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Stimulated emission induced by exciton–exciton scattering in ZnO/ZnMgO multiquantum wells up to room temperature

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The mechanism of ultraviolet stimulated emission was investigated in ZnO/ZnMgO multiquantum wells. Stimulated emission induced by exciton–exciton scattering occurred throughout a range of temperatures from 5 K to room temperature. At temperatures higher than 160 K, stimulated emission due to electron-hole plasma recombination was also observed with a higher excitation threshold than that of exciton–exciton scattering. The exciton binding energies of multiquantum wells were larger than that of bulk ZnO and increased with a decrease in the well widths. This enhancement of exciton binding energy is due to the quantum-confinement effect and is favorable for the stability of exciton states. © 2000 American Institute of Physics. [S0003-6951(00)00652-5]

ZnO-based semiconductors and related heterostructures are attracting increasing attention because of their promising optoelectronic applications in the ultraviolet wavelength range.^{1–3} Compared with other wide band gap materials, ZnO has larger exciton binding energy (~ 60 meV), which assures more efficient excitonic emission at higher temperatures. A notable discovery in ZnO thin-film materials was the observation of stimulated emission induced by the exciton–exciton (ex–ex) scattering at moderate pumping intensity.^{1–3} This process occurs at a threshold lower than the recombination of electron-hole plasma (EHP) and is therefore desirable for the realization of low-threshold lasers. The ex–ex scattering process has also been observed in other II–VI and III–V bulk materials and heteroepitaxial layers.^{4–7} It is expected that, in quantum wells, the observation of this phenomenon should be favored by the enhanced binding energy of excitons and hence by the larger stability of the exciton states.⁸ However, in contrast to this expectation, the emission in quantum wells induced by the exciton-related scattering process has been mostly observed at low temperatures in II–VI materials and rarely demonstrated at room temperature.^{9–11}

Recently, Ohtomo *et al.* reported the observation of stimulated emission in ZnO/ZnMgO multiquantum wells (MQWs) at room temperature or above,¹² but the mechanism of the recombination process has not been elucidated. In this letter, we will discuss the mechanism of stimulated emission in ZnO/ZnMgO MQW structures. The stimulated emission spectra were investigated at various excitation intensities and

at various temperatures from 5 to 300 K. Throughout the whole temperature range, stimulated emission induced by ex–ex scattering with a low excitation threshold was shown. The demonstration of stimulated emission induced by an excitonic process paves the way toward the realization of low-threshold MQW laser diodes operating in the ultraviolet region.

The ZnO/ZnMgO MQWs were grown by the L–MBE method on a $S_c\text{-ALMGO}_4$ (0001) substrate.^{3,13} The active regions were made up of alternating ZnO well layers and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ barrier layers with ten periods. The Mg content of the barrier layers was chosen at $x = 0.12$, corresponding to a barrier height of about 0.2 eV. The thickness of the barrier layers was kept at about 50 Å, while those of well layers ranged from 6.9 to 46.5 Å.

The ZnO/ZnMgO MQWs were optically pumped in an edge emission geometry using a dye laser (351 nm). The dye laser was pumped by a XeCl excimer laser (308 nm) with a pulse width of ~ 13 ns and a repetition rate of 10 Hz. The excitation laser beam was focused on the sample surface using a cylindrical lens to form a rectangular stripe with area of $\sim 800 \times 100 \mu\text{m}^2$. The emission was collected from one edge of the sample and coupled into a 300 mm monochromator with a 1200 line/mm grating, and it was detected by an electrically cooled charge coupled device. Surface photoluminescence (PL) was measured in a conventional back-scattering geometry using a cw He–Cd laser (325 nm) as the excitation source.

Figure 1(a) shows the evolution of edge emission spectra of a ZnO/ZnMgO MQW sample with a QW width (L_z) of 17.5 Å taken at 5 K, where the excitation density varied from 6 to 410 kW/cm². Figure 1(b) shows the absorption and PL spectra plotted for the same sample. At the lowest pumping

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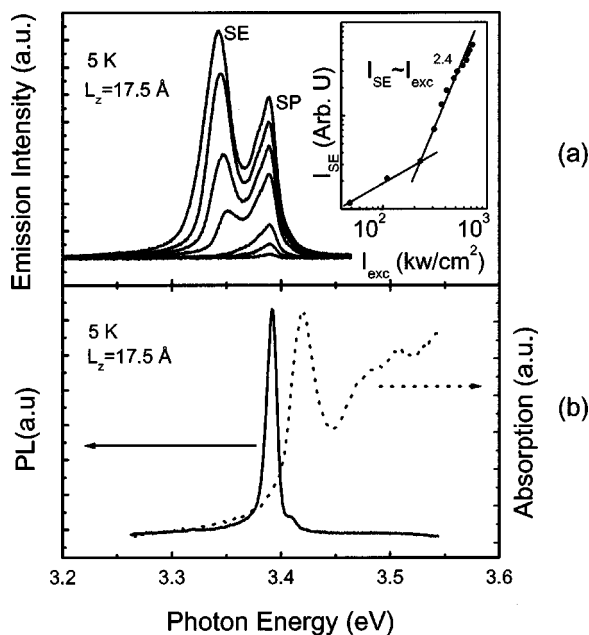


FIG. 1. (a) The evolution of edge emission spectra of ZnO/Zn_{0.88}Mg_{0.12}O MQWs with well width of 17.5 Å as the excitation intensity increases from 6 to 410 kW/cm². The inset shows the spectrally integrated stimulated emission intensity as a function of the excitation intensity. (b): Surface PL spectrum under the weak excitation by a cw He–Cd laser (solid line), and optical absorption spectrum (dotted line) taken at 5 K.

intensity, only one spontaneous emission (SP) peak was observed. This peak was located at the same position as the PL peak and can be attributed to the recombination of localized excitons. With an increase in pumping density, a new peak appeared at the lower energy side of the SP band. Above a certain threshold, this peak grew superlinearly with respect to the excitation density [as shown in the inset of Fig. 1(b)], indicating the appearance of stimulated emission (SE). The peak of stimulated emission exhibited a considerable redshift just above the threshold intensity but very little at higher intensities. Here, we denote the stimulated emission peak at high excitation intensity as *P* band.

Figure 2 shows the normalized emission spectra of the earlier-mentioned sample under an excitation density of about 2 MW/cm² taken at various temperatures (*T*). There appeared a second stimulated emission peak at the lower energy side of the *P* band at *T* > 160 K. The threshold of this peak was higher than that of the *P* band. Moreover, this new peak exhibited a remarkable redshift as the excitation density increased. Therefore, it can be attributed to the recombination of EHP. The relevant redshift with increasing excitation density is due to the band gap renormalization effect.⁸ The simultaneous observation of both stimulated emission peaks may be attributed to the lack of spatial and temporal resolution¹⁴ and/or coexistence of excitons and EHP.¹⁵ The appearance of an EHP band provides strong evidence that the *P* band is of excitonic origin. Furthermore, the peak energy of the *P* band is about 86 meV lower than the free exciton energy determined from the absorption spectrum at 5 K. This energy difference, defined as a Stokes shift, is comparable to the exciton binding energy of ZnO and implies that *P*-band emission is induced by ex–ex scattering. At a very low excitation density, photocreated excitons rapidly relax into localized exciton states so that luminescence due to the recom-

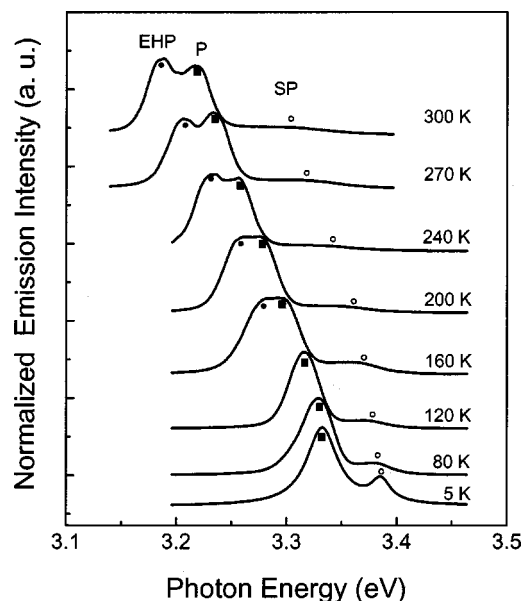


FIG. 2. Normalized stimulated emission spectra of ZnO/Zn_{0.88}Mg_{0.12}O MQWs at various temperatures at an excitation power density of about 2 MW/cm².

ination of localized excitons is dominant in the corresponding spectra. At higher excitation density, the localized exciton states become saturated and a large number of excitons occupy the free exciton states. Thus, the scattering process occurs between free excitons. The threshold excitation densities of the *P* band, determined by the excitation density dependence of stimulated emission, were around 220 and 480 kW/cm² at 5 and 300 K, respectively, which were somewhat higher than those reported for a ZnO epilayer on sapphire.¹ This is because the loss induced by reflected and transmitted light has not been subtracted. Another reason for the difference in thresholds is probably due to the difference in laser pulse duration.

It is notable that ex–ex scattering may occur in two ways; namely, one of the excitons may be scattered into an excited state (*P_n*-band emission) or into a continuum state (*P*-band emission).¹⁰ Both of these processes contribute to the emission spectrum. With increases in the excitation density, the *P*-band becomes predominant, while *P_n*-band becomes saturated. As a result, the emission peak shifts to the lower energy side and finally converges at the *P* band.

The recombination mechanism of stimulated emission induced by excitonic origin can be better understood by studying the temperature dependence of the SE peak position.⁴ Figure 3 shows the temperature dependence of peak energies of the *P* band and free exciton energies for two ZnO/ZnMgO MQW samples with different well widths. For comparison, the corresponding plot for a ZnO single layer on a sapphire substrate is shown in the upper part. The *P* band in ZnO was unambiguously assigned to the stimulated emission induced by ex–ex scattering.¹ It was positioned at the lower energy side of excitonic resonance energy by exciton binding energy (E_b^x) plus a mean kinetic energy proportional to temperature *T*.¹⁶ The dotted lines in Fig. 3 represent the calculated temperature dependence of peak energy according to Klingshirn.¹⁶ They agree quite well with the corresponding *P* bands. It can be clearly seen that the temperature de-

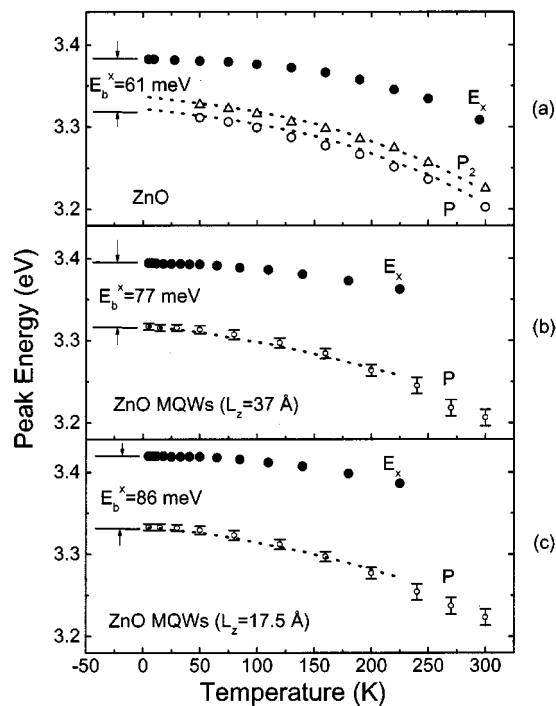


FIG. 3. Temperature dependence of peak energy of the P band (open circles) and free exciton energy (filled circles) in a ZnO epitaxial layer (a) and in ZnO/Zn_{0.88}Mg_{0.12}O MQWs (b) and (c).

pendence of the P -band energy in the MQWs has the same feature as that in a ZnO single layer. This result strongly supports the notion that the P band in ZnO/ZnMgO MQWs is due to ex-ex scattering. In fact, other exciton-related scattering processes were ruled out by considering the relative peak energy position and its temperature dependence. For example, the temperature dependence of a LO-phonon replica of the exciton recombination should show the opposite tendency.¹⁶ Moreover, the PL results showed that the LO-phonon energy of our investigated MQWs was the same as that of bulk ZnO (~ 72 meV). Therefore, the inconsistency of the energy position should also exclude the possibility of a LO-phonon mechanism. Another exciton-related mechanism is exciton-electron scattering. In this process, the excitonic energy is reduced by kinetic energy of electrons so that the recombination emission position starts from the free exciton position at a low temperature and the Stokes shift is proportional to temperature.⁴ This feature is inconsistent with that shown in Fig. 3.

The exciton binding energy can be easily determined by the energy difference between the P line and the excitonic resonance position at a low temperature because the kinetic energy is negligible. Table I shows the exciton binding energies for various samples. The estimated binding energy of ZnO/sapphire was a little higher than the value reported in the literature,¹ probably because the effective temperature of excitons was slightly higher than the lattice temperature. The exciton binding energies of MQWs are considerably enhanced compared with those of bulk ZnO and increase as the well widths decrease. Such enhancement can be understood by the quantum-confinement effect.

TABLE I. Exciton binding energies (E_b^x) of different ZnO samples.

Material	Thickness (Å)	E_b^x (meV)
ZnO	bulk	61 ^a
	46.5	71.3
	42.3	72.2
ZnO/ZnMgO MQWs	37	77
	27	81
	17.5	86

^aSee Ref. 1.

In summary, strong stimulated emission was observed in ZnO/ZnMgO MQWs. The stimulated emission induced by exciton-exciton scattering occurred throughout the range of temperatures from 5 K to room temperature. At a certain excitation density, radiative recombination processes induced by both exciton-exciton scattering (P band) and EHP contribute to the stimulated emission at higher temperatures, but the excitation threshold of the P band is much lower than that of EHP emission. The demonstration of stimulated emission with excitonic origin at room temperature contributes to the possibility of realization of a low-threshold violet diode laser composed of ZnO-based MQWs. The exciton binding energies of the samples were deduced from the energy difference between the P line and the free exciton. The enhancement of exciton binding energy due to quantum confinement was confirmed. Such enhancement is favorable for the preservation of excitons at higher temperatures.

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