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## Lithium-related states as deep electron traps in ZnO

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Carrier trapping in Li-doped ZnO was studied using Electron Beam Induced Current technique, as well as cathodoluminescence spectroscopy and persistent photoconductivity measurements. Under electron beam excitation, the minority carrier diffusion length underwent a significant increase, which was correlated with growing carrier lifetime, as demonstrated by the irradiation-induced decay of CL intensity of the near-band-edge transition. Variable-temperature cathodoluminescence and photoconductivity experiments showed evidence of carrier trapping and yielded activation energies of 280 and 245 meV, respectively. These observations are attributed to the presence of a deep, Li-related acceptor state. © 2005 American Institute of Physics. [DOI: [10.1063/1.2136348](https://doi.org/10.1063/1.2136348)]

ZnO is a wide bandgap semiconductor with great prospects for optoelectronic device applications, due both to its attractive optical and electronic characteristics (particularly, high exciton binding energy) and technological advantages, such as the availability of large area lattice-matched substrates, low cost, and the use of wet chemical etching, as opposed to reactive ion etching in GaN technology.

Although ZnO technology is still in its development stages, a number of ZnO-based heterojunction<sup>1,2</sup> as well as homojunction<sup>3-6</sup> devices have already been reported. In the present state of the technology, the latter group is characterized by rather poor performance attributable in part to low *p*-type carrier densities.<sup>6</sup> As for heterojunction devices that employ *n*-type ZnO, their quality, although currently superior to all ZnO-based junctions, is intrinsically limited by the defects arising from the lattice discontinuities at the interface. Consequently, the availability of device quality *p*-type ZnO is crucial for fully realizing the potential of the ZnO technology in bipolar device applications.

The *p*-type doping of ZnO, however, presents considerable challenges. Similar to GaN, compensation by native donors is at the root of the problem, since even nominally undoped material is generally *n* type, due to the electrical activity of native defects, such as zinc interstitials, zinc antisites, and oxygen vacancies,<sup>7,8</sup> as well as hydrogen impurity.<sup>9</sup> On the other hand, potential acceptors, such as nitrogen,<sup>10</sup> phosphorus,<sup>11</sup> and arsenic,<sup>12</sup> form states deep within the bandgap (about 160, 130, and 100 meV above the valence band maximum, respectively), and therefore, have low ionization fractions at room temperature.

Lithium has also been considered as a potential acceptor dopant, since Li<sub>Zn</sub> (substitutional Li on the Zn site) was predicted to form an acceptor level much shallower than those of group V elements.<sup>13,14</sup> However, because of its small radius, the incorporation of Li leads to the formation of Li interstitials (Li<sub>i</sub>), which act as shallow donors and further suppress the net hole concentrations.

Despite the encouraging theoretical predictions, the experimental reports on the energetic position of the Li<sub>Zn</sub> acceptor suggest that its levels are actually located deeper than

expected. Several independent studies on Li-doped ZnO show the presence of a Li-related acceptor with the activation energies ranging from 165 to over 500 meV.<sup>15</sup> In this letter, we present further evidence for the deep nature of a Li acceptor state in ZnO and explore its role in carrier transport. Temperature- and time-dependent cathodoluminescence (CL), Electron Beam Induced Current (EBIC), and persistent photoconductivity (PPC) measurements were used to probe the dynamics of electron trapping on Li-related levels.

The experiments were carried out on commercially available bulk ZnO (Tokyo Denpa Co.). The samples were weakly *n* type, showing electron concentrations of  $\sim 10^{14}$  cm<sup>-3</sup> and mobility of  $\sim 150$  cm<sup>2</sup>/V s at room temperature. Secondary Ion Mass Spectroscopy (SIMS) measurements revealed the Li concentration of about  $3 \times 10^{16}$  cm<sup>-3</sup> (Ref. 16) (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 nonpolar *a* plane of the ZnO crystal by electron beam evaporation of an 80 nm thick Au layer and subsequent liftoff.

Time-dependent cathodoluminescence measurements were conducted *in-situ* in the Phillips XL30 scanning electron microscope (SEM) using an integrated Gatan MonoCL3 system. This setup allows combining periodic acquisition of CL spectra with continuous excitation of the sample by scanning the beam over the same location. For temperature-dependent CL measurements, the sample temperature was varied *in-situ* from 25 °C to 125 °C using a specially designed hot stage and an external temperature controller (Gatan). At each temperature, the electron beam irradiation and CL measurements were conducted at a different location. The excitation for CL measurements was provided by a 20 kV electron beam, corresponding to an electron penetration depth of about 1.5 μm.

Room temperature minority carrier diffusion length measurements were conducted to relate the changes in carrier lifetime to the diffusion length. The experiments were performed *in-situ* in the SEM using the EBIC method. A detailed description of the EBIC technique, especially as it pertains to electron irradiation studies, can be found elsewhere<sup>17</sup> (and references therein). To monitor the effects of electron irradiation on the diffusion length, the beam of the SEM was

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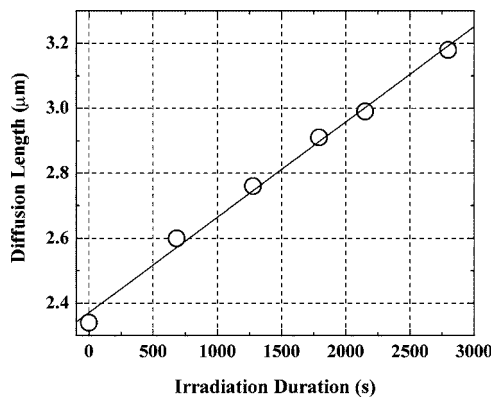


FIG. 1. Room temperature dependence of minority carrier diffusion length on the duration of electron irradiation (open circles) and the linear fit (solid line).

repeatedly scanned over the same location, with EBIC measurements taken intermittently.

Photoconductivity measurements were performed in the temperature range of 34 °C to 93 °C at the excitation wavelength of 360 nm using a Xe-arc source with a Jobin-Yvon Triax 320 monochromator. Photocurrent was measured under a constant bias of 2.0 V. The signal was processed using a Keithley 428 current amplifier and a Keithley 2000 multimeter, and recorded with a Labview-based software.

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 ( $L$ ) increases linearly with the duration of electron irradiation (Fig. 1). This appears to be a common occurrence in wide bandgap semiconductors doped with species that create deep acceptor levels, as similar observations were made not only in phosphorus-doped ZnMgO,<sup>18</sup> but also in (Al)GaN doped with Mg, Mn, Fe, and C.<sup>19–21</sup> It is also noteworthy that no irradiation-induced changes in diffusion length were observed in either  $n$ -GaN or nominally undoped  $n$ -ZnO.

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 nonequilibrium carriers generated by the electron beam. The inset of Fig. 2(a) 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 ( $\tau$ ), which is manifested by the systematic decay of the luminescence intensity ( $I$ ), since  $I$  is proportional to  $1/\tau$ . To characterize the intensity decay, we relate it to the diffusion length,  $L$ , which is known to vary linearly (cf. Fig. 1) with the 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 2(a) shows that this is indeed the case, indicating that the observed increase of the diffusion length is attributable to the growing lifetime of nonequilibrium carriers.

CL measurements conducted at elevated temperatures confirmed the same trend for the irradiation-induced change of luminescence intensity. It can be seen from Fig. 2(a) that

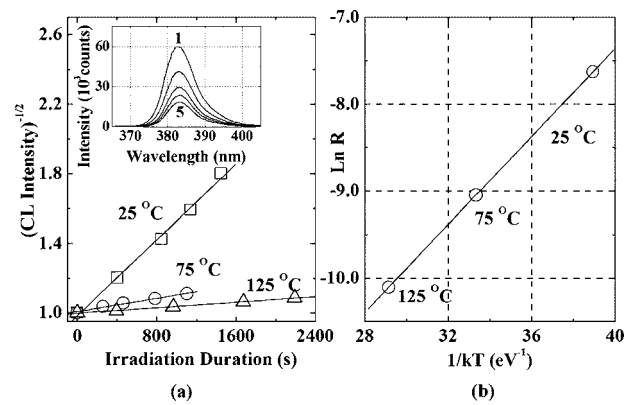


FIG. 2. (a) Variable temperature dependence of the inverse square root of normalized CL intensity on the duration of electron irradiation and the linear fit with the rate  $R$ . **Inset:** Room temperature cathodoluminescence spectra taken under continuous excitation by the electron beam. **1** is the preirradiation spectrum and **5** is the spectrum after 1450 s of electron irradiation. (b) Arrhenius plot of  $R$  as a function of temperature yielding an activation energy  $\Delta E_{A,I}$  of  $283 \pm 9$  meV.

the inverse square root of intensity increases linearly for all temperatures. The temperature dependence of rate  $R$  can be used to determine the activation energy of the irradiation-induced processes according to the following expression:<sup>18,22</sup>

$$R = R_0 \exp\left(\frac{\Delta E_{A,I}}{kT}\right) \exp\left(-\frac{\Delta E_{A,T}}{2kT}\right), \quad (1)$$

where  $R_0$  is a scaling constant,  $T$  is temperature,  $k$  is the Boltzmann's constant,  $\Delta E_{A,I}$  is the activation energy of electron irradiation effect, and  $\Delta E_{A,T}$  is the activation energy of thermally induced intensity decay. Our earlier studies of the temperature-dependent CL intensity yielded the activation energy of about 60 meV for  $\Delta E_{A,T}$ .<sup>22</sup> From the equation (1), the value for  $\Delta E_{A,I}$  of  $283 \pm 9$  meV was obtained using the Arrhenius plot shown in Fig. 2(b).

It should be noted that we have extensively applied the above-explained approach to acceptor-doped GaN as well as ZnO compounds.<sup>18–21</sup> In all cases, the activation energy determined from the temperature dependence of irradiation-induced intensity decay coincided with the ionization energy of the dominant deep acceptor species. The deep nature of these acceptors prevents their complete ionization at room temperature, and the neutral (nonionized) acceptor atoms act as traps for nonequilibrium electrons generated by the SEM beam. The filled traps are thereby removed from participating in carrier recombination, resulting in a greater lifetime of nonequilibrium minority holes in the valence band (due to a lower rate of recombination with nonequilibrium electrons) and, consequently, greater diffusion length. The fact that the rate  $R$  diminishes with increasing temperature indicates that there exists a competing, thermally activated process that counteracts the capture of non-equilibrium electrons by neutral acceptor levels, namely, the release of the trapped electron. As the temperature increases, the balance between capture and release shifts toward the latter, reducing the impact of electron irradiation on the carrier lifetime and diffusion length.

Therefore, in light of our prior findings and given the analogous response of ZnO:Li studied in this work, 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 ioniza-

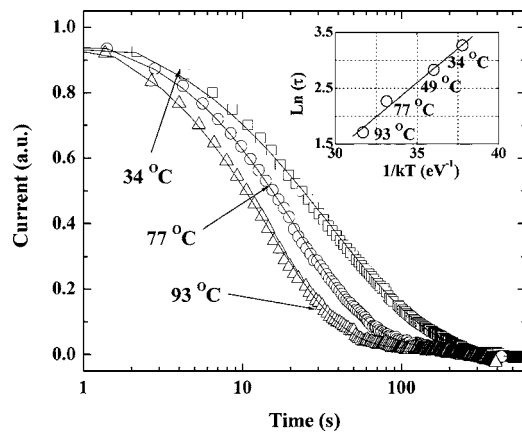


FIG. 3. Decay of photocurrent at variable temperatures under a constant bias of 2 V (open symbols) and the stretched-exponential fit (solid lines). The decay curve at 49 °C is omitted for clarity. **Inset:** Arrhenius plot of the PPC decay time constant as a function of temperature, corresponding to the activation energy of  $245 \pm 22$  meV.

tion energy of around 280 meV. Although several theoretical works have predicted a very shallow  $\text{Li}_{\text{Zn}}$  level,<sup>13,14</sup> these predictions have not been substantiated experimentally, as most studies find a rather deep Li acceptor with activation energies of several hundreds meV.<sup>15,23</sup> In fact, recent first-principles calculations by Wardle *et al.* also suggest that the  $\text{Li}_{\text{Zn}}$  state lies at about 0.2 eV above the valence band maximum,<sup>15</sup> 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 the presence of deep electron traps, persistent photoconductivity takes place when the probability of electron capture is greater than the probability of recombination.<sup>24</sup> Figure 3 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:<sup>25</sup>

$$I(t) = I_0 + A \exp[-(t/\tau)^\beta], \quad (2)$$

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.

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 the Arrhenius plot shown in the inset of Fig. 3. 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-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 the presence of deep electron traps, the Fermi level may lie far below these states. Although shallow donors may capture nonequilibrium 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.<sup>24</sup>

In summary, the impact of Li doping on nonequilibrium carrier transport in ZnO was explored. A Li-related acceptor state with an activation energy of approximately 260 meV was determined to play a key role in electron trapping phenomena. Although its chemical nature is unclear at the moment, this level is associated with an electron irradiation-induced increase of the nonequilibrium carrier lifetime and diffusion length, as well as with strong persistent photoconductivity.

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