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# Group I elements in ZnO

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## ABSTRACT

In this report we focus on the lithium doping of ZnO epitaxial films grown on GaN templates and ZnO substrates. We compare the results with diffusion studies of Li into ZnO single-crystal substrates. The diffused and in-situ doped layers were studied using mass spectroscopy, low temperature photoluminescence and Raman spectroscopy. Li is known to produce a deep acceptor state which takes part in a shallow donor to deep acceptor recombination in the visible spectral region. We will demonstrate that also shallow Li acceptors are introduced depending on the growth/diffusion temperature. The shallow Li-related acceptor has a binding energy around 300 meV. A donor-acceptor pair recombination with its zero phonon line at 3.05 eV followed by LO phonon replica is observed.

The intensity ratio of the zero phonon line compared to the replica indicates weak electron phonon coupling, hence small lattice relaxation in contrast to the recombination with the deep Li acceptor.

## INTRODUCTION

First principles calculations predict shallow levels for the group-I elements Li: 0.09 eV and Na: 0.17 eV [1] with almost no relaxation around the $Li_{Zn}$ acceptor [2], and a small outward relaxation for the surrounding oxygen atoms in the case of $Na_{Zn}$. This is in contrast to the EPR investigations reported by Schirmer in 1968 [3] on ZnO:Li. The interpretation of the hyperfine data showed that the hole is primarily located on one neighbouring oxygen atom along the c-axis and induces a substantial distortion. It is the reason why $Li_{Zn}$ is a deep acceptor with a binding energy of 800 meV. $Na_{Zn}$ behaves similar, the binding energy is 600 meV [4]. Both defects are responsible for broad strong phonon coupled luminescence bands in the visible spectral range with maxima at 2.1 eV (Li) and 2.17 eV (Na). The acceptors show up in shallow donor to deep acceptor recombinations as demonstrated by optically detected magnetic resonance experiments [5, 6]. For the conversion from n-type to high resistive ZnO:Li Zwingel [7] showed that the conductivity decreased in inverse proportion to the square of the Li concentration. Only 1% of the total Li concentration was effective in the compensation of the donors already present in the crystal. Zwingel assumed equal concentrations for the interstitial Li donors and $Li_{Zn}$ acceptors and postulated the existence of another Li acceptor, needed to model the reaction kinetics. It should arise from the pairing of two Li centres. Up to now this defect has not shown up in the radiative recombinations of ZnO:Li.

## EXPERIMENTAL DETAILS

ZnO epitaxial films doped with Li were grown by CVD either on GaN/Sapphire templates (metallic Li as precursor, growth temperature 580 °C) or on ZnO substrate (Tokio Denpa) with $LiNH_2$ as precursor at a growth temperature of 700 °C. Figure 1 shows the low temperature photoluminescence of the homoepitaxially grown ZnO:Li film.

The quality of the films can be directly deduced from the line width of the excitonic recombinations. For the homoepitaxial films it is 0.1 meV, and it is a factor of 30 larger on the heteroepitaxial film (see Figure 1). This reflects the lower structural quality, but also the higher background concentration of donors, since Ga diffuses from the template diffuses into the ZnO layer as shown by SIMS experiments. The recombinations shown in Figure 1 are numbered according to Reference [8]. $I_6$ and $I_7$ are caused by neutral donor bound excitons [9], for $I_{10}$ magnetic field experiments (Zeeman splitting) are not yet available to allow for a definite assignment. $I_0$ to $I_2$ are in the energy range where ionized donor bound exciton recombinations have been observed [8, 9]. The free exciton transition (FX in Figure 1) is observable already at 2 K, again an indication of high crystalline quality.

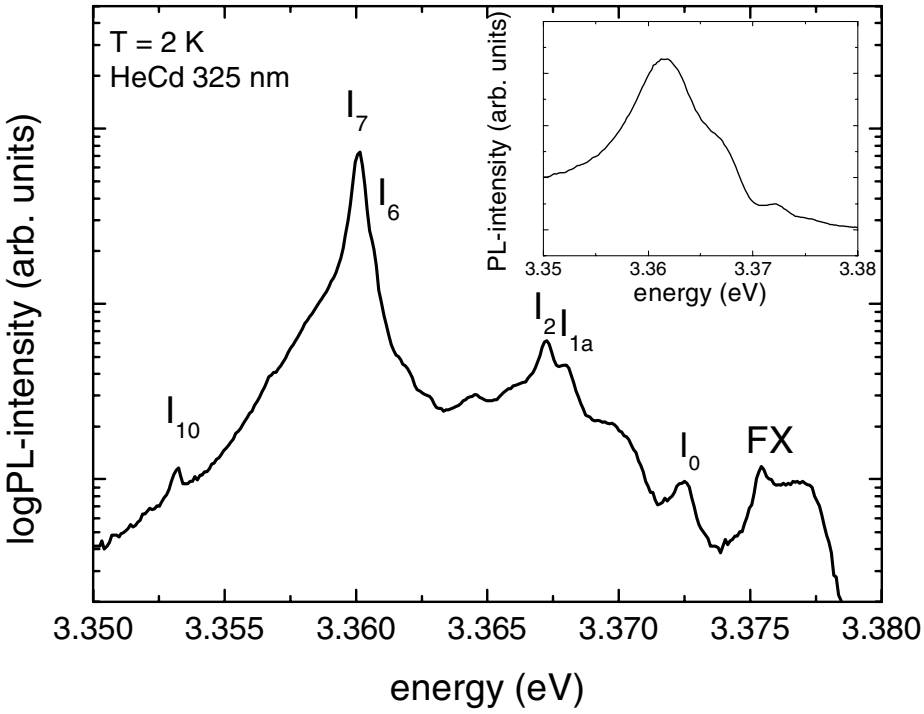


**Figure 1:** Band edge luminescence of epitaxial ZnO:Li on ZnO substrate, the inset shows the result for a heteroepitaxially grown ZnO:Li film on GaN-templates.

Figure 2 gives an overview of the recombinations occurring between 3.1 and 1.8 eV. In the range from 3.1 to 2.8 eV a series of lines show up which have so far not been reported. The luminescence starts at around 3.05 eV (see Figure 2.a) and shows pronounced coupling to longitudinal optical (LO) phonons separated by 72 meV. This is typical for a donor-acceptor pair (DAP) recombination. The coupling strength given by the Huang-Rhys factor S is estimated from the Poisson distribution $I=I_0 S^n/n!$ where n runs from 0, 1, 2 .. and $I_0$ is the intensity of the first, the zero-phonon line (ZPL). For S one obtains a value of $0.35 \pm 0.05$, i.e. weak electron phonon coupling. If we assume a value of 50 meV for the donor binding energy $E_D$, and neglect the coulomb interaction one obtains an acceptor binding energy $E_A$ around 300 meV (from the transition energy $E(h\nu)=E_g - E_D - E_A$, $E_g$=3.44 eV at 2K). The DAP transitions is obviously more pronounced in the heteroepitaxial sample. In the homoepitaxial film only the first two lines can be resolved. The transition energy is shifted to lower energies which indicates lower background carrier densities n ($E(h\nu)= E_g - E_D - E_A + \alpha n^{1/3}$, $\alpha$ being a constant) .

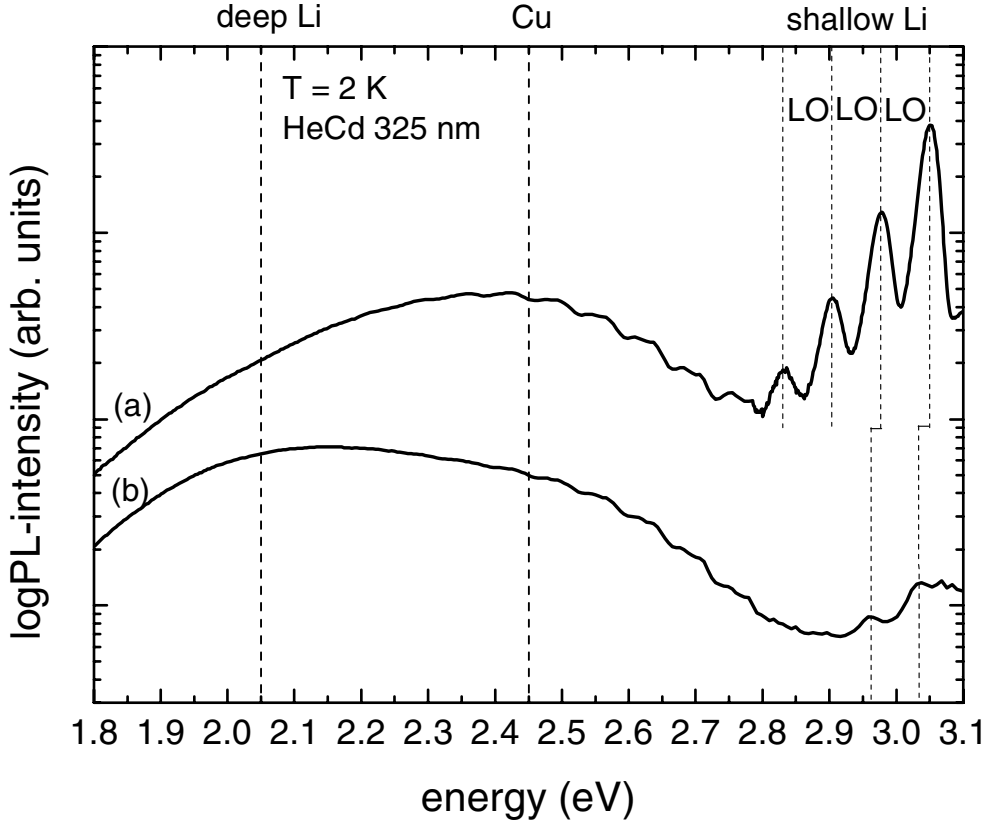


**Figure 2:** Photoluminescence in the blue and visible spectral range showing donor acceptor pair recombination at 3.05 eV with LO replicas, the Cu emission and the deep Li acceptor related band at 2.05 eV (a: ZnO:Li/GaN; b: ZnO:Li/ZnO)

In the visible spectral range the Cu green emission is found in both samples, it starts around 2.77 eV and has a pronounced phonon structure. For the homoepitaxial film in addition a deeper recombination band around 2.05 eV is superposed. The differences between the two samples – apart from structural quality – are related to the different growth temperatures as shown by diffusion experiments.

For the diffusion experiments we used state of the art ZnO bulk crystals from CrysTec. Salts containing group-I elements (mainly nitrates and carbonates) were brought into aqueous solutions, the surfaces of the crystals were covered with the solutions and carefully dried by a fan before being put into the diffusion oven. Diffusions were carried out in nitrogen atmosphere in a temperature range between 300 and 800 °C for 10 minutes. The samples were removed from the oven at the diffusion temperatures and quenched to room temperature.

Depending on the diffusion temperature the same DAP band at 3.05 eV is found. Its intensity is strongest for the temperature interval between 450 and 650 °C (see Figure 3). The lower growth temperature of ZnO/GaN is reflected in a higher intensity of the DAP band at 3.05 eV. This is in contrast to ZnO/ZnO film with a growth temperature of 700 °C where the DAP band is very much reduced in intensity. However, the deep recombination at 2.05 eV which is caused by the deep Li acceptor has gained in intensity considerably. This leads us to the conclusion that the shallow acceptor connected with the 3.05 eV band is i) Li related, and ii) is introduced only in a narrow temperature range. At temperatures above 750 °C only the deep Li acceptor is formed in agreement with previous diffusion studies carried out at a temperature of 850 °C.

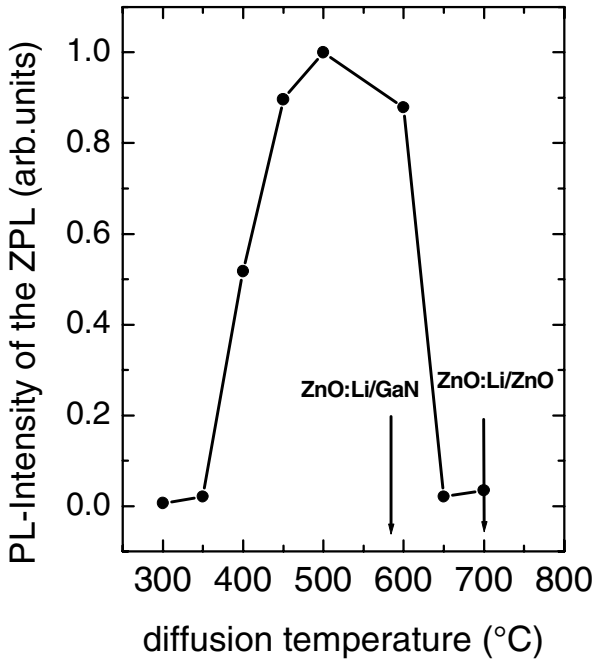


**Figure 3:** Intensity of the zero phonon line (ZPL) of the recombination at 3.05 eV in Li diffused ZnO as a function of the diffusion temperature. The growth temperatures of the two ZnO films are indicated.

The DAP band around 3.05 eV shows weak electron phonon coupling which indicates very small lattice relaxation. If we assume that also for the shallow Li acceptor Li is incorporated on a Zn site, we have the same core for the acceptor structure - a shallow centre without significant relaxation and a deep one with significant relaxation. Zwingel [7] postulated the existence of another Li acceptor, which is needed to model the reaction kinetics. It should arise from the pairing of two Li centers. If both were on lattice sites there was no driving force for pairing (coulomb repulsion). A substitutional-interstitial configuration would result in a neutral defect pair. It is obvious that another partner is needed to stabilize the binding and reduces the distortion on the Li-O distance in order to be compatible with the weak electron phonon coupling found in the luminescence experiments. A single acceptor state could result from a configuration where a positively charged hydrogen atom is involved, i.e. a $Li_{Zn}$-H-$Li_{Zn}$ complex. This defect model would be similar to the one proposed for the Cu(III) center in ZnO [10]. Raman experiments could not detect any Li related vibrational modes, the Li doped films only showed the lattice modes of ZnO.

## CONCLUSION

In conclusion, Li doping of ZnO in comparison with Li diffusion into ZnO produces a new donor acceptor pair recombination at 3.05 eV. The Li related acceptor has a binding energy around 300 meV. This shallow acceptor state can effectively be introduced only if the growth/diffusion temperature is below 700 °C, otherwise the 800 meV deep acceptor state is formed. The limited range of stability is an indication of pair formation, and a possible defect model has been presented in which hydrogen may play an essential role.

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