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2007 J. Phys. D: Appl. Phys. 40 6541

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J. Phys. D: Appl. Phys. **40** (2007) 6541–6544 doi:10.1088/0022-3727/40/21/012

Room temperature excitonic spontaneous and stimulated emission properties in ZnO/MgZnO multiple quantum wells grown on sapphire substrate

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Received 13 July 2007, in final form 11 September 2007
Published 19 October 2007
Online at stacks.iop.org/JPhysD/40/6541

Abstract

$ZnO/Mg_{0.2}Zn_{0.8}O$ multiple quantum wells (MQWs) were grown on a *c*-plane sapphire (Al_2O_3) substrate by plasma-assisted molecular beam epitaxy. Both the spontaneous and the stimulated emission properties at room temperature (RT) in MQWs were studied under lower and higher excitation densities. The strong emission at 3.330 eV was observed in the MQWs at RT, which was attributed to the free exciton transition by the temperature-dependent photoluminescence measurement. Significantly, RT stimulated emission caused by inelastic exciton–exciton scattering was observed in the $ZnO/Mg_{0.2}Zn_{0.8}O$ MQWs grown on Al_2O_3. Thus, the exciton binding energy was determined to be 122 meV in our MQWs.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO and its alloys, such as MgZnO and BeZnO, have recently attracted much attention due to their potential applications in ultraviolet light emitting diodes (LEDs) and laser diodes (LDs) [1–4]. In particular, room temperature (RT) excitonic ultraviolet lasing has been observed in ZnO/BeZnO multiple quantum wells (MQWs) both optical and electrical pumping [4]. Due to the toxicity of BeO, much effort has been devoted to fabrication and understanding of ZnO/MgZnO MQWs [2, 3, 5–7]. Makino *et al* have grown ZnO/MgZnO MQWs on a scarce substrate $ScAlMgO_4$ and observed the strong exciton emissions up to RT [5]. In addition, stimulated emission induced by exciton–exciton scattering in their MQWs has been demonstrated with a low threshold density (11 kW cm^{-2}) at RT [3]. In our progress to ZnO-based LEDs and LDs, blue-violet electro-luminescence has been observed from the homojunction LEDs fabricated on a common substrate Al_2O_3 [8, 9]. To further enhance the device performance, it is very necessary to fabricate and study the ZnO/MgZnO MQWs grown on Al_2O_3. However, there are very few works focused on this issue while much effort is devoted to the MQWs on $ScAlMgO_4$. Ohtomo and co-workers have grown ZnO/MgZnO MQWs on Al_2O_3 but no photoluminescence (PL) was observed above 150 K [5, 10]. In our previous works, the structural and optical properties of $ZnO/Mg_{0.12}Zn_{0.88}O$ heterostructures with various well widths have been studied [11, 12]. In addition, the low-temperature (5 K) stimulated emission caused by exciton–exciton scattering in $ZnO/Mg_{0.1}Zn_{0.9}O$ single-quantum well has been observed in our early report [13]. However, there are very few reports

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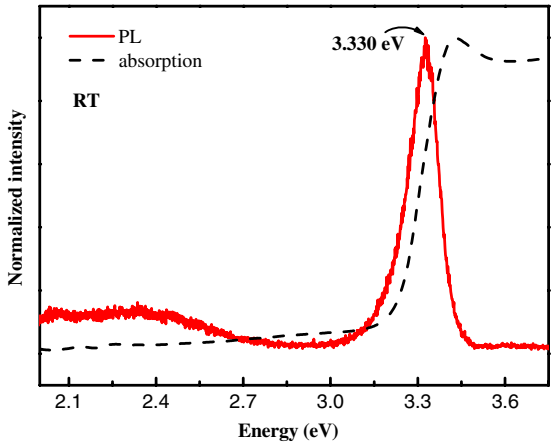

Figure 1. The RT absorption spectrum and the PL spectrum excited by a He–Cd laser for ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs.

about the RT stimulated emission in ZnO MQWs on a *c*-plane Al_2O_3 substrate [3].

In this paper, ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs were grown on a *c*-plane Al_2O_3 substrate by plasma-assisted molecular beam epitaxy (P-MBE). The RT spontaneous emission at 3.330 eV was attributed to the free exciton transition by the temperature-dependent PL measurement. Significantly, the RT stimulated emissions induced by exciton–exciton scattering were demonstrated in the MQWs grown on Al_2O_3.

2. Experimental details

The ZnO MQWs used in this study were grown on *c*-plane Al_2O_3 by P-MBE, following the deposition of a 100 nm thick $Mg_{0.2}Zn_{0.8}O$ buffer layer. The structures consist of 10 MQWs with 1.5 nm thick ZnO wells and 10 nm thick $Mg_{0.2}Zn_{0.8}O$ barriers. The film was grown at 550 °C before exposure to oxygen plasma for 30 min. Details of the growth procedure can be found in a previous work [11]. X-ray diffraction and reflection high-energy electron diffraction measurements revealed the high quality of the alloy films [11]. Temperature-dependent PL spectra were measured using the 325 nm line of a 5 mW He–Cd laser. The stimulated emission experiments were performed using the pulse laser output (350 nm) from an optical parametric amplifier (OPA) in an active passive mode-locked femtosecond Ti : sapphire laser operating at a repetition rate of 1 KHz. The excitation light was focused on the sample surface using a cylindrical lens. Emission from the sample edge was collected into a spectrometer (the spectral resolution was approximately 0.5 nm) and detected by an electrically cooled charge-coupled device.

3. Results and discussion

Figure 1 shows RT PL and absorption spectra in ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs. The PL spectrum is dominated by the near band-edge emission at 3.330 eV with weak deep-level emission, indicating high optical quality. Compared with the ZnO PL peak of 3.290 eV at RT [11], the luminescence in ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs shows an obvious blueshift of about 40 meV due to the quantum confinement effect [11]. Also shown in figure 1, the absorption spectrum is located on the higher energy side of the PL peak. In our previous works, it has been demonstrated that the RT luminescences in ZnO/MgZnO heterostructures were composed of localized exciton emissions at the lower energy side and the free exciton emissions at the higher energy side by the time-resolved PL measurements [12].

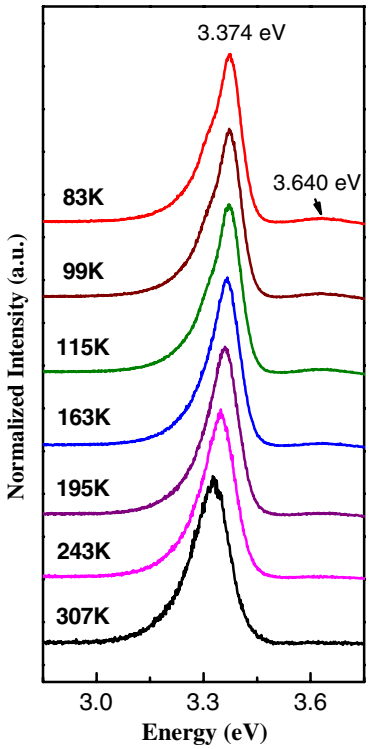

Figure 2. Temperature-dependent PL spectra of the ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs. The spectra were normalized and shifted vertically for clarity.

In order to further understand the origin of 3.330 eV emission in ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs, the temperature-dependent PL spectra are displayed in figure 2. At 83 K, the spectrum is dominated by a strong emission at 3.374 eV with a more weak line at 3.640 eV. According to our earlier works, the former is attributed to localized exciton emission and the latter is assigned to the recombination from the barrier layers [11]. As the temperature increases from 83 to 307 K, the dominant peak energy shifts from 3.374 to 3.330 eV and the barrier layer emission rapidly disappears. This phenomenon has been explained by the potential barrier existing in the interface between the ZnO and MgZnO layers [11].

Figure 3 shows the temperature dependence of the PL peak energy in the MQWs. As the temperature increases from 82 to 163 K, the PL peak exhibits a slight redshift of about 5 meV. However, when the temperature is increased further from 163 to 307 K, the PL peak redshifts 39 meV. As is well known, the redshift of the free exciton with increasing temperature results from the band gap shrinkage, which derives from both thermal expansion and exciton–phonon interaction. Sun *et al* have studied the temperature dependence of the 1S exciton absorption peak of ZnO MQW samples with various well widths, and fitted their results by the Bose–Einstein expression [7]:

$$E(T) = E(0) - \frac{\lambda}{\exp(\beta/T) - 1}, \qquad (1)$$

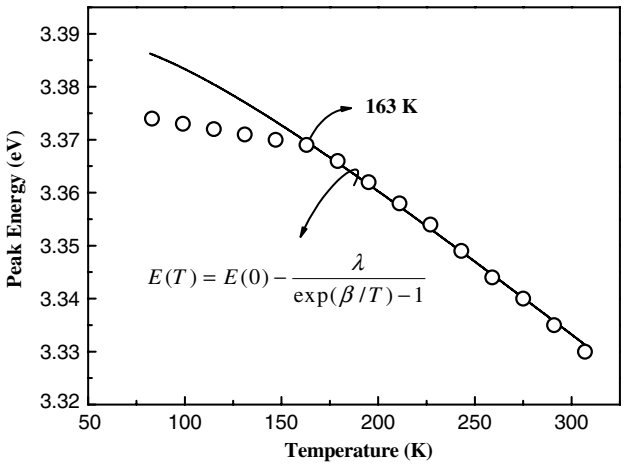

Figure 3. Temperature-dependent peak energy of the PL spectra in the ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs and the fitting curve using equation (1).

where λ and β are fitting parameters and $E(0)$ is the band gap at a temperature of 0 K. They have found that except for $E(0)$, all the ZnO/$Mg_{0.12}Zn_{0.88}O$ MQWs with various well widths have the same fitting parameters with $\lambda = 0.070 \pm 0.005$ eV and $\beta = 250 \pm 10$ K [7]. To further elucidate the origin of the luminescence in our MQWs, the temperature dependence of the peak energy is fitted by equation (1), as shown in figure 3. It is found that the data for temperatures above 163 K can be well fitted by equation (1) with $\lambda = 0.073$ eV and $\beta = 248$ K, while the data are obviously below the fitted curve over the temperature range from 83 to 163 K. In general, when a dominant PL peak is assigned to the radiative recombination of localized excitons, its peak energy blueshifts with increasing temperatures at low temperatures and redshifts at high temperatures [6]. The blueshift is associated with the thermal activation of localized excitons to free excitons. The redshift is due to the band gap shrinkage. Then, the recombination mechanism of our MQWs in a different temperature range can be explained as follows: at temperatures below 163 K, the PL spectrum is dominated by the localized exciton emissions, which are gradually dissociated to the free excitons component due to thermal activation. This behaviour increases the higher energy side emission and results in blueshift, which partly compensates the redshift of the band gap. Thus, the peak energy exhibits a slight redshift of 5 meV, a value much smaller than the expected band gap shrinkage of 16 meV over this temperature range (this is estimated from the fitted curve by equation (1)). For temperatures above 163 K, the free exciton emission gradually dominates the PL spectrum and exhibits a continuous redshift agreed with the band gap shrinkage. Thus, we conclude that the PL spectrum in ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs is dominated by localized exciton emission at low temperatures (below 163 K) while the free exciton transition gradually dominates the spectrum at higher temperatures up to RT.

Figure 4 shows the stimulated emission spectra of ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs, measured under strong-pulsed laser output of the OPA at RT. At the excitation density of 200 kW cm^{-2}, a new peak (P_2) is observed at 3.200 eV with a full width at half maximum (FWHM) of 135 meV,

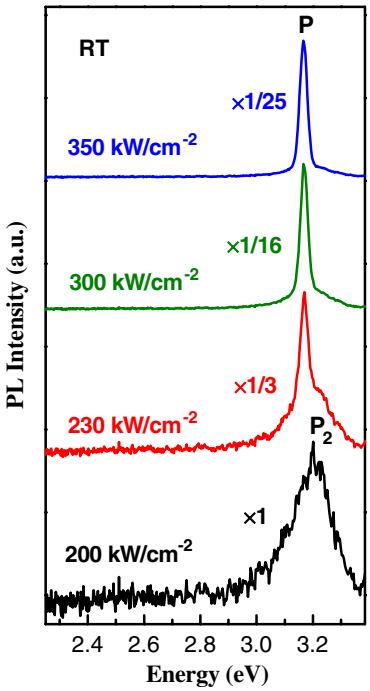

Figure 4. The evolution of the RT PL spectra in the ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs as the excitation density increases from 200 to 350 kW cm^{-2} by a pulse laser output of the OPA.

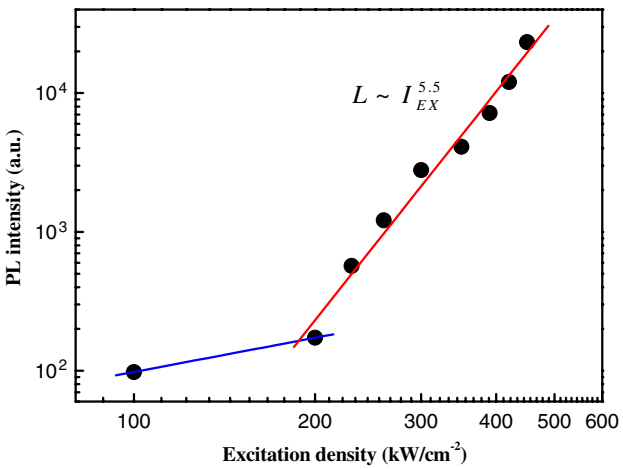

Figure 5. The integrated intensity of the stimulated emission as a function of the excitation density.

which is lower than the spontaneous PL peak in figure 1 by about 130 meV. As the excitation density increases further to 230 kW cm^{-2}, a sharp peak (P) at 3.170 eV with an FWHM of 25 meV emerges rapidly from the lower energy side of the P_2 peak and dominates the spectrum. When the excitation density reaches 350 kW cm^{-2}, the intensity of the P peak increases further with no change in the energy position and the P_2 peak is thoroughly suppressed. As shown in figure 5, the intensity (L) of the P band increases superlinearly with the excitation density (I_{EX}). The dependence of L on I_{EX} can be fitted by $L \propto I_{EX}^{5.5}$. Thus, the superlinear increase of the P peak intensity, as well as the narrow linewidth with the total suppression of the other emissions, clearly indicates that stimulated emissions have occurred in our sample.

Compared with previous reports on stimulated emission from ZnO MQWs at RT [2–4], the positions of the P and P_2 peaks are in good agreement with that expected from an inelastic collision between excitons, in which one of the two excitons obtains energy from the other and scatters into a higher exciton state with a quantum number $n > 1$, while the other recombines radiatively. The photons emitted in this process have the energies of P_n given by [4]

$$P_n = E_{ex} - E_{ex}^{b}\left(1 - \frac{1}{n^2}\right) - \frac{3}{2}kT \qquad (n = 2, 3, \cdots, \infty), \tag{2}$$

where E_{ex}, E_{ex}^{b} and kT are the free exciton energy, the exciton binding energy and thermal energy, respectively. If the value of E_{ex} is estimated to be 3.330 eV by the spontaneous emission peak in figure 1, the exciton binding energy is determined to be about 122 meV by equation (2) using $P_n = 3.170$ eV, which is very close to the exciton binding energy of 115 meV in ZnO/MgZnO MQWs reported by Sun *et al* [14] and much lower than that obtained in ZnO/BeZnO MQWs [4]. Then, the energy difference between P_∞ and P_2 is calculated to be about 31 meV by equation (2) using $E_{ex}^{b} = 122$ meV. Fortunately, this calculated value is in good agreement with the observed peak shift between the P and P_2 emissions in figure 4. Thus, the mechanism of the stimulated emission in our ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs can be reasonably attributed to inelastic exciton–exciton scattering. Moreover, the large exciton binding energy of 122 meV further confirms the excitonic nature of the RT spontaneous emission in the MQWs discussed above.

4. Conclusion

In conclusion, the ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs film was grown on *c*-plane Al_2O_3 by P-MBE. The strong emission at 3.330 eV was observed in the MQWs at RT, which was attributed to the exciton transition by the temperature-dependent photoluminescence (PL) measurement. Strong RT stimulated emission caused by inelastic exciton–exciton scattering was observed in ZnO/$Mg_{0.2}Zn_{0.8}O$ MQWs. Thus, the exciton binding energy was determined to be 122 meV in our MQWs.

Acknowledgments

This work is supported by the Key Project of the National Natural Science Foundation of China under Grant Nos. 60336020, 50532050, the '973' program under Grant No. 2006CB604906, the Innovation Project of the Chinese Academy of Sciences and the National Natural Science Foundation of China under Grant Nos. 60429403, 60506014, 50402016, 60576040 and 10674133.

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