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<tr>
<td>Citation</td>
<td>Applied Physics Letters, Vol. 77, No. 26, 2000, 12</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://scitation.aip.org/content/aip/journal/apl">http://scitation.aip.org/content/aip/journal/apl</a></td>
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Stimulated emission induced by exciton–exciton scattering in ZnO/ZnMgO multiquantum wells up to room temperature

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(Received 15 June 2000; accepted for publication 24 October 2000)

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.

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 scattering (ex–ex) 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. 5 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. 6–11

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 ALMGO 4 (0001) substrate. 3,13 The active regions were made up of alternating ZnO well layers and Zn 1−x Mgx 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 beam was focused on the sample surface using a cylindrical lens to form a rectangular stripe with area of ~800×100 μm 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 x ) of 17.5 Å taken at 5 K, where the excitation density varied from 6 to 410 kW/cm 2. Figure 1(b) shows the absorption and PL spectra plotted for the same sample. At the lowest pumping...
Figure 2 shows the normalized emission spectra of the $P_n$-band at $\sim 160$ K. The threshold of this peak was observed at the lower energy side of the SP band. Above a certain threshold, this peak grew superlinearly with respect to the excitation density, and can be attributed to the recombination of localized excitons so that luminescence due to the recombination process occurs between free excitons. The threshold ex–ex scattering may occur in two ways; namely, one of the excitons may be scattered into an exciton bound state or into a continuum state. The recombination mechanism of stimulated emission induced by ex–ex scattering can be better understood by the stimulated emission peak energies of the $P_n$-band and free exciton energies for two excitation densities of the $P_n$-band, determined by the excitation intensity. 

It is notable that ex–ex scattering may occur in two ways; namely, one of the excitons may be scattered into an exciton bound state or into a continuum state. The recombination mechanism of stimulated emission induced by ex–ex scattering can be better understood by the stimulated emission peak energies of the $P_n$-band and free exciton energies for two excitation densities of the $P_n$-band, determined by the excitation intensity. 

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/cm$^2$. The inset shows the spectrally integrated stimulated emission for a ZnO epilayer on a sapphire substrate. This is because the loss induced by reflected and scattered light. The emission peak shifts to the lower energy side and finally converges at the exciton binding energy ($E_b$) of ZnO and implies that the calculated temperature dependence of peak energy according to the absorption spectrum at 5 K. This is because the loss induced by reflected and scattered light.
dependence 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. Moreover, the PL results showed that the LO-phonon energy of our investigated MQWs was the same as that of bulk ZnO ($\sim 72$ 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 energy difference between the excitonic and free exciton is exciton–electron scattering. In this process, the excitonic energy is reduced by kinetic energy of electrons so that the excitonic energy is reduced by kinetic energy of electrons so that the excitonic energy is reduced by kinetic energy of electrons so that the energy difference between the excitonic and free exciton.

**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$_{0.8}$Mg$_{0.2}$O MQWs (b) and (c).

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.

This work was supported by the Proposal Based Program of NEDO (Grant No. 99S12010).

**TABLE I.** Exciton binding energies ($E_b$) of different ZnO samples.

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<tr>
<th>Material</th>
<th>Thickness (Å)</th>
<th>$E_b$ (meV)</th>
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<tr>
<td>ZnO bulk</td>
<td></td>
<td>61$^*$</td>
</tr>
<tr>
<td>ZnO/ZnMgO MQWs</td>
<td></td>
<td>46.5, 71.3</td>
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<tr>
<td></td>
<td>42.3</td>
<td>72.2</td>
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<tr>
<td></td>
<td>27</td>
<td>77</td>
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<tr>
<td></td>
<td>17.5</td>
<td>86</td>
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$^*$ See Ref. 1.