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Negative thermal quenching in undoped ZnO and Ga-doped ZnO film grown on c-Al_2O_3 (0001) by plasma-assisted molecular beam epitaxy

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Abstract Negative thermal quenching (NTQ) was observed in bound exciton emission line in undoped ZnO and the donor-to-valence-band emission in heavily Ga-doped ZnO thin films grown on c-Al_2O_3 (1000) through low temperature photoluminescence spectra. In both cases, the enhanced feature of PL peak intensity occurred in the temperature range of 35–45 K corresponding to the energies of either excitation to the vibrational/rotational resonance states or the involvement of B-valence band considering the activation energy of about 5 meV.

Keywords Negative thermal quenching · ZnO · Ga-doped ZnO · B-valence band · Vibrational/rotational resonance states

1 Introduction

In solids such as semiconductors and ionic crystals, the intensity of photoluminescence (PL) emission generally decreased as temperature is increased due to the increase of the nonradiative recombination probability of electrons and holes, which is called "thermal quenching" [1, 2]. However, it was observed in some semiconducting materials of GaAs [3, 4] and ZnS [5] in some temperature range that the PL intensity increases with the increment of temperature. This phenomenon is called "negative thermal quenching (NTQ)". Bebb et al. [3, 4] proposed that NTQ for the ($e-A^o$) emission in GaAs was due to the thermal dissociation of the (D^o, X) system, which resulted in the ejection of a free electron into the conduction band. They could explain qualitatively the NTQ, but did not develop any analytical formula to describe the NTQ curve quantitatively. ZnO has been emerged as a good candidate for high efficient UV/blue LED due to its large exciton binding energy of 60 meV at room temperature, high radiation resistance, and optical gain [6–8]. Recently, this NTQ was also observed in II-VI ZnO semiconductor material with large band gap (3.37 eV at RT) and the analytical formula was proposed by both Shibata and Meyer et al. Shibata [9, 10] suggested that the principal mechanism of NTQ is the thermal excitation of electrons to the initial state of the PL transition from the eigenstates with smaller energy eigenvalues. Meyer et al. [11] reported that in undoped ZnO crystal excited rotational states of the donor bound excitons could be seen in low temperature PL measurements and at high temperature the appearance of the excitons bound to the B-valence band was observed, which were approximately 4.7 meV higher in energy. In this study, we use the high quality undoped ZnO and Ga-doped ZnO thin films epitaxially grown by plasma-assisted molecular beam epitaxy (PA-MBE) and NTQ behaviors are investigated through low-temperature PL spectra.

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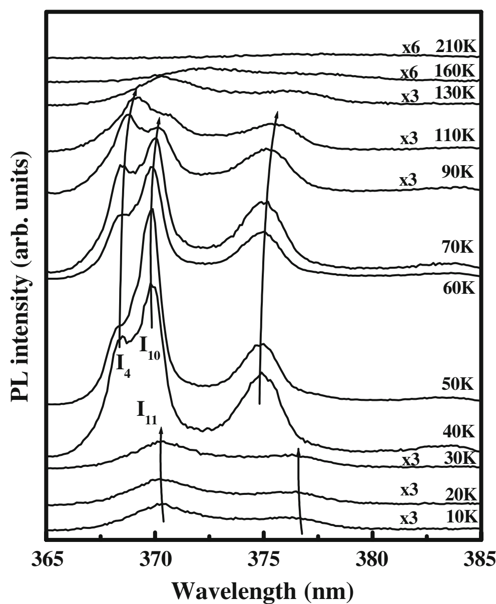

Fig. 1 Photoluminescence spectra of undoped ZnO thin film at temperatures 10–300 K grown on low-temperature buffered ZnO/ Al_2O_3(1000) at 760 °C

2 Experimental

The ZnO films were deposited on α-Al_2O_3(0001) single crystals by plasma-assisted molecular beam epitaxy (PA-MBE). An elemental Knudsen cell was used to supply zinc atoms of 6N purity, and the temperature of the cell was maintained at 355 °C during deposition. Active oxygen species was generated and spread over the sapphire substrate through a radio-frequency plasma source activated at the power of 450 W. Detailed conditions for preparing and cleaning sapphire substrate were reported elsewhere [12, 13]. Low-temperature buffer layer with the thickness of 15 nm was grown at 500 °C, and was thermally-treated at 800 °C for 30 min. Then, the growth was restarted at 720 °C and continued for 3 h. The total thickness of the film was about 500 nm. In order to control the n-type doping concentration, Ga cell temperature was varied from 450 °C to 650 °C and grown at the same conditions with the undoped ZnO.

In situ RHEED (Oxford Applied Research, LEG 110) patterns were observed to monitor the growth mode and surface status of the films during deposition. The crystalline quality of the deposited films was estimated by XRC (Bruker AXS, D8 Discover). Temperature-dependent photoluminescence was obtained with the excitation source of λ=325 nm He–Cd laser (25 mW).

3 Results and discussion

3.1 NTQ in undoped-ZnO

Figure 1 shows PL spectra taken for the undoped ZnO grown at 760 °C from 10–300 K. Below 30 K, a bound exciton emission is observed at 3.3485 eV (3.3492 eV) which can be attributed to the bound exciton recombination, I_{11}, as reported through magneto-photoluminescence experiments [14, 15]. Two peaks in the lower energy side, at 3.2958 and 3.223 eV are clearly observed and show the energy separation of about ΔE=72.8 meV (not shown here) which is consistent with previous observations of the energy of LO phonon [16]. Therefore, they can be easily conjectured to relate with optical phonon replicas of bound exciton, BE_x–mLO (I_2=3.3678 eV) which has been commonly assigned to ionized donor bound excitons. As the temperature increases, I_{11} disappears at higher temperatures above 30 K. Instead, a new peak is clearly observed around 3.352 eV at 40 K and shows the maximum intensity at 50 K. Since the photon energy of this luminescence is slightly higher than I_{11}, and is very close to the 3.3531 eV line from [15], it can be temporarily assigned as another bound exciton, I_{10}. The chemical nature of these two bound exciton emissions I_{10} and I_{11} still remains to be determined.

Figure 2 represents the variations of PL intensity as a function of temperature for I_{10} line. As temperature decreases, the PL intensity is also decrease initially up to 30 K and then it starts increasing showing peak intensity at 20 K and then finally decreases at high temperature $T<$ 20 K. In general as temperature increases the PL intensity was known to be decreased due to the increase of nonradiative electron-hole recombination probability. On the other hand, an increase in the PL intensity with the increase of temperature was observed in the temperature range of $30<T<50$ K and this phenomenon was known as "negative thermal quenching (NTQ)".

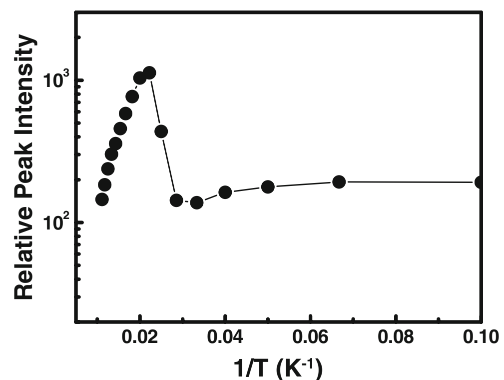

Fig. 2 The variation of integrated PL intensity for undoped ZnO grown at 760 °C as a function of temperature (1/*T*; K^{-1})

Besides, the complete disappearance of I_{11} line at the temperature of 40 K, it is worthwhile to note that the luminescence intensity of I_{10} greatly increased and has the maximum value at 50 K. This feature can be ascribed to the following two processes. Firstly we can think about the thermal effect. As the localization energy of bound exciton line I_{11} is 27.5 meV [12], it can be presumed that bound exciton of I_{11} is thermally excited to as much as 4.3 meV (=50 K) by thermalization effect, and this is very close to the energy difference of 4.7 meV between I_{10} and I_{11} lines.

Secondly, the energy level of the excitation resonance states of two exciton lines should be compared. Goutowski et al. [16] reported that the excited states of bound excitons were composed of mainly three different groups with respect to their position from the main luminescence line. The group I resonances were treated with regard to possible vibronic or rotational excited states 1 to 3 meV above the main recombination lines. The group II resonances around 5 meV above the main lines were explained in terms of acceptor-exciton complexes involving one hole from the B valence band corresponding to the second lower Γ_7 band among three split valence bands, one Γ_9 and two Γ_7's, by spin-orbit interaction. The resonances of group III were shown to belong to excited electronic states of the (A^0, X_A) systems. For example, in the excitation spectra of the luminescence line I_{6a} for polarization perpendicular to the crystal c axis ($E \perp c$), group I lying 0.6 to 1.8 meV, group II between 4.3 and 6.5 meV, and group III locating 8.1 to 14.9 meV were found on the high-energy side of I_{6a}, respectively. [16] These groups of excitation resonances also occurred in the excitation spectra of all other luminescence lines of I_5 to I_{11}. It is plausible that the disappearance of I_{11} and the emergence of I_{10} around 40 K stem from the excitation to the vibronic/rotational resonance states or involvement of B-valence level, considering the range of the obtainable thermal activation energy ($k_B T$~2.58–4.30 meV) in the temperature range of 30~50 K.

3.2 NTQ in Ga-ZnO

Figure 3 shows the low temperature-dependent PL result of the highly Ga-doped ZnO with $N_{Ga}=2.5\times10^{20}$ cm^{-3}. As the temperature increases from 10 K to 80 K, the PL peak intensity gradually decreases. But it is noteworthy that PL intensity at 45 K is higher than that at 30 K, which is very similar behavior to the undoped ZnO as shown in Fig. 1. It's been well known that PL intensity decreases with measurement temperature due to thermal quenching effect (i.e. increase of nonradiative transition probability at higher temperatures). In contrast, the bound excitonic (BE) emissions spectra [11] and the donor-acceptor pair (DAP) and bound-to-free (BF) emissions of ZnO have been reported to show negative thermal quenching (NTQ) effect in low temperature range [10]. For the PL spectra measured at 10 K, a small but clear shoulder in the energy range of Ga-bound-exciton emission is observed at around 3.36 eV, and it rapidly disappears as the temperature goes up. Because of the fluctuation in doping concentration, there could exist excitons bound to isolated Ga-dopants, which are so apart from other dopants that they do not form an impurity-band. It can be suggested that the disappearance of the small shoulder is due to the separation of bound-excitons from donors by thermal activation. The localization energy was estimated as 16.8 meV by calculating the activation energy of the change of PL intensity [17]. At well below the Debye temperature ($\theta_{D,ZnO}$=200–600 K), increased electron-phonon scattering with the increase of temperature reduces the peak energy, while lattice thermal expansion plays a major role at higher temperatures. For heavily doped ZnO, the temperature dependence cannot be described by the Varshini's equation [18] because, in addition to the electron-phonon scattering, collective effects such as the participation of B-valence band in the transition and the band gap renormalization effect as well as screening due to the abruptly increased number of free carriers should be simultaneously considered. The amount of the abrupt jump of emission energy in the range of 30–35 K is approximately 5.7 meV, which is comparable with difference in the energy gap due to the splitting of A- and B-valence bands (4.7–4.9 meV). The similar behavior was previously observed in PL studies of undoped ZnO epitaxially grown thin films. According to Shibata, the principal mechanism of NTQ was explained by the thermal excitation of the electron to the initial state of the PL transition from the intermediate states with smaller energy eigenvalues [9, 10].

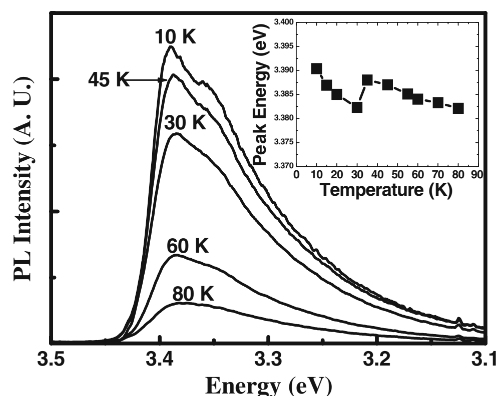

Fig. 3 The variation of integrated PL intensity for heavily doped Ga-ZnO at different low temperature region (*inlet* presents the change of the PL peak position)

The formula for temperature-dependent negative thermal quenching, expressed as in Eq. 1, was well fitted with the experimentally determined values of the PL intensity in GaAs and ZnS. Recently this Eq. 1 was also employed for the explanation to illustrate the relationship of observed bound exciton peaks with the doped impurities in ZnO crystal and high quality ZnO thin film [10].

$$I(T) = I(0)\left\{1 + D_1 \exp\left(-E_1'\Big/k_B T\right)\right\}/ \\ \{1 + C_1 \exp(-E_1/k_B T) + C_2 \exp(-E_2/k_B T)\}, \quad (1)$$

where E_1' is the activation energy for thermal excitation of electrons to the initial state for intermediate state, E_1 and E_2 is the activation energy for nonradiative recombination processes. We carefully analyze the results and the accurately estimated fitted values of the parameters are summarized as E_1' 46 meV, E_1 64 meV, and E_2 8.4 meV respectively. Meyer et al. [11] reported that, the A–B valence band splitting observed not only I_4, but also for all other lines from I_6 to I_9. In particular B-band involved lines represented by $I_i(B)$ show a thermally activated behavior, initially showed an increase in intensity and then drop as the main exciton lines do while the main bound exciton line does not. In case of $I_i(B)$ the dependence can be fitted by Eq. 2

$$I_x = B \frac{1}{1 - A \exp\left\{\frac{-E_x}{kT}\right\}\left(C + \exp\left\{\frac{-E_{AB}}{kT}\right\}\right)}, \quad (2)$$

where B and C are constants and E_{AB} is the splitting between the A- and B-valence bands and E_x is the localization energy of the corresponding A bound exciton.

In this research, NTQ behavior around the temperature of 35–45 K in undoped ZnO and Ga-doped ZnO and thus it can be proposed that mainly the holes in B-valence band participate in the recombination and emission above the temperature of 35 K. It is plausible that the enhancement of PL peak intensity at 45 K originate from the excitation to the vibrational/rotational resonance states (group I) or the involvement of B-valence band, considering the obtainable thermal activation energy ($k_B T$~2.58–4.3 meV) in the temperature range of 30–50 K.

4 Conclusions

Bound exciton emission line in undoped ZnO and the donor-to-valence-band emission in also showed the negative thermal quenching phenomena through low temperature photoluminescence. It can be suggested that the enhancement of PL peak intensity around the temperature 35–45 K result from the excitation to the vibrational/rotational resonance states or the involvement of B-valence band considering the activation energy of about 5 meV.

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