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Variation of N acceptor energy induced by Al–N codoping in ZnO films

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ABSTRACT

Recombination mechanisms of Nitrogen-related emissions in undoped and Al–N codoped ZnO films were investigated by low temperature photoluminescence spectra. The peak near 3.312 meV was existed both in these two kinds of ZnO films. This peak was classified as the transition of the acceptor-bound exciton (A^0X) related to N_O acceptor. The A^0X transition peak in Al–N codoped ZnO films shifted to lower energy comparing with the position of A^0X in undoped ZnO films. This phenomenon was induced by the incorporation of Al. A photoluminescence recombination possibly due to free-electron-to-acceptor (FA) transition was observed at temperatures higher than 40 K in Al–N doped ZnO films. The acceptor ionization energy was estimated from the energy position of the FA luminescence to be 183.7 meV. Moreover, the excitation intensity-dependent PL spectra which taken at 80 K in Al–N codoped ZnO film was measured. The luminescence band labeled donor–acceptor pair (DAP) shifts to higher energies with increase excitation intensity.

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1. Introduction

Zinc oxide has a high exciton binding energy of 60 meV at room temperature [1], and it is considered to be a new photo-electric material in shortwave length as GaN. For fabricating ZnO-based optoelectronic devices, however, both n-type and p-type materials are required. Nitrogen has been proved to be the most promising dopant for the growth of p-type ZnO [2], and many groups have reported p-type ZnO by doping or codoping methods [3–7]. Recently, we produced the N monodoped and Al–N codoped ZnO films by RF-assisted MOCVD. The Hall measurement shown that the Al–N codoped ZnO films display p-type properties with resistivity of 560 Ω cm, carrier density of 1.2×10^{17} cm^{-3} and Hall mobility of 0.093 cm^2/Vs, and the results unchanged two weeks later. While the resistance of N doped ZnO films was rather high. In this letter, the acceptor-bound exciton (A^0X) transition in the temperature-dependent photoluminescence spectra was observed both in undoped and Al–N codoped ZnO films. We shall focus on the difference of A^0X position in undoped and Al–N codoped ZnO films and the observation of the free-electron-to-acceptor (FA) transition to reveal the different Nitrogen-related recombination mechanisms.

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2. Experimental procedure

Undoped and Al–N codoped ZnO films were grown on quartz substrates by RF-assisted MOCVD. In this system, the orientation of electric field generated by RF equipment is parallel to the substrate, and the RF equipment is very close to the susceptor. Carrier gas which is introduced from the top of the chamber can bring N atoms into reaction surface timely. For undoped ZnO film, the growth proceeded at 620 °C for 40 min under vacuum with Diethylzinc (DEZ) and CO_2 as sources precursors, and purified N_2 as carrier gas. For Al–N codoped ZnO film, the growth proceeded with following steps: firstly, intrinsic ZnO was grown for 10 min as buffer layer, then Trimethylaluminum (TMA) was introduced, and turn on the button of RF power simultaneously. The doping process was maintained at 620 °C for 30 min. In order to improve the quality of ZnO films, all samples were annealed in N_2 ambient (humidity: 23%) at 700 °C for 1 h after growth. Photoluminescence spectra were measured using a He–Cd laser excited at 325 nm at a temperature ranging from 10 K to 250 K.

3. Results and discussion

The PL spectra range from 3.0 eV to 3.4 eV taken at 10 K for undoped and Al–N doped ZnO films are compared in Fig. 1. Curve a and curve b correspond to undoped ZnO film and Al–N codoped ZnO film, respectively. The UV PL spectrum for undoped ZnO film consists of three main emission bands, located at 3.360 eV, 3.313 eV, 3.24 eV, respectively, and a weak broad band centered at 3.17 eV. The peak at 3.360 eV has earlier been classified as an acceptor-bound exciton associated with an acceptor, whose ionized energy is 79 meV [8]. However, it is too shallow for a simple substitutional acceptor. Some researches assigned it to a transition of excitons

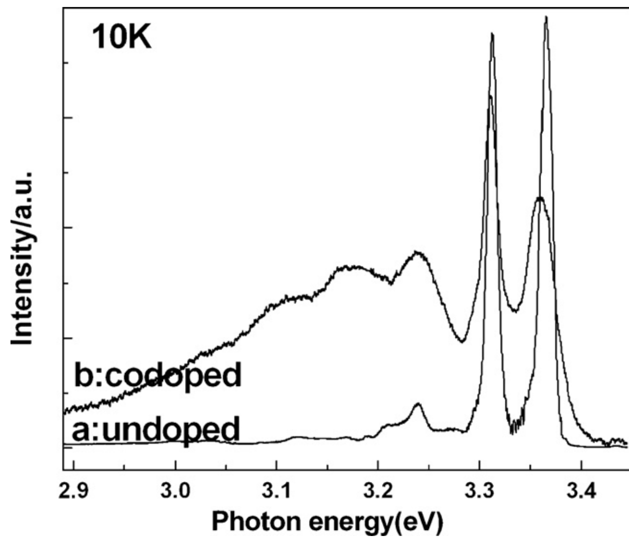

Fig. 1. Low-temperature PL spectra of undoped ZnO (a) and Al–N codoped ZnO (b) measured at 10 K.

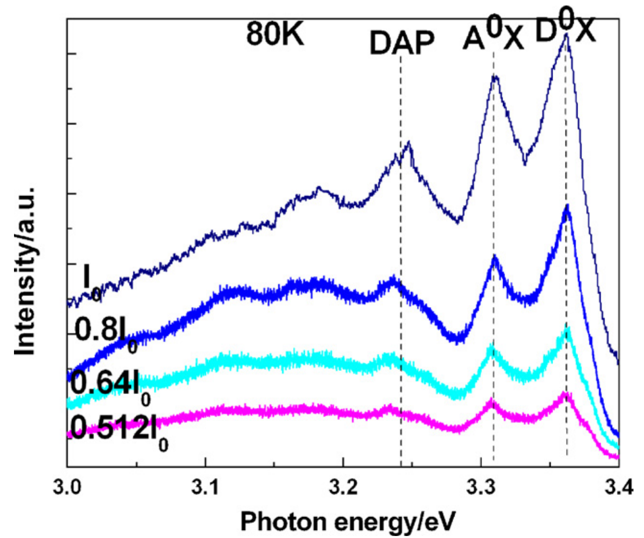

Fig. 2. Excitation intensity-dependent PL spectra of Al–N codoped ZnO film measured at 80 K.

bound to ionized donors or the rotator state of the neutral-bound-exciton [9–11]. Another sharp excitonic-type line at 3.313 eV has been observed in many undoped ZnO films, and been classified as A^0X recombination associated with N_O acceptor. The shoulder of this peak at lower energy corresponds to the LO replicas of D^0X-LO. The broad bands centered at 3.24 eV can be attributed to the superposition of a donor–acceptor pair (DAP) and LO replicas of A^0X-LO, respectively.

In comparing the undoped and Al–N doped ZnO films, it can be seen that the line at 3.312 eV nearing the "deep" A^0X line at 3.313 eV in the undoped sample, dominated over the D^0X line which is located at 3.359 eV. The increase of the intensity of A^0X line may be induced by the large number of N_O centers in Al–N codoped ZnO film. The position of the A^0X line in the codoped sample is a little below than that in the undoped samples, and this phenomenon has also been seen by Look et al. [9]. While, compared with the undoped sample, the A^0X line in the codoped sample shifts to the band gap energy of itself. The peak locate at 3.170 eV, 3.102 eV, 3.03 eV are the LO replicas of DAP.

Moreover, in order to investigate the Nitrogen-related recombination mechanisms, the excitation intensity-dependent PL and temperature-dependent PL measurements of Al–N codoped sample were performed, respectively. It is known that the peak energy of the DAP recombination follows the general form [12]:

$$E_{\mathrm{DAP}} = E_{\mathrm{g}} - (E_{\mathrm{D}} + E_{\mathrm{A}}) + \frac{e^2}{4\pi\varepsilon R_{\mathrm{DA}}} \quad (1)$$

where E_g, E_D, E_A, and e, ε are band gap energy, donor binding energy, acceptor binding energy, elementary electric charge and dielectric constant, respectively, R_{DA} is the distance between the involved donor and acceptor. When the excitation intensity increased, the number of occupied donor and acceptor centers increases, resulting in decrease of their average distance R_{DA}, so that DAP luminescence peak shows a blue-shift. Fig. 2 shows excitation intensity-dependent PL spectra taken at 80 K. It indicates that the emission of the peak assigned as DAP shifts to higher energy with the increase of excitation intensity, which is consistent with the characteristics of DAP mentioned above. This phenomenon further supports our assignment of DAP.

Fig. 3 shows the temperature-dependent PL spectra for Al–N doped ZnO film, which shows that the 3.359 eV and 3.311 eV band reveal red shift with increasing temperature, while the 3.242 eV band shows no obvious shift with the increase of temperature. A new luminescence line which located at the higher energy side of DAP appeared at temperatures exceeding 40 K, which is assumed to be free-electron-to-acceptor (FA) transition. And it is evident that the DAP peak quenches rapidly with increasing temperature and the FA intensity gradually exceeds the intensity of DAP. In standard PL, the ionization energy of an acceptor impurity can be accurately determined from the energy position of the free-electron-to-acceptor (FA) transition at a low temperature. On the other hand, the energy position of DAP band can only give a rough estimate of the level of acceptor ionization energy. FA luminescence has been observed at higher temperatures at which the donors are efficiently ionized [11]. The temperature dependence of FA band centered at 3.246 eV can be well described as the following [13]:

$$E_{\mathrm{FA}}(T) = E_{\mathrm{g}}(T) - E_{\mathrm{A}} + \frac{KT}{2} \quad (2)$$

where $E_g(T)$ is the temperature-dependent band gap, and following the Varshni-type equation [14], E_A, K, and T are acceptor level, Boltzmann constant, and temperature, respectively. By fitting the energies of the FA band at different temperatures with Eq. (2),

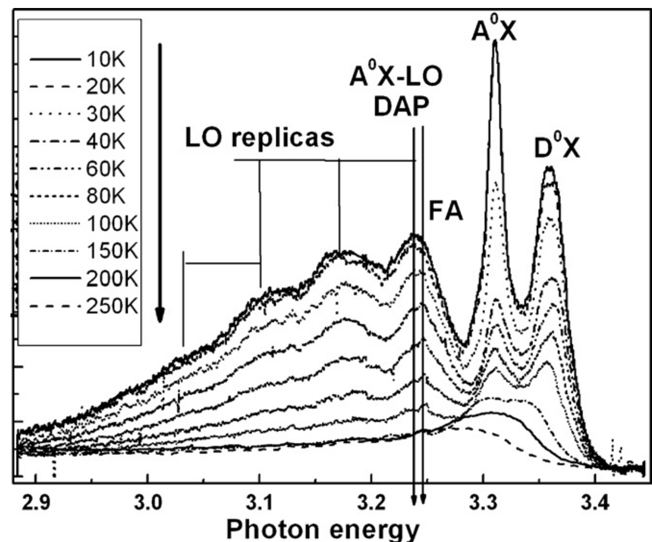

Fig. 3. Temperature-dependent PL spectra of Al–N doped ZnO film measured at temperatures from 10 K to 250 K.

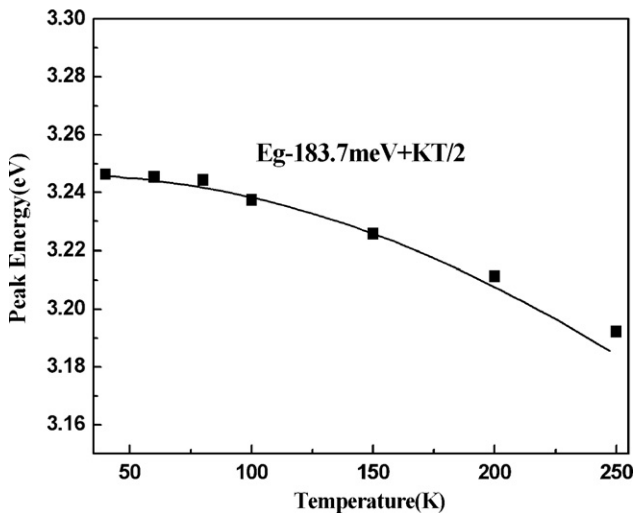

Fig. 4. Temperature-dependent photon energies of FA indicated in Fig. 3. The solid lines represent the fitting to the data.

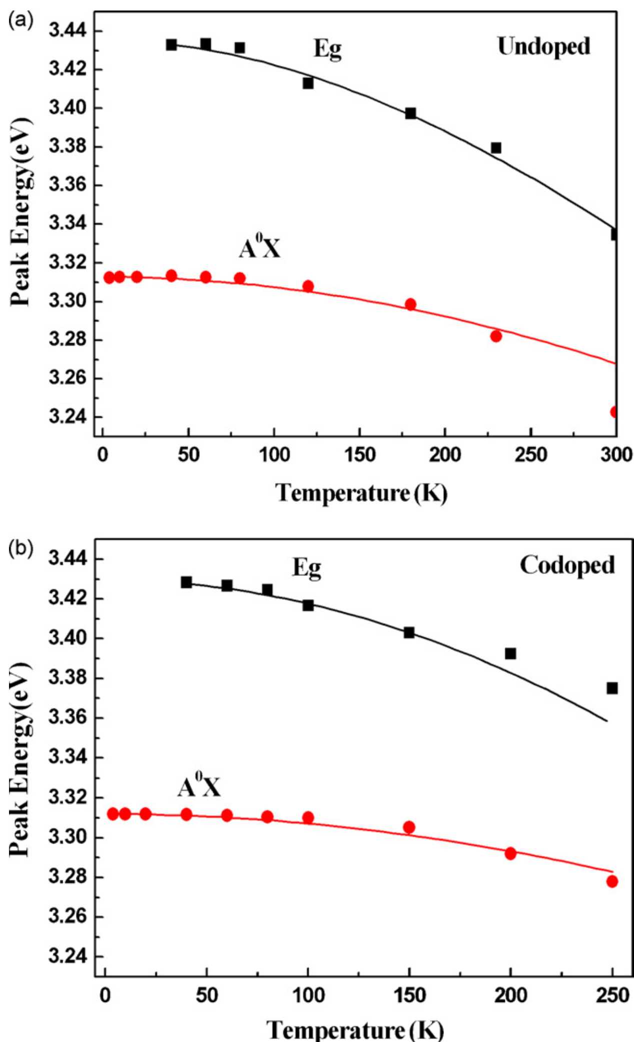

Fig. 5. PL peak energies as functions of temperature for undoped (a) and Al–N codoped (b) ZnO films. The dots are experimental data and the solid lines are fitting curves.

as shown in Fig. 4, the N_O acceptor level can be estimated to be about 183.7 meV. Using the Haynes rule $E_{loc} = A + B \times E_A$, where $A = -3.8$ meV, $B = 0.365$ [10], E_A is the binding energy between the acceptor and free exciton, the E_{loc} is estimated to be 63.24 meV. Also it is too large for the binding energy to the acceptor, while, there is no strong evidence that Haynes Rule even applies in ZnO, especially for acceptors. On the other hand, if there real being large binding energy to the acceptor, the A^0X will exist in room temperature, so the origin of UV luminescence in room temperature is consist of A^0X and FX.

The band gap variation with temperature can be described adequately using Varshni equation,

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \quad (3)$$

where α and β are constants. For undoped ZnO, the parameters in Eq. (3) are $E_g(0) = 3.435$ eV, $\alpha = 0.0015$ eV/K, $\beta = 1091$ K; For Al–N codoped ZnO, the parameters in Eq. (3) are $E_g(0) = 3.429$ eV, $\alpha = 0.0039$ eV/K, $\beta = 3647$ K.

The temperature dependence of A^0X exciton transition energy also can be described by Varshni equation,

$$E(T) = E(0) - \frac{\alpha T^2}{\beta + T} \quad (4)$$

where $E(0)$ is the A^0X exciton energy at zero temperature, α and β are the temperature coefficients. For undoped ZnO, the parameters in Eq. (4) are $E(0) = 3.313$ eV, $\alpha = 0.0022$ eV/K, $\beta = 4100$ K; For Al–N codoped ZnO, the parameters in Eq. (4) are $E(0) = 3.312$ eV, $\alpha = 0.0041$ eV/K, $\beta = 8600$ K. Fig. 5 shows that the experimental data can be well fitted by Eqs. (3) and (4).

Applying Haynes' Rule which has been referred in last paragraph, the 3.3126 eV line in undoped ZnO film corresponds to an acceptor at about 184.8 meV. While the 3.311 eV line in Al–N codoped ZnO film corresponds to an acceptor at about 166.6 meV. These results are in agreement with the value calculated using FA. The codoping method results shallower acceptor energy level. The small binding energy is helpful for acceptor ionization, resulting in a higher hole concentration in the codoping epilayer.

4. Conclusions

In summary, the photoluminescence properties in undoped and Al–N codoped ZnO films have been investigated by temperature-dependent PL spectra. The peak at 3.312 meV was existed both in all samples was classified as the transition of the acceptor-bound exciton (A^0X) related to N_O acceptor. Moreover, the excitation intensity-dependent PL spectra, which taken at 80 K in Al–N codoped ZnO film, show that the DAP emission peak shifts to higher energies with increase excitation intensity. By fitting the experimental data using Varshni equation, the acceptor-bound energies for undoped and Al–N codoped epilayers are about 184.8 meV and 166.6 meV, respectively. And the acceptor ionization energy decreased due to the incorporation of Al. A photoluminescence recombination possibly resulted from free-electron-to-acceptor (FA) transition was observed at temperatures higher than 40 K in Al–N codoped ZnO films. Activation energy of the Nitrogen-related acceptor level was estimated to be 183.7 meV. This value is in agreement with the results calculated by Varshni equation and Haynes rule.

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