Short communication

Optical investigations of Be doped ZnO films grown by molecular beam epitaxy

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A B S T R A C T

In this article, the optical properties of ZnO:Be films grown by plasma-assisted molecular beam epitaxy were investigated by the excitation density-dependent and temperature-dependent photoluminescence measurements. The low temperature photoluminescence spectra showed a dominant excitons bound to neutral donors (D°X) emission centered at 3.3540 eV and strong donor-acceptor pair (DAP) transitions at 3.3000 eV. In addition, it showed that the intensity ratio of the DAP and D°X peaks changed with background electron concentration. Furthermore, a shallow acceptor state with ionization energy of 116 meV was found and attributed to Zn vacancy. The present study further suggests that Be and N codoping ZnO might be suitable for fabricating reliable p-type ZnO materials.

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1. Introduction

Due to the wide band-gap ($E_g = 3.37$ eV at room temperature) and large exciton binding energy ($E^b = 60$ meV), zinc oxide (ZnO) has attracted great attention in recent years [1–4]. However, the lack of reliable p-type ZnO materials hindered the development of ZnO-based photoelectric device. BeZnO alloys were proposed recently to engineer the energy band-gap of ZnO materials. The structural, optical, electrical and piezoelectric properties were investigated experimentally and theoretically in several groups [5–13]. However, beyond band-gap engineering, it was suggested that alloying BeO into ZnO:N films may be a promising way to solve the p-type doping problem, since the solubility and thermal stability of nitrogen (N) acceptor in ZnO:N film were highly enhanced by adding Be atoms [14,15], and the fact that the N acceptor transition energies became shallower when the number of its nearest neighbor Be atoms increases [16,17]. Furthermore, the formation of intrinsic hole-killers, e.g., oxygen vacancies (O_V), was greatly suppressed in BeZnO alloys [18]. However, Be and N co-doping ZnO with a high Be dose were unfavorable since a certain amount of Be atoms moved into interstitial sites at a high Be flux [19–21]. The interstitial Be atoms (Be_i) are double donors

which can efficiently compensate N acceptor and also reduce carrier mobility. Despite reports of progress results, the information available in this area is still very limited. The evolution of intrinsic defects in Be doped ZnO (ZnO:Be) films is unclear at this stage.

Photoluminescence (PL), as a non-destructive and sensitive method, was widely used to gain information on crystal quality and defect properties. In the present work, the optical properties of ZnO:Be films were investigated by the excitation-power density-dependent and temperature-dependent PL measurements. The low temperature ($T = 30$ K) PL spectra of ZnO:Be films showed a dominant excitons bound to neutral donors (D°X) emission centered at 3.3540 eV and strong donor-acceptor pair (DAP) transitions at 3.3000 eV. Intrinsic Zn vacancies (Zn_V) acceptor defects were found in ZnO:Be films. One interesting feature in ZnO:Be films was that the intensity ratio of the DAP and D°X emissions varied with background electron concentration.

2. Experimental

The ZnO:Be films under investigated were grown by plasma-assisted molecular beam epitaxy, with Zn (6N) and Be (4N) supplied by solid source effusion cells, and O supplied from 6 N oxygen through an RF plasma generator. Before growth, designed buffer layers were inserted between c-sapphire substrate and the epitaxial film. The experimental details can be found elsewhere [22]. After the buffer layer annealed at 750 °C, a series of ZnO:Be

films with different Be compositions were deposited at 650 °C [18]. During the growth, conditions were kept unchanged except for Be flux. Here, the Be composition in ZnO:Be film was modulated by tuning the temperature of Be source (T_{Be}, T_{Be} = 950, 960, 970 and 980 °C). The higher temperature, the more Be composition, as confirmed by quantitative elemental analysis [18]. The Be compositions in ZnO:Be films were measured by time-of-flight secondary ion mass spectrometry (TOF-SIMS). The background electron concentration of ZnO:Be films were quantified by van der Pauw configured Hall effect system. The room temperature electron concentration of ZnO:Be films are $\sim 2 \times 10^{16}$ cm^{-3}, 3×10^{15} cm^{-3}, 1×10^{16} cm^{-3} and 3×10^{16} cm^{-3} for T_{Be} = 950 − 980 °C, respectively. High resolution XRD (HRXRD) was performed to investigate the structural properties of the as-grown films. PL measurement was conducted at temperatures ranging from 30 to 300 K, and the emitted light was dispersed by an Omni-λ500 spectrometer with a 1200/mm grating. The surface of the films was illuminated by 325 nm UV light emitting from a *cw* He–Cd laser. The power of the incident light beam upon the sample was varied from 0.8 to 4 mW.

3. Results and discussion

Fig. 1 shows the low temperature (*T* = 30 K) PL spectrum of ZnO:Be film prepared at T_{Be} = 960 °C. The PL spectrum of ZnO film prepared under same condition is also illustrated. As can be seen, the two samples show similar PL spectra. The PL spectra are dominated by a strong emission line at 3.3540 eV which can be attributed to D°X (Figs. 1 and 4). The full width at half maximum (FWHM) of the D°X emission line for ZnO and ZnO:Be films are 6.5 meV and 6.0 meV, indicating that the crystalline quality of the obtained ZnO:Be film is comparable to the ZnO film. This is consistence with HRXRD observations [18]. In addition, a weak band on the high energy side centered at 3.3660 eV could be attributed to I_8 emission line [23]. Another weak emission at 3.3697 eV could be assigned to free exciton (FX) emission. In contrast, the ZnO:Be film shows obviously two emission peaks located at 3.3117 eV and the satellite band at 3.300 eV. These two emissions are attributed to the FA and DAP transitions, respectively, as will be demonstrated below. Besides, the energy difference between DAP and 3.2288 eV shoulder peak is 71.2 meV. This value is similar to the longitudinal-optical (LO) phonon energy of 72 meV obtained from ZnO bulk [24]. Therefore, the 3.2288 eV band could be attributed to the first longitudinal optical-phonon replica (1LO) related to DAP recombination.

The origin of emission band at 3.30 ∼ 3.31 eV was controversially discussed in the previous literatures [25,26]. However, the band appeared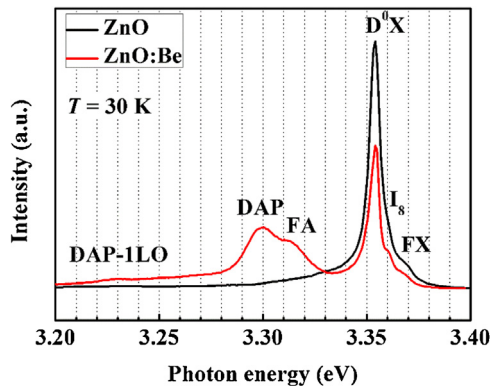 in ZnO:Be film can be assigned to DAP transition. To confirm the spectra assignment of DAP recombination, the spectra have been measured under different excitation densities, as illustrated in Fig. 2. The emission peak of DAP moves to high energy side with excitation density increases, while the emission peak of FA keeps unchanged. This is the typical feature of the DAP recombination process [27]. The energy of the DAP luminescence is given by:

$$\hbar\omega = E_g - E_D - E_A + \frac{e^2}{4\pi\varepsilon R_{DA}} \tag{1}$$

where E_D, E_A are the donor and acceptor ionization energies, R_{DA} is donor-acceptor pair distance, *e* is elementary electric charge, ε is dielectric constant. With increasing the excitation density, the number of occupied donor and acceptor increases and their average distance R_{DA} necessarily decreases. Thus, one can find that the DAP emission line shifts to the high energy side with increasing excitation density. We attribute the DAP emission line to the transitions between O_V, Be_i donors and Zn_V acceptors. Some amount of Be atoms move to interstitial sites due to its small atomic radius [20], and O_V defects have low formation energies and are commonly formed in as-grown ZnO film [28]. The Zn_V acceptor defects can be further verified by temperature-dependent PL spectra analysis.

Fig. 3 shows the temperature-dependent PL spectra of ZnO:Be film prepared at T_{Be} = 960 °C. These spectra were taken at temperatures ranging from 30 to 150 K. With an increase in temperature, the positions of the emission peaks tend to shift to the low-energy regions, and these intensities continue to quench. The D°X line is almost disappeared as the temperature increases to 125 K and the I_8 line is disappeared at 80 K. On the contrary, the DAP luminescence is gradually varied to a luminescence such as FA transition. The energy position of FA is given by:

$$\hbar\omega_{FA} = E_g - E_A + (1/2)k_B T \tag{2}$$

where k_B and *T* are Boltzmann constant and temperature. The E_g can be estimated by $E_x + E^b$, where E_x is free exciton energy. As shown in Fig. 3, the energy of free exciton observed at 100 K is 3.3616 eV, and the corresponding FA is 3.3096 eV. Thus, we obtain the acceptor ionization energy E_A, equaling to 116 meV. Such transition energy is comparable to the value reported in Ref. [29] and close to the density functional theory calculated value of $E_A[Zn_V^{0/-}]$ [30]. This means that intrinsic Zn_V defects were formed in ZnO:Be films. Previous observations showed that the incorporated Be atoms markedly suppressed formation of O_V donor defects [18]. However, it seems that Zn_V acceptor defects might be energetically favored in ZnO:Be films. This further suggests that Be and N
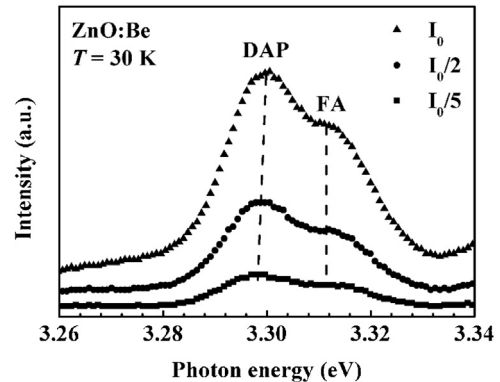

Fig. 1. 30 K PL spectra of ZnO:Be (T_{Be} = 960 °C) and ZnO films.

Fig. 2. Excitation-power density-dependent PL spectra of ZnO:Be film (T_{Be} = 960 °C) measured at *T* = 30 K. The I_0 is 4 mW. A blue-shift of DAP line with increased excitation density is clearly observed.