely is the ionization of the acceptor by a valence band electron ($A^0 + e \rightarrow A^-$); since an ionized level does not participate in recombination via the ($e, A^0$) route, the rate of these transitions (i.e., the intensity of the luminescence) decreases with $E_A$ at any given temperature. Conversely, for a constant $E_A$, the intensity decays with increasing temperature as more and more acceptors are ionized.

It is apparent from Figure 11 that the activation energy shows a systematic dependence on the carrier concentration. The values of $E_A$ are $212 \pm 28$, $175 \pm 20$, $158 \pm 22$, and $135 \pm 15$ meV for samples 1, 2, 3, and 4, respectively. These values are in reasonable agreement with the ionization energy of a $\text{Sb}_{2n-2}\text{V}_{2n}$ complex predicted by Limpijumnong et al. to have a value of about 160 meV [57]. Furthermore, the decay of activation energy with carrier density, $p$, follows a common pattern observed previously in other semiconductors [83, 86, 87] and is described by an equation of the type:

$$E_A(N_A^-) = E_A(0) - \alpha(N_A^-)^{1/3}$$  \hspace{1cm} (9)

where $N_A^-$ is the concentration of ionized acceptors, $E_A(0)$ is the ionization energy at very low doping levels, and $\alpha$ is a constant accounting for geometrical factors as well as for the properties of the material. Figure 12 demonstrates that Equation 9 provides a reasonable fit to the experimentally obtained activation energies under the approximation that $N_A^- - N_D^+ = p$, where $N_D^+$ is the density of ionized shallow donors.
(due to compensation, the p-type conductivity is determined by the difference between the concentrations of ionized donors and acceptors). The value of $\alpha$ was found to be equal to $6.4 \times 10^{-7}$, which is comparable to that in other semiconductors [83,86]. $N_d^-$ can be estimated from the electron concentration in undoped, n-type ZnO samples grown by the same method and is about $5 \times 10^{18}$ cm$^{-3}$ [32]. We note that this is a rough estimate and does not account for the earlier observation that background donor concentration in Sb-doped samples may be different from that in undoped ZnO films due to the creation of Zn vacancies induced by Sb doping. The concentration of Zn vacancies was shown to depend on Sb doping level [88], which would in turn lead to the variations in shallow donor density among the samples under investigation.

Figure 12. Decrease of activation energy as a function of ionized acceptor concentration. (After reference [74]).
It should be noted that earlier PL measurements performed on sample 4 showed a consistent activation energy of 140 meV [88].

The phenomenon of variation of the dopant activation energy with carrier concentration in semiconductors has been attributed to a number of causes. Among these are the formation of the band-tail states that extend into the forbidden gap, the broadening of the acceptor band in the gap, and the reduction of binding energy due to Coulomb interaction between the holes in the valence band and the ionized acceptor states [82,83,87].

3.2 Studies of the Effects of Electron Irradiation on Minority Carrier Transport in GaN and ZnO Compounds

Extensive studies aimed at achieving p-type conductivity in GaN and ZnO reveal that most potential acceptors tend to form acceptor levels far from the valence band maximum [24,89]. Since the ionization fraction of such acceptors is low (due to their high activation energy), there is a large concentration of neutral states that may act as traps for non-equilibrium electrons. Deep carrier traps have pronounced implications on minority carrier transport and often give rise to such undesirable phenomena as radiation-induced optical metastability, persistent photoconductivity, and optical quenching of photocurrent [90-92]. On the other hand, it has been demonstrated that capture of minority carriers by deep metastable traps is associated with the increase of
minority carrier diffusion length and lifetime [61,63,65]. Moreover, in GaN photodiodes, this increase was shown to result in a significant (several-fold) improvement of photoresponse in agreement with Eq. (3) [62].

The effects of electron trapping on the diffusion length and lifetime of minority carriers can be probed by subjecting the material of interest to the excitation by the electron beam of the scanning electron microscope or, alternatively, by applying forward bias (solid-state electron injection) to a p-n junction or a Schottky barrier. This section discusses the effects of electron irradiation on the minority carrier diffusion length and lifetime in a number of GaN- and ZnO-based materials.

### 3.2.1 Electron Irradiation-induced Effects in C-doped GaN

GaN:C was exposed to the SEM beam for several hundred seconds (Figure 13), while carrier diffusion length was measured periodically using EBIC technique. Figure 13 shows that irradiation by the electron beam clearly results in a significant increase of the carrier diffusion length, and that this increase is linear with respect to the duration of electron irradiation (t). It should be noted that this long-lasting (days) increase has been previously observed in a number of GaN-based materials [93-95].
Figure 13. Dependence of electronic carrier diffusion length on duration of electron beam irradiation at room temperature in GaN:C. (After reference [85]).

The increase of the electronic carrier diffusion length can occur due to either increased diffusivity or due to greater lifetime of the carriers in the conduction or valence band. Since it has been reported that the mobility (and hence the diffusivity) of carriers is not affected by electron injection [96], this effect of electron irradiation has to be attributed to the increase of carrier lifetime.

Cathodoluminescence measurements were performed to demonstrate that the increase of $L$ is, indeed, associated with growing lifetime. a shows a series of near-band-edge cathodoluminescence spectra for GaN:C collected at fixed time intervals under continuous excitation by the electron beam. The spectra feature a relatively broad band, which includes the band-to-band and the conduction band-to-neutral acceptor
transitions [21,33]. It is clear from Figure 14a that the rate with which these transitions occur decreases steadily as a consequence of irradiation by the electron beam. A 1-2 nm red shift of CL spectra (compare spectra 1 and 4) may be related to the continuous electron trapping on the neutral acceptors, which create a band in the forbidden gap (see discussion below).

Since luminescence intensity is inversely proportional to $\tau$, the systematic decay of intensity indicates that irradiation by the electron beam increases the lifetime of non-equilibrium electronic carriers [95]. Carrier diffusion length is proportional to the square root of lifetime ($L=(D\tau)^{1/2}$); the diffusion length, in turn, was shown by EBIC measurements to be directly proportional to duration of irradiation. Therefore, lifetime can be expected to increase quadratically with $t$, as is manifested experimentally by the decay of intensity of the NBE luminescence. The inset of Figure 14a shows that there exists a linear dependence between $I^{-1/2}$, which is proportional to the diffusion length of the non-equilibrium carriers, and the duration of irradiation. In Figure 14a (and also in Figure 14b below) intensity was normalized with respect to its initial value.

The decay of intensity with duration of irradiation by the electron beam can also be characterized by the rate, $R$, of the linear relationship between $t^{1/2}$ and $t$, as shown in Figure 14b. This figure presents the results of variable-temperature cathodoluminescence measurements carried out on GaN:C and reveals that irradiation-induced decay of intensity slows down with increasing temperature. This indicates that
there exists a competing, thermally activated process that opposes the irradiation-induced increase of electronic carrier lifetime and diffusion length. The dependence of $R$ on temperature can be represented as follows:

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

(10)

where $R_0$ is a scaling constant, and $\Delta E_A$ is the activation energy. The factor of $2kT$ accounts for both electron excitation-induced effect on $R$ ($\propto \exp(\Delta E_A/kT)$) and its temperature dependence ($\propto \exp(-\Delta E_A/2kT)$) [95]. It is assumed that activation energies for both contributions are similar. Applying Equation 10 to the values of $R$ obtained by temperature-dependent CL measurements yielded activation energy of about 210 meV (see Arrhenius plot in the inset of Figure 14b). This value is in good agreement with both theoretically and experimentally obtained estimates for the ionization energy of a C$_N$ (carbon on nitrogen site) acceptor state [18,21,97,98]. This fact, combined with previous findings showing that transport properties of undoped GaN are not affected by electron irradiation [99], suggests that carbon acceptor level plays a crucial role in the electron irradiation effect.
Figure 14. a) Cathodoluminescence spectra for GaN:C taken at 55 °C after 0, 273, 536, and 779 of continuous irradiation, with 1 corresponding to the pre-irradiation spectrum and 4 to 779 s of electron irradiation. Inset: Experimentally obtained values of $I^{-1/2}$ (open circles) versus duration of irradiation; the solid line represents linear fit. Intensity was normalized with respect to its pre-irradiation value. b) Variable-temperature dependence of inverse square root of normalized intensity on duration of electron irradiation for GaN:C and the linear fit with the rate R. Inset: Arrhenius plot of R as a function of temperature, yielding $\Delta E_A$ of about 210 meV.
The impact of C acceptor states is not surprising, taking into account the abundance of neutral carbon atoms in the material. Due to the high ionization energy, only a small fraction of carbon impurities is ionized at room temperature. As a consequence, the resultant material contains high concentrations of non-ionized acceptor species, which are capable of trapping non-equilibrium electrons generated by the electron beam of the SEM.

Figure 15. Schematic representation of electron irradiation-induced processes. Electron beam generates non-equilibrium electron-hole pairs (Ia). Non-equilibrium carriers recombine either via the band-to-band transition (Ib) or through unoccupied (non-ionized) acceptor states (Ic). However, if a non-equilibrium electron is trapped by the acceptor level, recombination cannot proceed (II), leading to increased lifetime of non-equilibrium carriers. Release of the trapped electron with an activation energy $\Delta E_A$ restores the original recombination pathway (III), resulting in a slower rate of lifetime increase at elevated temperatures.
Generally, non-equilibrium electrons recombine with holes in the valence band by undergoing either a band-to-band transition or a transition that involves a neutral acceptor level (Figure 15, Ib and Ic). However, if an electron is trapped by one of the acceptor levels, the latter can no longer provide a recombination pathway (Figure 15, II). As excitation proceeds, more of these traps become occupied by electrons, decreasing the rate with which recombination occurs. Lower recombination rate translates directly to greater lifetime of non-equilibrium carriers in the band and, consequently, greater diffusion length.

An acceptor level can again become available for recombination if the trapped electron gains sufficient energy to overcome the energy barrier and escape to the valence band (Figure 15, III). This energy barrier, in fact, prevents an immediate hole capture by the acceptor level (trapped electron transition to the valence band) and ensures a long-lasting nature of the effect of electron irradiation. As the temperature increases, the transitions in Figure 15, III occur more frequently, re-establishing the original recombination pathway and thus contributing to the slower rate of lifetime increase, as demonstrated in Figure 14b. Furthermore, it has been reported that the energy necessary for an electron to be emitted from a deep acceptor state is comparable to its ionization energy [100]. This suggests that the activation energy obtained by us from the temperature-dependent CL measurements is, indeed, related to a deep $C_N$-acceptor level.
3.2.2 Electron Irradiation-induced Effects in Mn-doped GaN

Figure 16 shows the decay of EBIC signal in Mn-doped GaN as the SEM beam is moved away from the Schottky contact (Section 2.1.3.2). Curves 1-3 demonstrate the increase of the diffusion length after several hundred seconds of electron irradiation. As displayed in the inset of Figure 16, the increase of $L$ as a function of $t$ is linear. Note that EBIC measurements carried out on undoped GaN and GaN:Mn layers codoped with Si did not reveal any noticeable increase of $L$ with $t$ suggesting that both the presence of Mn and the position of the Fermi level (changes with Si codoping) are important for the observed behavior.

![Figure 16. Room temperature EBIC signal decay for a GaN:Mn sample as a function of distance from the Schottky barrier. Curve 1 corresponds to the initial line-scan, curves 2 and 3 correspond to $t$ of 60 and 210 s, respectively. Inset: $L$ vs $t$ experimental dependence and the linear fit. (After reference [93]).](image-url)
Figure 17 shows the room temperature CL spectra for the Mn-doped GaN layer. The full-range CL spectrum is shown in the right inset. Besides a relatively narrow band-to-band peak, it features a broad luminescence band, which remains unaffected by electron irradiation and is attributed to defect-induced recombination across the band gap. In contrast, the intensity of the band-to-band CL, located at about 367 nm, exhibits a continuous decay with $t$ (left inset of Figure 17). The minority carrier diffusion length and the band-to-band CL intensity are related via the non-equilibrium minority carrier lifetime $\tau$. $L$ increases linearly with $t$, as seen in Figure 16, and its dependence on the
minority carrier lifetime is given by Equation 1, with carrier diffusivity $D$ unaffected by electron irradiation [96]. According to Equation 1, the inverse CL intensity, which is directly proportional to the lifetime of carriers in the band, (larger is the value of $\tau$, the longer is the none-equilibrium carrier stay in the band, and, as a result, the lower is the rate of radiative recombination), should depend quadratically on $t$. This is, indeed, observed in Figure 18, where the square root of the inverse normalized (with respect to its initial maximum value) intensity, $I^{-1/2}$, is plotted versus $t$.

Figure 18. Variable temperature dependence for the square root of inverse normalized intensity on the time of electron irradiation. 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. (After reference [93]).
It has been recently shown that Mn forms a deep neutral acceptor level (Mn$^{3+}$) in GaN, with only a very small number of acceptors being ionized to Mn$^{2+}$ [101]. Si co-doping results in a shift of the Fermi level position towards the conduction band and almost complete ionization of Mn acceptors. Since no dependence of the band-to-band CL or $L$ on electron that irradiation was found in GaN:Mn:Si samples or undoped GaN layers, it can be concluded the effects observed in GaN:Mn are caused by the presence of neutral Mn acceptors in the initially non-irradiated samples.

Temperature-dependent CL measurements in the range between −50°C and 80°C were carried out to further illuminate the possible physical origin of the experimental findings. Figure 18 shows the dependence of $I^{1/2}$ on $t$ at different temperatures. The slopes of the linear dependencies in Figure 18 are the rates $R$ for CL decrease. Evidently, an increase in temperature results in a decrease of $R$, suggesting existence of thermally activated process, which counteracts the effect of electron irradiation, thereby leading to a decrease of $t$. The activation energy of 360 meV for this process was calculated using Equation 10 from the Arrhenius plot shown in the inset of Figure 18. The model summarized in Figure 19 follows the defect molecule picture for Mn$^{3+}$ in GaN [1]. Initially, Mn impurities are present in the neutral acceptor state Mn$^{3+}$, characterized by two filled $e$ orbitals and three $t_2$ orbitals [left side of Figure 19a.] While electrons occupy two of the latter orbitals, the third one is empty. Recombination of non-equilibrium electron-hole pairs created by SEM electron beam causes the band-to-band cathodoluminescence. In addition, electron beam injection can lead either to electron
transfer from e to an empty t2 orbital or, competitively, to direct ionization of the Mn$^{3+}$ state to Mn$^{2+}$ [process (1) in Figure 19a].

Figure 19. Possible mechanism for the observed electron irradiation-induced effects. 1) Ionization of Mn$^{3+}$ to Mn$^{2+}$ due to electron beam excitation and a consequent electron transition to a vacant t2 orbital [dashed arrow in (a), left]. 2) Band-to-impurity recombination through a vacant Mn$^{3+}$ e orbital [(a), right]. 3) Thermally activated hole emission (electron capture) from the e orbital of the Mn$^{3+}$* state to the valence band. This leads to ionization of Mn$^{3+}$* to Mn$^{2+}$ and, thus, to a suppression of (2).

In the first case, electron transfer causes generation of the energetically higher Mn$^{3+}$* state (one electron on e orbital and three electrons on t2 orbitals), shown on the right side of Figure 19a. This lead to activation of a non-radiative recombination channel (2) via a vacant e orbital and therefore to a decrease in the intensity of the band-to-band cathodoluminescence, as is seen in Figure 17. Here, we have to assume that the transition (2) in Figure 19a dominates over the band-to-band transition after the electron
irradiation is started, while a recombination through the \( t2 \) orbitals of the \( \text{Mn}^{3+} \) ground state [cf. Figure 19a, left] is not allowed. Although the exact reason for this is unclear at the moment, the experimental evidence exists. Note that the process of \( \text{Mn}^{3+} \) ionization to \( \text{Mn}^{2+} \) creates a hole in the valence band and, thus, would not lead to the observed increase of the minority carrier diffusion length. This is because the non-equilibrium electrons of the conduction band, induced by electron beam irradiation, would then recombine with the non-equilibrium holes available in the valence band, leading to a decrease of the non-equilibrium carrier lifetime and \( L \).

Because the Fermi level in GaN:Mn samples is close to the middle of the band gap, the carrier diffusion length determined from EBIC most likely represents the effective diffusion length for the non-equilibrium electron-hole pairs. Therefore, the longer the non-equilibrium carrier lifetime, the longer is \( L \) (cf. Figure 16), and the smaller is the number of recombination events including those through the band-to-band transition. As a result, the band-to-band CL continues to decay with increasing duration of electron irradiation. Two different mechanisms can cause a reactivation of the band-to-band channel when the temperature is increased. A thermally activated charge neutral transition of a metastable \( \text{Mn}^{3+*} \) to a \( \text{Mn}^{3+} \) state [Figure 19b] establishes the initial situation and quenches the electron irradiation effects. Up to now, such a transition has not been reported in the literature. On the other hand, a thermally activated hole emission from an \( e \) orbital of the \( \text{Mn}^{3+*} \) state to the valence band is also likely to occur [process (3) in Figure 19a, right]. According to Ref. [101], this process exhibits an
activation energy of 300 meV. The temperature-dependent rate of CL decrease observed in this work shows the activation energy $E_A=360$ meV. The relatively large difference between the above activation energies indicates that a charge-neutral thermally activated transition from Mn$^{3+*}$ to Mn$^{3+}$ may be the preferred pathway.

Figure 20. Dependence of electronic carrier diffusion length on duration of electron beam irradiation at room temperature in GaN:Fe and Al$_{0.2}$Ga$_{0.8}$N:Fe. (After reference [85]).

3.2.3 Electron Irradiation-induced Effects in Fe-doped (Al)GaN

EBIC measurements on Fe-doped GaN and Al$_{0.2}$Ga$_{0.8}$N were performed at room temperature in order to confirm that electron irradiation results in an increase of minority carrier diffusion length. The results of these measurements are shown in Figure 20.
Figure 21. Decay of NBE cathodoluminescence intensity in GaN:Fe at room temperature. The spectra were taken at 0, 524, 810, 1073, and 1362 s of electron irradiation, with 1 corresponding to initial spectrum and 5 to the spectrum after 1362 s of continuous irradiation. Inset: CL spectra of the NBE region of Al\(_{0.2}\)Ga\(_{0.8}\)N:Fe under continuous electron irradiation (0, 247, 392, 587, and 761 s of irradiation), with 1 corresponding to pre-irradiation spectrum and 5 to the spectrum after 761 s of continuous irradiation. (After reference [85]).

The characteristic decay of NBE luminescence intensity was observed in both compounds (Figure 21 and its inset for GaN:Fe and Al\(_{0.2}\)Ga\(_{0.8}\)N:Fe, respectively), indicating that the increase in the diffusion length is associated with growing lifetime of electronic carriers. Similar to GaN:C and GaN:Mn, the intensity decayed quadratically with duration of excitation, and variable temperature CL studies confirmed that \(R\) decreases with temperature (Figure 22), indicating a thermally activated process that counteracts the effects of electron irradiation. These temperature-dependent
measurements allowed to estimate an average activation energy of about 230 meV for GaN:Fe (Figure 22, top) and 360 meV for AlGaN:Fe (Figure 22 bottom).

Figure 22. Normalized peak $I^{1/2}$ versus duration of irradiation at different temperatures for GaN:Fe (top) and Al$_{0.2}$Ga$_{0.8}$N:Fe (bottom). Note that graphs at some temperatures are not shown for clarity. Insets: temperature dependence of the rate of $I^{1/2}$ and the fit, yielding $E_A$ of $\sim$230 meV for GaN:Fe, and $\sim$360 meV for AlGaN:Fe.
Taking into account the similarities in the response to the electron irradiation of all studied compounds, it stands to reason that the same process (i.e., electron trapping on deep acceptor levels) is the cause of this behavior. However, if this were indeed the case, then, per above discussion, one would expect that the experimentally obtained activation energies for GaN:Fe and Al\textsubscript{0.2}Ga\textsubscript{0.8}N:Fe are comparable to the ionization energy of Fe acceptor in the corresponding material.

The literature reports on the ionization energy of the Fe acceptor in GaN are contradictory. Heitz \textit{et al.} found the Fe\textsuperscript{3+/2+} charge transfer level to be located about 3.2 eV above the valence band maximum [39], while other authors place it at about 2.5 eV [38]. Regardless of the true value, it is clear that this level is located far from the valence band edge and that the activation energy of electron irradiation-induced phenomena is roughly 10% of the ionization energy of the Fe acceptor ground state. However, it is not unlikely that irradiation by the electron beam contributes to the formation of an excited state of Fe acceptor. In a photoluminescence excitation (PLE) study of the electronic states of Fe\textsuperscript{3+} in GaN, Heitz \textit{et al.} observed the formation of a relatively shallow electron-hole complex (Fe\textsuperscript{3+}, e, h) [39], which is essentially an excited state of Fe\textsuperscript{3+}. Such states are formed when the ionization does not proceed to completion and the emitted hole remains electrostatically attracted to the transition metal (TM) center. In GaN:Fe, this complex was shown to have a binding energy of (280 ± 100) meV, a value that is in good agreement with our results.
Note that these findings represent a general trend in the binding energies of TM-hole complexes. Review of the literature reveals that in a wide range of III-V [102] as well as II-IV [103] semiconductors, these binding energies are consistently about an order of magnitude lower than the ionization energies of the TM acceptor ground states. Therefore, higher activation energy in AlGaN:Fe is also in agreement with our model, since incorporation of aluminum in GaN lattice leads to increased ionization energies of acceptors and, consequently, to the greater binding energy of the (Fe$^{3+}$, e, h) complex.

A more quantitative estimate of these energies in AlGaN:Fe can be obtained by applying the internal reference rule suggested by Langer et al. [43] to the results obtained in GaN. This rule states that in isovalent compounds (e.g., all III-V semiconductors), TM impurity levels are aligned with respect to each other, as if pinned to a fictitious reference level common in all host materials. In fact, one of the first predictions for the band discontinuities at GaN/AlN interface was obtained by treating the ($A^0/A^-$) charge transfer level of iron as a common reference [38]. Currently, available data converge on the estimate that about (35±5)% of the band gap difference between GaN and Al$_x$Ga$_{1-x}$N is accommodated in the valence band offset ([104] and references therein). For $x = 0.20$, this amounts to (180±20) meV. Using this value and based on the results obtained by Heitz et al. for GaN [39], Fe$^{3+/2+}$ charge transfer level in Al$_{0.2}$Ga$_{0.8}$N should then be located at about 3.4 eV above the valence band maximum. Hence, the binding energy of (Fe$^{3+}$, e, h) complex in Al$_{0.2}$Ga$_{0.8}$N is expected to be roughly 340 meV.
This is in good agreement with the electron irradiation effect activation energy of 360 meV obtained by us in this work for Al$_{0.2}$Ga$_{0.8}$N:Fe.

### 3.2.4 Electron Irradiation-induced Effects in ZnMgO:P

As in GaN, room-temperature EBIC measurements revealed that minority electron diffusion length increases with electron injection (Figure 23). Same experiments on nominally undoped bulk ZnO showed no response to electron injection, suggesting the involvement of phosphorus-related levels.

![Graph showing diffusion length vs. injection duration](image)

Figure 23. Experimental dependence of minority electron diffusion length on duration of electron injection in Zn$_{0.9}$Mg$_{0.1}$O at 300K. Inset: calculated minority electron lifetime dependence on duration of electron injection. For lifetime calculations, minority electron mobility was assumed to be 50 cm$^2$/Vs. (After reference [80]).
Provided that the increase of \( L \) is a consequence of increasing lifetime of electrons in the conduction band, \( \tau \) can be estimated according to Equation 1. The results of this estimate, assuming the mobility of minority electrons to be around 50 cm\(^2\)/Vs, are shown in the inset of Figure 23.

![Figure 24. Room temperature CL spectra of Zn\(_{0.9}\)Mg\(_{0.1}\)O measured in the same location at different times of electron irradiation. 1 is a pre-irradiation spectrum; 2, 3, and 4 correspond to the duration of electron irradiation of 359, 793, and 1163 s, respectively. Inset: pre-irradiation broad-range CL spectrum taken in a different location than spectra 1 through 4. (After reference [80]).](image)

Cathodoluminescence spectrum of ZnMgO:P (cf. Figure 24) is dominated by strong emission starting at about 355 nm (3.49 eV), which is in good agreement with 10% Mg concentration in ZnO lattice, since each atomic percent of Mg is known to increase the
ZnO band gap (3.30 eV) by 0.02 eV [105]. This feature is attributed to band-to-band as well as to band-to-impurity (P-acceptor) transitions. The spectrum also reveals a broad luminescence band that is likely defect-related [27].

Figure 25. Variable temperature dependence for the square root of inverse normalized intensity on duration of electron irradiation in ZnMgO:P. 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 $E_A = 256 \pm 20$ meV. (After reference [80]).

CL measurements were performed at temperatures ranging from 25 °C to 125 °C. Figure 24 shows a series of room temperature spectra collected under continuous electron beam excitation. As in GaN, the intensity of the near-band-edge (NBE) transition can be seen to fall steadily with increasing $t$, which correlates with the growth
of the diffusion length as shown by EBIC experiments. It should be noted that the broad luminescence feature remained unaffected by electron irradiation.

Repeating the experiment at increased temperatures showed a systematic decrease in the rate of decay of CL intensity of the NBE transition (Figure 25). Using Equation 10, the results were treated to extract an activation energy of $256 \text{ meV} \pm 20 \text{ meV}$ from the slope of the Arrhenius plot in the inset of Figure 25. This activation energy is in good agreement with that for the phosphorus acceptor obtained based on the simple hydrogenic model. The model assumes phosphorus substitution on the oxygen site and predicts the activation energy of 250-300 meV [106].

Since no electron injection effects were observed in undoped ZnO, it stands to reason that phosphorus acceptor plays a crucial role in this phenomenon. Because of the high ionization energy of the P acceptor, most of the phosphorus atoms are initially in the neutral state and, therefore, readily accept non-equilibrium electrons generated by the SEM beam. This prevents recombination of the minority electrons through these levels and leads to an increase in lifetime, as is evidenced by injection-induced decay in NBE luminescence intensity, as well as increasing diffusion length. At higher temperature, however, electrons captured on P-levels can gain sufficient thermal energy to escape the trap, thus restoring the original recombination pathway, which manifests itself in the slower rate of luminescence decay.
3.2.5 *Electron Irradiation-induced Effects in ZnO:Li*

The effects of exposure of ZnO:Li to the electron beam were monitored over the irradiation period of ~ 2500 s. Intermittent EBIC measurements revealed that the minority carrier (hole) diffusion length increases linearly with duration of electron irradiation (Figure 26).

![Graph showing the relationship between diffusion length and irradiation duration.](image)

**Figure 26.** Room temperature dependence of minority carrier diffusion length in ZnO:Li on duration of electron irradiation (open circles) and the linear fit (solid line). (After reference [84]).

The results of EBIC measurements were correlated with those of cathodoluminescence spectroscopy in order to demonstrate that the increase in the diffusion length is associated with growing lifetime of non-equilibrium carriers generated by the electron
beam. The inset of Figure 27a shows a series of room temperature CL spectra numbered in order of increasing duration of irradiation. The figure features the dominant near-band-edge (NBE) transition at about 382 nm (3.25 eV) and demonstrates that exposure to the electron beam results in the increase of carrier lifetime, which is manifested by the systematic decay of the luminescence intensity, since \( I \) is proportional to \( 1/\tau \).

![Figure 27](image)

**Figure 27.** Variable-temperature dependence of inverse square root of normalized intensity on duration of electron irradiation and the linear fit with the rate \( R \) (a) and Arrhenius plot of \( R \) as a function of temperature yielding an activation energy \( \Delta E_{A,I} \) of 283±9 meV (b). Inset: Room temperature cathodoluminescence spectra taken under continuous excitation by the electron beam. 1 is the pre-irradiation spectrum and 5 is the spectrum after 1450 s of electron irradiation. (After reference [84]).
To characterize the intensity decay, we relate it to $L$, which is known to vary linearly (cf. Figure 26) with duration of excitation. Since $L$ is proportional to $\tau^{1/2}$, the inverse square root of normalized (with respect to the initial maximum value) intensity must also be proportional to $L$, and consequently, would be expected to vary linearly with duration of electron irradiation. Figure 27(a) shows that this is indeed the case, indicating that the observed increase of the diffusion length is attributable to the growing lifetime of non-equilibrium carriers.

CL measurements conducted at elevated temperatures confirmed the same trend for the irradiation-induced change of luminescence intensity. It can be seen from Figure 27 that the inverse square root of intensity increases linearly for all temperatures.

The temperature dependence of $R$ can be used to determine the activation energy of the irradiation-induced processes according to Equation 10. The factor of $2kT$ in this equation accounts for both electron irradiation-induced effect on $R$ ($\propto \exp(\Delta E_{A}/kT)$) and its temperature dependence ($\propto \exp(\Delta E_{A}/-2kT)$), since generally it is safe to assume that the activation energies for both contributions are similar [95]. On the other hand, earlier studies of the temperature-induced CL intensity decay yielded the activation energy of about 60 meV (cf. Section 3.1.1), thus allowing us to separate the two components as follows:

$$R = R_o \exp\left(\frac{\Delta E_{A,I}}{kT}\right)\exp\left(-\frac{\Delta E_{A,T}}{2kT}\right)$$  \hspace{1cm} (11)
where $\Delta E_{A,I}$ is the activation energy of electron irradiation effect and $\Delta E_{A,T}$ is the previously determined activation energy of thermally induced intensity decay. From the Equation 11, the value for $\Delta E_{A,I}$ of 283±9 meV was obtained using the Arrhenius plot shown in Figure 27.

In light of our prior findings and given the analogous response of ZnO:Li, it is likely that the observed irradiation-induced increase in lifetime and diffusion length is caused by the trapping of non-equilibrium electrons on a Li-acceptor level with the ionization energy of around 280 meV. Although several theoretical works have predicted a very shallow Li$_{Zn}$ level [45,46], these predictions have not been substantiated experimentally, as most studies find a rather deep Li-acceptor with activation energies of several hundreds meV [47,49]. In fact, recent first-principles calculations by Wardle et al., also suggest that the Li$_{Zn}$ state lies at about 0.2 eV above the valence band maximum [47], which is in reasonable agreement with the results obtained in this work.

Variable temperature persistent photoconductivity measurements also showed evidence of the existence of deep traps in Li-doped ZnO. In presence of deep electron traps, persistent photoconductivity takes place when the probability of electron capture is greater than the probability of recombination [107]. Figure 28 shows the decay of photocurrent at several temperatures, which was normalized with respect to the steady-state photocurrent value at each temperature. After initial excitation, the lamp shutter
was closed, and the current was recorded as a function of time. The decay of photocurrent was fitted with a stretched exponential function of the following form [108]:

\[
I(t) = I_0 + A \exp\left[-(t / \tau)^\beta\right]
\]  

(12)

where \(I_0\) is the steady-state photocurrent value, \(\tau\) is the PPC decay time constant, \(\beta\) is the decay exponent (0<\(\beta\)<1), and \(A\) is a scaling constant.

Figure 28. Decay of photocurrent in ZnO:Li at variable temperatures (open symbols) and the stretched-exponential fit (solid lines). The decay curve at 45 °C is omitted for clarity. Inset: Arrhenius plot of the PPC decay time constant as a function of temperature, corresponding to the activation energy of 245 ± 22 meV. (After reference [95]).
In the studied temperature range, the decay exponent $\beta$ was approximately 0.6 and was not significantly affected by temperature. The decay time $\tau$ was observed to decrease exponentially with increasing temperature, yielding an activation energy of the process responsible for the PPC behavior. This activation energy was determined to be $245 \pm 22$ meV from Equation 12, as shown in the inset of Figure 28. This value is consistent with that obtained from variable temperature CL experiments, which suggests that the same level is involved in electron trapping that occurs under either photo- or electron excitation.

It should be clarified that the weak n-type character of the sample is not necessarily in contradiction with the dominant behavior of acceptor states observed in electron trapping phenomena. As was mentioned, the n-type conductivity in nominally undoped ZnO is due to the shallow donor states, whereas in presence of deep electron traps the Fermi level may lie far below these states. Although shallow donors may capture non-equilibrium electrons under excitation, those are quickly released if the temperature is sufficiently high. Therefore, if the difference in the energetic position between the donor and trap states is large, the latter dominate the kinetics of electron trapping [107].
Continuous irradiation of the p-type ZnO:Sb sample by the electron beam of the SEM was shown to result in an increase of the minority carrier diffusion length. The irradiation was performed at several temperatures, with the diffusion length exhibiting the same linear trend, as shown in Figure 29. Note that the values of $L$ were vertically offset to clearly show its increase with duration of irradiation and thus do not accurately represent the temperature dependence of diffusion length.

The irradiation-induced increase of $L$ is thought to have an origin similar to that of the thermally-induced increase: the non-equilibrium electrons generated by the electron beam are continuously trapped by the neutral acceptor levels ($A^0 + e^- \rightarrow A^-$), reducing the recombination rate and resulting in longer lifetime of electrons in the conduction band. As excitation proceeds, the concentration of neutral levels diminishes and the increase of $L$ continues up to its saturation value (cf. Figure 30 below).

It can also be seen from Figure 29 that the rate, $R$, of the diffusion length increase is reduced with increasing temperature. The increase of the diffusion length due to trapping is counteracted by the release of the trapped electrons that occurs if the carriers gain sufficient energy to escape the trap. As the temperature is raised, the likelihood of de-trapping increases, which dampens the irradiation-induced growth of the diffusion length.
The influence of electron irradiation and temperature on the rate R is shown in Equation 11, where $\Delta E_{A,T}$ is the thermal activation energy determined as described in Section 3.1.2. Using the above equation, the activation energy of irradiation-induced component of diffusion length increase can be obtained from the Arrhenius plot shown in the inset of Figure 29.

![Figure 29. Electron irradiation-induced increase of minority electron diffusion length in ZnO:Sb at different temperatures. The values of the diffusion length were vertically offset for clarity and are not intended to illustrate the temperature dependence (Section 3.1.2). Inset: Rate of irradiation-induced increase of diffusion length as a function of temperature (open circles). The fit with Equation 11 (solid line) gives activation energy of 219 ± 8 meV. (After reference [73]).](image)

The value of $\Delta E_{A,I}$ can be extracted from the slope of the linear fit, which from Equation 11 equals $(\Delta E_{A,I} - \frac{1}{2} \Delta E_{A,T})$. The treatment yielded a value of 219 ± 8 meV, which is
similar to the thermal activation energy obtained above and is in excellent agreement with that obtained in ref. [74] (212 ± 28 meV), which further supports the involvement of the same acceptor level in both irradiation- and temperature-induced processes.

While the nature of the acceptor responsible for the increase of $L$ cannot be deduced with absolute certainty, one of the possibilities is a Sb$_{Zn}$-2V$_{Zn}$ complex, predicted by Limpijumnong et al. [57] to have the activation energy of about 160 meV. As this value is somewhat lower than that determined by our experiments, it should be noted that it does not account for the strong dependence of the acceptor activation energy on the concentration of majority carriers. It has been shown that in Sb-doped ZnO, acceptor activation energy can increase from about 135 to 212 meV in the range of carrier concentrations spanning about one order of magnitude [74]. Therefore, the above theoretical prediction does not necessarily contradict our experimental results. On the other hand, the involvement of other Sb-related defects is highly unlikely. The substitutional defect (Sb$_O$) as well as the single-vacancy complex (Sb$_{Zn}$-V$_{Zn}$) are predicted to have ionization energies about an order of magnitude greater than those obtained experimentally, while other defects can also be ruled out based on their electrical behavior and/or high formation energies [57].
3.2.6.1 Saturation and Relaxation of Irradiation-induced Changes in Minority Carrier Diffusion Length in p-ZnO:Sb

The saturation and relaxation of irradiation-induced change of diffusion length was also studied. Figure 30 demonstrates that $L$ reaches its maximum value after about 50 min of continuous exposure to the electron beam.

![Graph showing the saturation and relaxation dynamics of minority carrier diffusion length in p-ZnO:Sb.](image)

Figure 30. Room temperature saturation and relaxation dynamics of minority carrier diffusion length in p-ZnO:Sb. The arrow marks the time at which the electron irradiation was discontinued. (After reference [73]).

Further monitoring revealed that irradiation-induced increase persists for at least one week at room temperature. Annealing the sample at 175°C for about 30 minutes resulted in a reduction of the diffusion length to about 1 μm. This behavior further
supports the involvement of deep electron traps in the phenomenon of interest, since temperature-induced de-trapping of carriers re-activates the original recombination route, thus reducing carrier lifetime and diffusion length.

Table 3. Room-temperature hole concentrations and activation energies ($E_A$) for the electron irradiation-induced lifetime increase in GaN:Mg

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Hole Concentration (cm$^{-3}$)</th>
<th>$E_A$(meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2 \times 10^{16}$</td>
<td>344 ± 43</td>
</tr>
<tr>
<td>2</td>
<td>$9 \times 10^{16}$</td>
<td>326 ± 48</td>
</tr>
<tr>
<td>3</td>
<td>$3 \times 10^{18}$</td>
<td>237 ± 20</td>
</tr>
<tr>
<td>4</td>
<td>$7 \times 10^{18}$</td>
<td>197 ± 7</td>
</tr>
</tbody>
</table>

3.2.7 Carrier Concentration Dependence for the Electron Irradiation Effects in $p$-GaN

The irradiation-induced decay of NBE luminescence intensity is demonstrated in Figure 31 on the example of sample 1 (cf. Table 3). The room-temperature spectra shown correspond to about 0, 1600, 2500, and 4000 seconds of continuous irradiation by the SEM beam. Since luminescence intensity, $I$, is inversely proportional to $\tau$, the systematic decay of intensity indicates that irradiation by the electron beam increases the lifetime of non-equilibrium electronic carriers. Carrier diffusion length is proportional to the square root of lifetime ($L=(D\tau)^{1/2}$), where $D$ is diffusivity; the diffusion length, in turn, had been shown by EBIC measurements to be directly proportional to duration of
irradiation (t) [61]. Therefore, lifetime can be expected to increase quadratically with t, as is demonstrated experimentally by the decay of intensity of the NBE luminescence.

Figure 31. Room-temperature cathodoluminescence spectra of GaN:Mg sample 1 under continuous irradiation by the SEM beam. Spectra 1 through 4 correspond to 0, 1611, 2529, and 4039 seconds of irradiation, respectively. Inset: Variable-temperature dependence of inverse square root of intensity on duration of electron irradiation and the linear fits (solid lines) with the rate R. Intensity values were normalized with respect to their initial values at each temperature; the data sets were vertically offset for clarity. (After reference [109])

The inset of Figure 31 shows that there exists a linear dependence between \((1/I)^{1/2}\), which is proportional to lifetime of the non-equilibrium carriers in the band, and the duration of irradiation. In this and subsequent figures, intensity was normalized with respect to its initial value.
The results of CL measurements performed on sample 1 at elevated temperatures are also shown in the inset of Figure 31. The progressively lower rates of intensity decay indicate that a concurrent, thermally activated process opposes the irradiation-induced lifetime increase. In the scheme of the mechanism suggested above, this process most likely consists of the transition of the electron from the Mg trap to the valence band. Thermal activation of this process indicates that there exists an energy barrier that must be overcome before the latter transition can take place. As the temperature increases, these transitions occur more frequently, re-establishing the original recombination pathway and resulting in the slower rate of lifetime increase.

The relationship of between the rate (\( R \)) and temperature (\( T \)) of the sample allows to estimate the activation energy of the irradiation-induced intensity decay according to the Equation 10. The activation energies for all for samples were extracted from the plots shown in Figure 32. For sample 1, the activation energy of \( 344 \pm 43 \) meV was obtained. While this value is considerably higher than the frequently quoted thermal activation energy of Mg acceptor (~ 200 meV), it is not in contradiction to the values of the optical ionization energy of Mg in GaN. Several photoluminescence studies, particularly those conducted in earlier years, when Mg doping yielded only moderate hole concentrations, resulted in the ionization energies on the order of 300 meV [110,111].
Figure 32. Arrhenius plots of $R$ as a function of sample temperature for samples 1 through 4 (plots (a) through (d), respectively). The linear fit with eq. 1 (solid lines) yielded activation energies shown in each plot. (After reference [109])

Note that the values of optical ionization energies (i.e., those obtained under non-equilibrium conditions, such as photo- and cathodoluminescence experiments) have been shown differ significantly from thermal activation energies (for instance, those derived from Hall measurements), implying the existence of significant relaxation energy of Mg dopants [16,110].

Further evidence of Mg involvement in irradiation-induced lifetime increase can be derived from the dependence of $\Delta E_A$ on carrier concentration, $p$, which is related to Mg doping levels. The activation energy of electron-irradiation effect was shown to
decrease systematically with increasing hole concentration (cf. Table 3). Incidentally, the relationship between acceptor activation energies and hole concentration is well-known and has been explored in GaN and other semiconductors [83,86]. It has been attributed to a number of causes, not necessarily mutually exclusive, including the formation of the band-tail states that extend into the forbidden gap, the broadening of the acceptor band in the gap, and the reduction of binding energy due to Coulomb interaction between the holes in the valence band and the ionized acceptor states [82]. The decrease of activation energy is often described by Equation 9, where \( \alpha \) is a constant accounting for geometrical factors as well as for the properties of the material and, according to theoretical calculations, has the following form:

\[
\alpha = \left( \frac{\Gamma(2/3) q^4}{\pi^2} \right) \left( \frac{q^2}{4\pi\varepsilon} \right), \tag{13}
\]

where \( \Gamma(x) \) is gamma function of argument \( x \), \( q \) is elementary charge and \( \varepsilon \) is dielectric constant, taken to be 9.5\( \varepsilon_0 \) [83].

The fit of experimentally obtained activation energies with Equation 13 is shown in Figure 33. The values of \( N_A^- \) were derived under the assumption that \( N_A^- - N_D^+ = \rho \), where \( N_D^+ \) is the density of ionized shallow donors and based on the manufacturer's specification, is approximately \( 1 \times 10^{17} \) cm\(^{-3} \). From the fit in Figure 33, \( \alpha = 9.74 \times 10^{-8} \) eV\( \cdot \)cm, which is comparable to the results of the calculation using Equation 13.
(3.32×10^{-8} \text{ eV} \cdot \text{cm}). Note, it is also within the order of magnitude of the value reported for acceptor activation energy in p-ZnO [74].

Figure 33. Decrease of activation energy of electron irradiation effect as a function of ionized acceptor concentration and the linear fit (solid line) with Equation 9. (After reference [109])

3.2.8 Effects of Solid State Electron Injection on the Performance of ZnO Homo junction Diodes

In addition to electron irradiation by the beam of the SEM, the increase of the minority carrier lifetime can be induced by solid-state electron injection carried out by applying forward bias to a p-n junction. Electron injection experiments were conducted on ZnO
homojunction photodiode in order to demonstrate that the injection-induced lifetime increase translates to the improved photoresponse of the junction in agreement with Equation 3.

Figure 34. SEM micrograph showing the cross-section of the device. Superimposed is the EBIC linescan, where the peak indicates the position of the p-n junction. Inset: Increase of the diffusion length as a function of injected charge (open circles) and the linear fit. (After reference [112]).

Figure 34 shows the cross-sectional view of the device with EBIC profile superimposed on the secondary electron (SE) micrograph. The maximum in the induced current signal reveals the physical location of the p-n junction. While the interface between Si substrate and p-ZnO is easily found due to SE contrast, the location of the junction between p-ZnO and n-ZnO can only be discerned via the EBIC signal.
Further EBIC measurements performed periodically after each electron injection interval demonstrated that the diffusion length of minority electrons in p-ZnO is significantly increased due to the application of the forward bias to the junction. The inset of Figure 34 illustrates that the value of $L$ is improved by roughly a factor of 2.5 after the injection of about 23 C. As was mentioned above, we observed a similar increase in other ZnO samples after irradiation by the electron beam of the SEM. The effect of electron irradiation on the diffusion length was attributed to the trapping of non-equilibrium electrons on the neutral acceptor levels. As the recombination of the non-equilibrium electron-hole pairs generally involves the levels of neutral acceptors located deep in the bandgap, trapping of electrons on these levels inhibits recombination and leads to an increase of carrier lifetime and, consequently, carrier diffusion length [80,84]. Since the presence of Sb has been shown to induce acceptor levels in the bandgap far from the valence band edge [32], it is likely that applying forward bias has similar effects: electrons injected into p-ZnO become trapped on the Sb-related levels, preventing the recombination through these levels and thus resulting in the increase of $L$.

Figure 35 displays a series of photocurrent spectra taken after several intervals of electron injection. The photoresponse appears at about 250 nm and increases steadily throughout the UV region. There is a shoulder near 350 nm, corresponding to the effective bandgap of ZnO (~3.54 eV) [113], after which the increase becomes less steep around the actual bandgap energy (3.39 eV or 365 nm). An increase of the photoresponse beyond this wavelength into visible region (ideally the response from
device should end there) is due to the collection of photogenerated carriers in the Si substrate [113].

Figure 35. Spectral photoresponse from a cross-section of a ZnO homojunction photodiode after different injection intervals. Spectrum 1 corresponds to the pre-injection state; spectrum 2 – 2.1 C injected; spectrum 3 – 12.6 C injected; spectrum 4 – 25.5 C injected. Inset: Photocurrent at 350 nm as a function of injected charge (open circles) and the linear fit. The values of $L$ are calculated based on the fit of the data in the inset of Figure 34. (After reference [112]).

In the case of front- or back-illuminated photodetectors and for above-bandgap excitation energies, the photoresponse is generally limited by the penetration depth of the exciting light. This is because the penetration depth (given by the inverse absorption coefficient in the NBE region, which is on the order of 100 nm in ZnO [59,60] is usually less than the diffusion length of minority carriers.
In the side-illuminated configuration such as shown in Figure 34 the situation is considerably different, since absorption of light and the carrier collection occur in mutually perpendicular planes, such that only the lateral component of the carrier diffusion contributes to the photocurrent. In this configuration, the collection efficiency is improved with increasing diffusion length, because more carriers are able to reach the space-charge region, where the collection occurs. Therefore, for lateral collection devices, the photoresponse is known to vary linearly with $L$ [114]. This is reflected in the inset of Figure 35, where the electron injection-induced increase of $L$ in the p-side of the junction (see also inset of Figure 34) manifests itself as a linear increase of the photocurrent in the device. Although EBIC measurements were conducted on a diode different from that used for photocurrent experiments, it can be deduced from the inset of Figure 34 and Figure 35 that injection of about 25 C of charge results in approximately 2.5-fold increase of both $L$ and the photocurrent. The values of $L$ shown in the inset of Figure 35 were calculated based on the linear fit to the data in Figure 34 and are shown to facilitate the comparison.

The stability of the injection-induced change was monitored over a period of several days, during which the diffusion length of electrons in p-ZnO persisted at the same elevated level as at the end of the last injection interval. Note that the diffusion length of minority holes in n-type ZnO (which was determined to be on the order of several hundred nanometers) was not affected by forward bias application. This further supports the idea that a significant concentration of acceptor levels is necessary to achieve the
increase of $L$, and therefore is consistent with earlier observations that electron irradiation has no effect on $L$ in undoped ZnO with intrinsic n-type conductivity [80].
CHAPTER 4 - SUMMARY AND CONCLUSIONS

This work covers several aspects of minority carrier transport in ZnO and GaN compounds. The summary and the implications of the major findings in this work are covered in this chapter.

4.1 Temperature-induced Increase of Minority Carrier Diffusion Length and Lifetime in ZnO

In n-ZnO and p-ZnO, the minority carrier diffusion length was shown to increase, while the cathodoluminescence intensity of the NBE transition decreased, indicating that the lifetime of non-equilibrium carriers in the band is greater at elevated temperatures. Activation energies obtained from both experimental techniques were in good agreement with each other, which suggests that both observations are manifestations of the same phenomenon. Since the carrier capture cross-section is inversely proportional to temperature, the rate with which non-equilibrium carriers undergo recombination decreases as the sample temperature is raised. This leads to longer carrier lifetimes and consequently to the increase in minority carrier diffusion length. Note that carrier diffusivity (a parameter which relates diffusion length and lifetime) is also affected by temperature, but its effect on the observed diffusion length increase was found do be minimal.
Variable-temperature measurements were also used to study the carrier concentration dependence of acceptor activation energy in p-type ZnO:Sb. It was shown that the activation energy for temperature-induced lifetime growth diminishes with increasing doping level. This behavior is consistent with other semiconductors and can be attributed to the broadening of the acceptor band.

4.2 Effects of Electron Irradiation on Minority Carrier Diffusion Length and Lifetime

The bulk of the research concentrated on studies of the trapping of non-equilibrium carriers in variety of GaN- and ZnO-related compounds. It was shown that irradiation by the beam of the SEM results in a notable increase of minority carrier diffusion length in compounds containing species that form deep acceptor levels. This increase was associated with irradiation-induced lifetime increase, as demonstrated by the decay of near-band-edge cathodoluminescence intensity. In all cases, the rate of this increase diminishes with increasing sample temperature, indicating that there exists a competing process that counteracts the effects of electron irradiation.

Based on these observations, the proposed mechanism for electron irradiation effects is based on the trapping of non-equilibrium carriers on non-ionized acceptor levels. In general, the ionization levels of most known acceptors in ZnO and GaN are located far from the valence band edge; therefore, a significant (>90%) fraction of all acceptor species remains neutral. Under equilibrium conditions, these levels are part of the near-
band-edge recombination pathway, and the balance between carrier trapping and de-trapping is maintained. Under electron excitation, however, with increased concentration of non-equilibrium carriers, the balance shifts towards the former, and carrier recombination rate decreases. The decrease in recombination rate translates directly to greater carrier lifetime.

The recombination pathway can be restored if the trapped electron gains sufficient thermal energy to escape the trap. This occurs more and more frequently as the sample temperature is raised and, therefore, explains the slower rate of lifetime increase at elevated temperatures.

Temperature-depended EBIC and CL measurements under continuous electron excitation allowed determining the activation energy for irradiation-induced changes. The findings of these measurements are summarized in Table 4, along with the independently determined ionization energies of the corresponding acceptors. Note that the trapping mechanisms of the transition-metal acceptors (Fe, Mn, and Sb) differ somewhat from the simple hydrogenic acceptors (P, Li, and C). The trapping of the carriers in Mn- and Fe-doped (Al)GaN was suggested to involve the more energetically accessible excited states, and the activation energy of electron irradiation effects in ZnO:Sb is consistent with the ionization energy of a Sb$_{2n}$-V$_{Zn}$ complex.
Table 4. Activation energies for the electron irradiation-induced effects in studied compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta E_A$ (meV)</th>
<th>Ionization Energy of Acceptor (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaN:C</td>
<td>210</td>
<td>230</td>
</tr>
<tr>
<td>GaN:Mn</td>
<td>360</td>
<td>300*</td>
</tr>
<tr>
<td>GaN:Fe</td>
<td>230</td>
<td>280*</td>
</tr>
<tr>
<td>AlGaN:Fe</td>
<td>360</td>
<td>340*</td>
</tr>
<tr>
<td>Bulk ZnO with Li</td>
<td>245</td>
<td>200</td>
</tr>
<tr>
<td>ZnMgO:P</td>
<td>260</td>
<td>200-300</td>
</tr>
<tr>
<td>ZnO:Sb</td>
<td>219</td>
<td>212</td>
</tr>
</tbody>
</table>

* Ionization energies of excited states (cf. Sections 3.2.2 and 3.2.3)

4.2.1 Device Implications of Electron Injection Effects

Solid-state electron injection (carried out by the application of forward bias to a ZnO homojunction) was shown to significantly improve the photoresponse of the p-n junction. This improvement was unambiguously correlated to the injection-induced increase of minority carrier diffusion length as measured by EBIC. Since for lateral collection photodetectors, the response varies linearly with $L$, and $L$, in turn, is proportional to the amount of injected charge, the 2.5-fold increase of diffusion length resulted in a
corresponding improvement of the photoresponse of the junction at 350 nm (near-peak sensitivity wavelength for ZnO).

This finding has significant implications for wide bandgap semiconductor technology, since it provides an opportunity for increasing the device performance without altering the current production technology. A simple electron injection procedure can significantly improve the peak photoresponse of an existing device, with the effects lasting for at least several days. Furthermore, it takes advantage of the intrinsic property of deep acceptor levels (i.e., carrier trapping), which is generally considered a drawback in these materials.
APPENDIX – BODY OF WORK
Book Chapter:


Journal Publications:


Presentations:


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