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Room-temperature stimulated emission of excitons in ZnO/(Mg, Zn)O superlattices

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We report on the observation of stimulated emission in $ZnO/Mg_xZn_{1-x}O$ superlattices well above room temperature. Two kinds of superlattices grown by laser molecular-beam epitaxy showed clear systematics on the quantum subband levels in absorption and spontaneous emission spectra. Stimulated emission with excitonic origin could be observed at very low optical pumping levels. The threshold excitation intensity changed from 11 to 40 kW/cm^2, and the emission energy could be tuned between 3.2 and 3.4 eV, depending on the well thickness and/or the Mg content in the barrier layers. The excitonic stimulated emission could be observed up to 373 K and the characteristic temperature was as high as 87 K. © *2000 American Institute of Physics.* [S0003-6951(00)04640-4]

As a wide band gap ($E_g = 3.37$ eV) oxide semiconductor, ZnO has attracted considerable attention due to potential applications, such as ultraviolet light-emitting devices and laser diodes. A large exciton binding energy (59 meV)[1] permits excitonic recombination well above room temperature (RT). In fact, RT lasing in ZnO epilayers on sapphire(0001) substrates having a very low threshold ($24\,kW/cm^2$) has been experimentally confirmed.[2–4] A lower pumping threshold can be expected, in principle, if an exciton-related recombination rather than an electron-hole plasma recombination is used. An example of the latter mechanism is the $In_xGa_{1-x}N/GaN$ based semiconductor laser.[5] For further improvement of efficiency, a quantum-well structure is an important approach. We fabricated ZnO/(Mg, Zn)O superlattices (SLs) on $ScAlMgO_4$ (SCAM) substrates because the use of this lattice-matched substrate significantly improved the semiconductor properties of epitaxial ZnO films in terms of surface flatness, crystallinity, electron mobility,[6,7] and optical spectra.[8] These SLs are expected to have negligibly small interface diffusion of Mg^{2+},[9] and consistently showed excellent optical properties.[10] The most salient feature is the observation of room-temperature photoluminescence (PL) of excitons accompanied by the quantum confinement effect in the SLs having various well widths and band offsets. In this letter, we report on the structural characterization and the characteristics of stimulated emission in $ZnO/Mg_xZn_{1-x}O$ SLs grown on the lattice-matched SCAM substrates. Stimulated emission was observed well above RT. We tested the high-temperature operation of the stimulated emission from the viewpoint of device applications.

Ten-period SLs, $[ZnO(L_w)/Mg_{0.12}Zn_{0.88}O]_{10}$ and $[ZnO(L_w)/Mg_{0.26}Zn_{0.74}O]_{10}$, were directly grown on SCAM substrates by laser molecular-beam epitaxy. This substrate has negligibly small lattice mismatch (0.08%) with the SL films.[6] The well layer thickness (L_w) was varied from 0.7 to 4.7 nm. The thickness of the barrier layer was fixed at approximately 5 nm. The thicknesses are the averages of 10 well layers. The Mg content of $x = 0.12$ is less than the solubility limit ($x = 0.15$).[11] Band gap energies of $Mg_xZn_{1-x}O$ are given elsewhere.[12] Nine SLs were integrated on a single substrate using a combinatorial masking system.[12] KrF excimer laser pulses were impinged on to a ZnO single crystal or $Mg_xZn_{1-x}O$ ceramic targets located 5 cm from the substrate surface. The films were grown at 600 °C in 1×10^{-5} Torr of pure oxygen. The energy diagrams of conduction and valence bands are shown in Ref. 10. Structural characterization was performed with a commercial x-ray diffraction (XRD) apparatus equipped with a masking system, which was specially designed for the combinatorial SL libraries. The surface morphology of the films was observed by means of contact-mode atomic force microscopy (AFM). A weak continuous wave (cw) He–Cd laser (325 nm) was the excitation source for spontaneous emission measurements. The arrangements related to the absorption and spontaneous emission measurements were the same as those adopted in a previous study.[9,13] Frequency-tripled pulses (355 nm, 10 Hz, 15 ps) from a mode-locked Nd:YAG laser were used for the pulsed excitation experiments at temperatures ranging from

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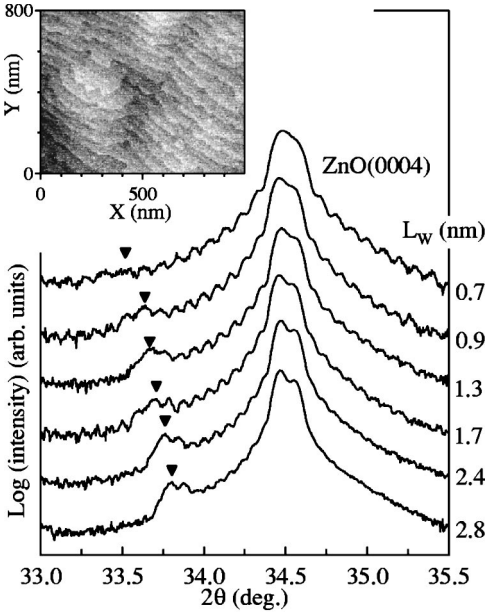

FIG. 1. XRD patterns of $ZnO/Mg_{0.26}Zn_{0.74}O$ SLs having various well layer thicknesses ($0.7 \leqslant L_w \leqslant 2.8$ nm), grown on a $ScAlMgO_4$ substrate. The triangles mark the Bragg diffraction peaks corresponding to the superlattice period. The inset shows a typical AFM image of the SL sample.

294 to 380 K. The maximum intensity of excitation was 58 kW/cm^2. Emission spectra were taken in the conventional side-emission geometry.[3]

Figure 1 shows the XRD patterns of SLs having various well layers thicknesses ranging from 0.7 to 2.8 nm grown on SCAM (0001) substrates. Bragg diffraction peaks from the superlattices, indicated by triangles, and clear intensity oscillations due to Laue patterns corresponding to the layer thickness were observed in all samples, indicating high crystallinity and high thickness homogeneity. The thicknesses of the well and the barrier layers were precisely determined by analyzing the XRD data. A typical AFM image is shown in the inset of Fig. 1. Here we note that the surface of the superlattices is composed of well-defined atomically flat terraces and 0.26-nm-high steps (charge neutral unit cell of ZnO). Therefore, the interface roughness in the heterostructure cannot be larger than 0.26 nm at most. We conclude that the ZnO and $Mg_xZn_{1-x}O$ alloy film grows in a two-dimensional growth mode on $ScAlMgO_4$ substrates, resulting in a sharp heterointerface between them.

Figure 2 shows stimulated emission spectra of SLs having $x=0.12$ and $L_w=1.8$ nm, measured under strong pulsed excitation at room temperature. Strong sharp emission peaks were observed at 3.24 eV above a very low threshold ($I_{\text{th}}=17$ kW/cm^2), and their integrated intensities rapidly increased as the excitation intensity (I_{ex}) increased, as can be seen in the inset. Almost all the SLs showed stimulated emission below the maximum excitation intensity used in this study. Spontaneous PL and absorption spectra are also shown for comparison. The energies of PL and lower absorption peaks coincide with the resonant energy of the lowest exciton state confined in the well layer.[10] The agreement between the spontaneous PL and absorption peaks is an indication of the well-regulated heterointerfaces as well as the small compositional fluctuations in the barrier layers (well-depth fluctuations). On the other hand, the stimulated emission peaks showed the Stokes shift (≈ 100 meV), i.e., the peak energies were lower than the absorption energy. The stimulated emission and absorption peak energies of the SLs are summarized in Figs. 3(a) and 3(b). The L_w dependence of the peak positions could be clearly seen not only in the absorption (open circles) but also in the stimulated emission spectra (closed squares). The L_w dependence of the spontaneous PL was shown in Ref. 10. The threshold values versus L_w are shown in Fig. 3(c) for $x=0.12$ (closed circles) and $x=0.26$ (open circles). Since the pumping laser energy was constant at 3.49 eV, when the absorption state was located

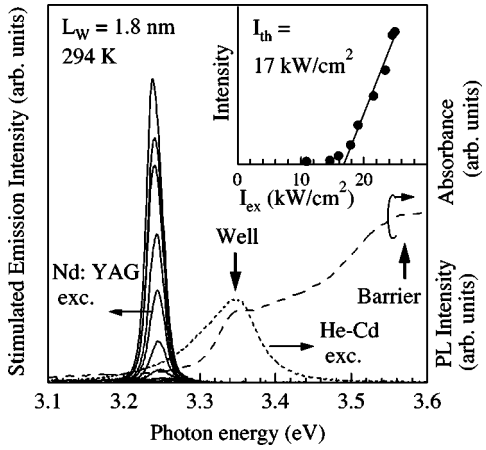

FIG. 2. Excitation intensity (I_{ex}) dependence of the stimulated emission spectra in a $ZnO/Mg_{0.12}Zn_{0.88}O$ SL ($L_w=1.8$ nm) under pulsed excitation measured at RT. Spontaneous PL (dotted line) under cw excitation and absorption (broken line) spectra are also shown. The inset depicts the integrated intensity of the stimulated emission peak as a function of I_{ex}. The threshold intensity (I_{th}) is 17 kW/cm^2.

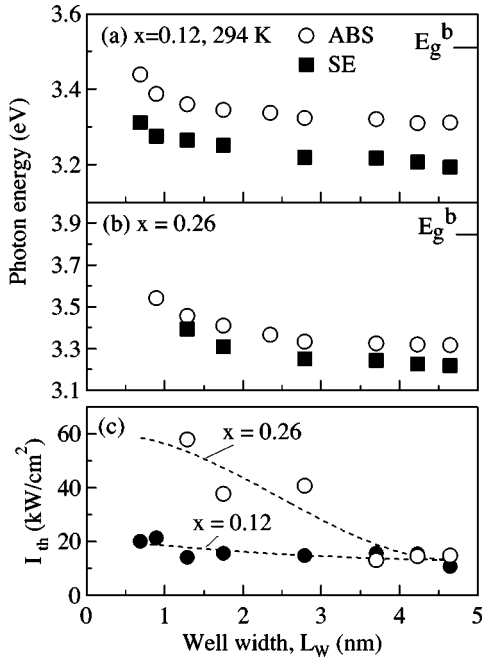

FIG. 3. Optical transition energies of subband absorption (open circles) and stimulated emission (closed squares) as a function of well layer thickness (L_w) for the $ZnO/Mg_xZn_{1-x}O$ SLs with $x=0.12$ (a) and 0.26 (b). The band gap energies of the barrier layers (E_g^b) are also shown. (c) L_w dependence of the stimulated emission threshold (I_{th}) in the SLs with $x=0.12$ (closed circles) and 0.26 (open circles). Stimulated emission did not take place for the $x=0.26$ films with L_w below 1 nm since the excitation energy is lower than the absorption energy.

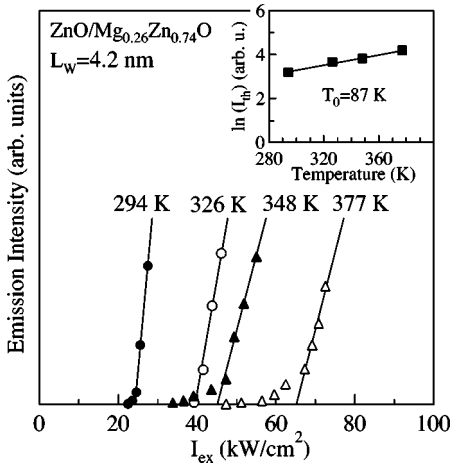

FIG. 4. Temperature dependence of the emission intensity as a function of excitation intensity (I_{ex}) in a $ZnO/Mg_{0.26}Zn_{0.74}O$ SL ($L_W=4.2$ nm). The inset shows the threshold intensity (I_{th}) as a function of temperature on a logarithmic scale.

higher than that energy, stimulated emission did not take place as seen in the case of $x=0.26$ films with L_w below 1 nm. All the SLs with $x=0.12$ had threshold below 22 kW/cm^2, and the lowest threshold was as small as 11 kW/cm^2 at $L_w=4.7$ nm. Figure 4 shows the temperature dependence of the $I_{stim}-I_{ex}$ curves of a SL with $x=0.26$ and $L_w=4.2$ nm in the temperature range between 294 and 377 K. Here, I_{stim} means the intensity of the stimulated emission, while I_{ex} denotes the excitation intensity. The threshold of the stimulated emission (I_{th}) increased gradually with increasing temperature. The inset shows the temperature dependence of I_{th} on a logarithmic scale. The relevant dependence could be fitted by the following equation:

$$I_{th}(T)=I_0\exp(T/T_0), \tag{1}$$

where I_0 is a constant, T is the measurement temperature, $I_{th}(T)$ is the threshold intensity, and T_0 is the characteristic temperature. The fitting result was in fairly good agreement with the experimental data and the T_0 was estimated to be 87 K. The Stokes shift of the stimulated emission was ≈ 100 meV and was comparable to the value of the exciton binding energy plus thermal energy.[14] It should be noted that the binding energy is likely to be enhanced due to the quantum confinement effect in the SL structures. The wavelength drift caused by the temperature change was estimated to be about 0.09 nm/K. This value is very close to the theoretical value of 0.085 nm/K (Ref. 14) for the stimulated emission due to the exciton–exciton (ex–ex) scattering process. Since the peak energy remained unchanged irrespective of the excitation intensity, we could safely rule out the possibility of electron-hole plasma. Exciton localization and the related effect on stimulated emission have been frequently observed in II–VI quantum wells at low temperatures. Various mechanisms such as localized excitons,[15] ex–ex scattering,[16] and localized biexcitons[17] have been proposed. The population inversion with very low threshold could be achieved by virtue of the small density of states in the localized states of excitons. In order to elucidate the emission mechanism of the present case, however, further work is necessary. According to our preliminary study,[18] the temperature dependence of the stimulated emission from the same set of specimens in the range of 5–300 K was found to be analogous to that of ZnO epilayers. The stimulated emission induced by the ex–ex scattering has been certainly confirmed in the latter case. Therefore, we could conclude that the stimulated emission due to the ex–ex process also occurred in the well layers of the SL samples. The characteristic temperature T_0 of 87 K was significantly higher than that of 55-nm-thick ZnO/sapphire (67 K),[19] which has shown excitonic laser action with a threshold of 24 kW/cm^2. We suggest that this kind of improvement can be explained by the enhanced binding energy of excitons due to the quantum confinement effect.[18]

In summary, excellent characteristics of the ZnO-based superlattices, such as high crystallinity and atomically flat surfaces and heterointerfaces, were confirmed. These samples also showed very high performance in terms of ultraviolet stimulated emission. We demonstrated efficient stimulated emission of up to 377 K by virtue of the combined effects of excitons and quantum confinement. These structures also have the big advantage of a tunable emission energy in the 3.2–3.4 eV range. The optimized threshold of the stimulated emission was 11 kW/cm^2, which is far better than the record value (24 kW/cm^2) observed in ZnO epilayers. The estimated characteristic temperature of 87 K was significantly higher than that of ZnO epitaxial layers grown on sapphire substrates (67 K).

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