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# Donor–acceptor pair luminescence of nitrogen doping p-type ZnO by plasma-assisted molecular beam epitaxy

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**Abstract**

We have grown N-doped p-type ZnO films by plasma-assisted molecular beam epitaxy. A dominant photoluminescence around 3.260 eV was observed at low temperature. By studying the dependence of photoluminescence on excitation density at 80 K, the emission around 3.260 eV can be attributed to a donor–acceptor pair transition. Time-resolved PL spectrum was also used to investigate the dynamics of the donor–acceptor pair recombination. The observed non-exponential decay curve was fitted by a fast component and long process. In long decay process, the curve was predicted to follow the power law $t^{-1}$. Therefore it can be concluded that the emission at 3.260 eV in our sample is of a tunnel-assisted donor–acceptor pair nature.


*Keywords:* p-Type ZnO; Optical properties; Donor–acceptor pair; Molecular beam epitaxy

## 1. Introduction

The recent progress in ZnO-based devices including efficient blue light-emitting diodes (LEDs) has demonstrated its potential [1]. As is well known, presently p-type ZnO doping is achieved more readily with N impurities [2,3]. Moreover, N-doped p-type ZnO films were obtained by all kinds of technologies such as molecular beam epitaxy (MBE) [2,3], metal organic chemical vapor deposition (MOCVD) [4], radio-frequency sputtering deposition [5], even many chemical methods. However, many aspects of the basic properties of p-type ZnO and related semiconductors remain to be not understood completely. Photoluminescence (PL), as a undestructive and sensitive method, is widely used to gain information on crystal quality, defect properties; especially, this method can present effectively the impurity energy level in band gap for the doing of semiconductors. The optical properties of the undoped ZnO have been widely studied [6], in which ultraviolet (UV) emissions originating from free and bound excitons and visible emission related to intrinsic defects such as oxygen vacancies were confirmed. However, for N-doped p-type ZnO, the origin of some newly observed PL emission bands located at 3.230–3.250 eV and 3.150–3.170 eV is not quite clear. One pointed out that these emissions are from bound exciton related to nitrogen acceptors [2]. Another one considered it to be originating from a donor–acceptor pair (DAP) [7].

This paper is concerned with the confirmation of PL spectrum at low temperature showing a dominant emission band at 3.260 eV in N-doped ZnO epitaixal layers grown on sapphire substrates by plasma-assisted molecular beam epitaxy (P-MBE). The measurements to determine the dependence of PL on the excitation density and temperature were carried out to investigate the optical properties of the N level. The time-resolved PL measurements on a p-type ZnO epilayers, by which the observed luminescence can be well understood in terms of the DAP recombination.

## 2. Experimental details

The ZnO epilayers used in this study were grown by P-MBE on *a*-plane sapphire substrates. Nitrogen dopant of

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p-type ZnO was produced by a radio-frequency NO plasma with a purity of 99.999%. The carrier concentration of p-type ZnO at 300 K is $2 \times 10^{16}\,cm^{-3}$ determined by Van der Pauw method in a magnetic field of 1 T by using Lakeshore Company Hall system 7407. The excitation source in PL measurement was the 325 nm line of a He–Cd laser, and the sample temperature was controlled between 80 and 300 K by using a liquid nitrogen cooling system. The time-resolved lifetime was measured using the time-correlated single photon counting technique with FL920-flurescence lifetime spectrometer, and a nF900 nanosecond flashlamp was used as excitation source.

## 3. Result and discussion

Fig. 1 shows the PL spectra at 80 K for the undoped ZnO and N-doped epilayers. The peak at 3.366 eV for the undoped ZnO epilayers is related to the excitons bound to shallow neutral donors ($D^0X$) [6], and the emission bands centered at 3.320 and 3.240 eV are attributed to the first and the second longitudinal optical-phonon replicas (1LO and 2LO) related to free exciton of ZnO. For N-doped p-type ZnO, a new and weaker UV emission peak located at 3.347 eV comparing to undoped ZnO is attributed to the emission of excitons bound to neural acceptors ($A^0X$). The dominant emission at 3.260 eV and the satellite band at 3.186 eV, which have the energy difference of 72 meV, are attributed to the DAP transition and its 1LO phonon replicas, respectively. The spectra have been measured under different excitation intensities. The 80 K emission spectra obtained at different excitation intensities are shown in Fig. 2. A blue shift in the peak position with increasing excitation intensity can be seen clearly. The inset of Fig. 2 shows the PL spectra at selected temperatures for N-doped ZnO. As the temperature is increased, the intensities of these peaks at 3.260 and 3.186 eV decrease rapidly by the same thermal quenching rate, as expected for the DAP transition.

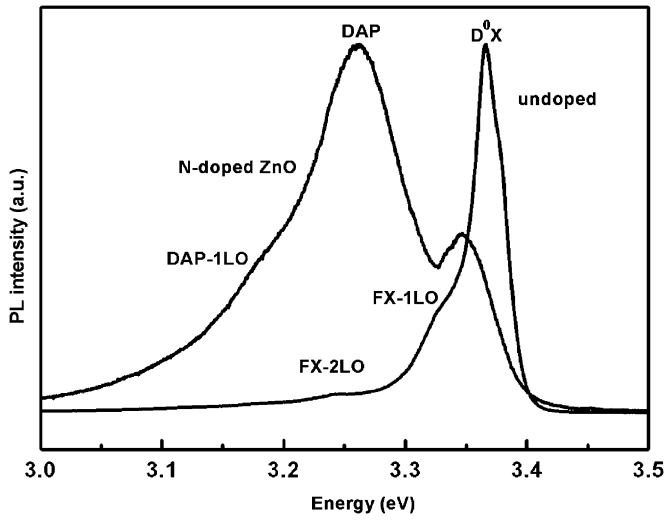


Fig. 1. PL of undoped and p-type ZnO.

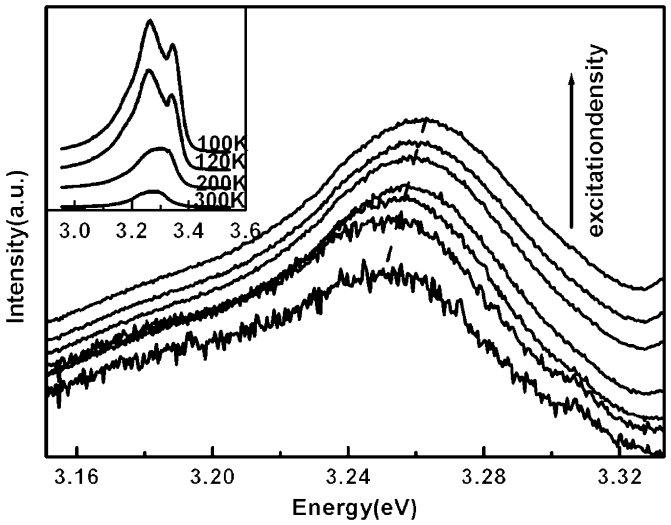


Fig. 2. PL spectra of p-type ZnO under different excitation density at 80 K. The inset shows the select temperature PL spectra of p-type ZnO.

For a distant DAP, the energy of photon resulting from radiative recombination is given by [8]

$$h\nu_{DA} = E_g - E_D - E_A + \frac{e^2}{4\pi\varepsilon R_{DA}},$$

where $E_g$ is the band gap of ZnO, $E_D$, $E_A$ are the donor and acceptor binding energies, respectively, $\varepsilon$ is the dielectric constant of ZnO, $R_{DA}$ is the distance between the involved donor and acceptor. With increasing the excitation intensity, the numbers of occupied donor and acceptor centers increase and their average distance $R_{DA}$ necessarily decrease. Consequently, it can be found that the emission line of pair-band shifts to the higher energy with increasing excitation intensity due to the Coulomb term in the above-mentioned equation. Here, we estimated the Coulomb energy from the residual donor density estimated by Hall measurements at room temperature on undoped ZnO layer. The residual donor density($N_D$) was about $5 \times 10^{17}\,cm^{-3}$ and the mean distance between donor and acceptor ($R_{DA}$) was roughly estimated by $(3/4\,\pi N_D)^{1/3}$. The Coulomb energy was calculated to about 21.543 meV. The value of acceptor binding energy was then obtained to about 142 meV by the above estimation and it accorded with the result of $160 \pm 45$ meV reported by Zeuner et al. [9].

In order to further understand the origin of the observed emission lines, their dynamical behaviors have been studied. Fig. 3 shows the PL temporal response of the 3.260 eV band measured at 80 K. At low temperatures, PL decay is non-exponential, but can be approximated by two exponential decays as illustrated by the dash-fitting curve in Fig. 3. At 80 K, the typical lifetime of the fast component is about 2.95 ns and the slow component is about 14 ns. Based on a theoretical model developed by Avouris and Morgan [10], the decay kinetics of both the band-to-impurity and DAP recombination are nor necessarily

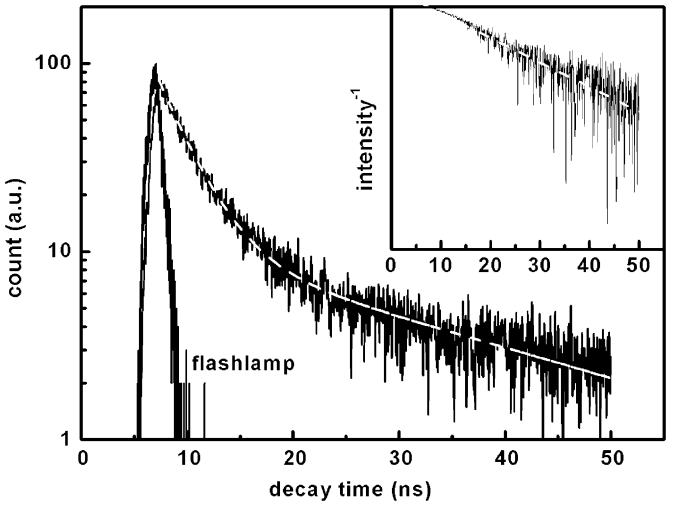


Fig. 3. Decay curves of the emission at 3.26 eV at 80 K. The inset shows PL intensity at longer decay time with the decay time. White dash line presents fitting result.

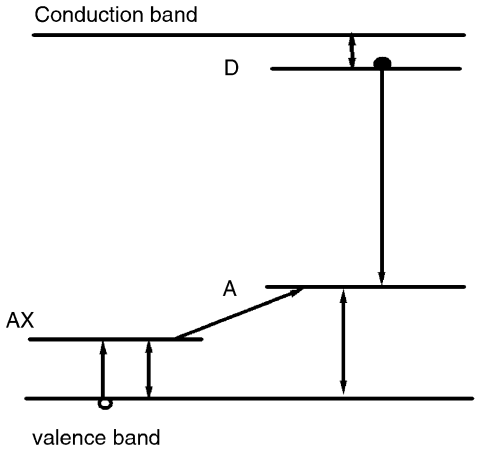


Fig. 4. Model of the tunnel-assisted DAP recombination of p-type ZnO.

exponential. The decay at longer delay can perfectly follow $t^{-1}$ as shown by dash line in the inset of Fig. 3. This observation agrees excellently with the predicted hyperbolic $t^{-1}$ decay at longer delay times for the radiative DAP recombination through tunneling [10]. To interpret the physical process, a hypothetical recombination model for the emission at 3.260 eV according to the reference 10 is shown in Fig. 4. In this figure, the D, A and AX present the donor level, acceptor level and hole traps. For the N-doped ZnO, nitrogen may form the AX centers capturing the holes besides the effective acceptors A, as predicted Park et al. [11]. In the N-doped ZnSe [11] and Mg-doped GaN [12], it can be seen that the dopants can form stable "AX" centers as hole traps. According to the results above, the acceptor level A is located at the 140 meV above the valence band; since the ionization energy of level A is larger than the thermal energy, the carrier transitions from the level A to the valence band can be neglected. The AX level captures non-equilibrium holes from the valence band during the optical excitation process and it competes with the level A for obtaining excess holes. With the increase in temperature, the holes captured by the AX level tunnel to the A level. The luminescence occurs when the electrons bound to donors recombinating radiatively with the holes bound to the nitrogen acceptors.

## 4. Conclusion

In summary, the optical properties of nitrogen-doped p-type ZnO grown by P-MBE were investigated. It has been demonstrated that the p-type ZnO exhibits a strong near band edge luminescence at 3.260 eV. The origin of this emission is attributed to the tunnel-assisted DAP recombination by (a) the emission peak blue shift with the excitation intensity and (b) the luminescence intensity at longer decay times follows the power law of $t^{-1}$.

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