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Room-temperature luminescence of excitons in ZnO/(Mg, Zn)O multiple quantum wells on lattice-matched substrates

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We report on the optical properties of ZnO/(Mg, Zn)O multiple quantum wells (MQWs) on lattice-matched $ScAlMgO_4$ substrates fabricated by laser molecular-beam epitaxy. As the well layer thickness decreased down to 7 Å, the photoluminescence (PL) and absorption peaks showed a systematic blueshift, consistent with the quantum-size effect. Moreover, a bright PL of free excitons could be observed even at room temperature. As a result, the PL could be tuned in the energy range of 3.3–3.6 eV by choosing the appropriate barrier height and well layer thickness. The widest tunability on the room-temperature luminescence of the excitons could be attained on the basis of the ZnO quantum structure. These favorable properties could not be attained in the MQWs on lattice-mismatched sapphire substrates. © *2000 American Institute of Physics.* [S0003-6951(00)04533-2]

Recently, ZnO and related oxides are attracting much attention as promising candidates for optoelectric applications in visible and ultraviolet (UV) regions. A large exciton binding energy [(EBE), 59 meV][1] permits excitonic recombination even at room temperature (RT). In fact, RT lasing in ZnO epilayers on sapphire(0001) substrates has been experimentally demonstrated.[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. A representative example of the latter is an $In_xGa_{1-x}N$–based laser diode.[5] The quantum-well approach is effective toward the goal of a current-injection laser.

We previously fabricated ZnO/(Mg, Zn)O multiple quantum wells (MQWs) on sapphire substrates with negligibly small interface diffusion of Mg^{2+}.[6] Excitonic photoluminescence (PL) accompanied by the quantum confinement effect was clearly observed at 4.2 K. These MQWs, however, showed the following drawbacks that are attributable to the rough interface due to lattice-mismatched substrates (in-plane, 18%): (1) controllability of layer thickness is not sufficient to realize the proper quantum confinement effect, and (2) PL efficiency is not high enough to enable observation of the exciton emission at RT. These problems must be overcome for an optoelectrical device to be operatable at RT. We used $ScAlMgO_4$ (SCAM) with (0001) orientation as a substrate, the lattice constant of which matches that of ZnO with 0.08%. Epitaxial ZnO and $Mg_xZn_{1-x}O$ films showed significantly improved structural[7] and optical[8] properties.

In this letter, we describe the optical properties of MQWs grown on lattice-matched substrates. The problem of the undesirable properties, which was unavoidable when the sapphire substrate was used, could be eliminated. Such a breakthrough is favorable from the viewpoint of practical application of ZnO devices.

MQWs of ten period, $[ZnO(L_w)/Mg_{0.12}Zn_{0.88}O]_{10}$ and $[ZnO(L_w)/Mg_{0.27}Zn_{0.73}O]_{10}$, were fabricated by laser molecular-beam epitaxy on SCAM substrates. The films had a *c*-axis orientation. The well layer thickness (L_w) was varied from 6.9 to 46.5 Å, and the thickness of the barrier layer was approximately 50 Å, both of which were precisely determined from x-ray diffraction analysis. The thicknesses, indicated below in units of angstroms, are the averaged ones of ten well layers, while those in units of unit cell height ($L=5.2$ Å) were rounded so as to be integers of the height of the ZnO charge neutral molecular layers (2.6 Å). All the layer thicknesses were set as integer of molecular layers by prescribed deposition time. The samples did not have buffer layers, unlike those on sapphire.[6] The Mg content of $x=0.12$ is slightly less than the solubility limit ($x=0.15$) of this alloy film,[9] while the content of $x=0.27$ is far above it. The band gap energies of $Mg_xZn_{1-x}O$ were summarized in Ref. 10. A combinatorial masking method[11] was adopted. Excimer laser pulses were impinged to $Mg_xZn_{1-x}O$ targets (99.999%). The films were grown at 600 °C in 1×10^{-5} Torr of pure oxygen (99.9999%). The SCAM is transparent in the spectral region of interest. The sample was kept in a cryostat. The PL was excited by a continuous wave (cw) He–Cd laser (325 nm) and was monitored using a monochromator with a charge-coupled device. Absorption measurements were carried out using a xenon lamp. Spectral resolution was ≈0.4 nm.

Figure 1 shows PL and absorption spectra in

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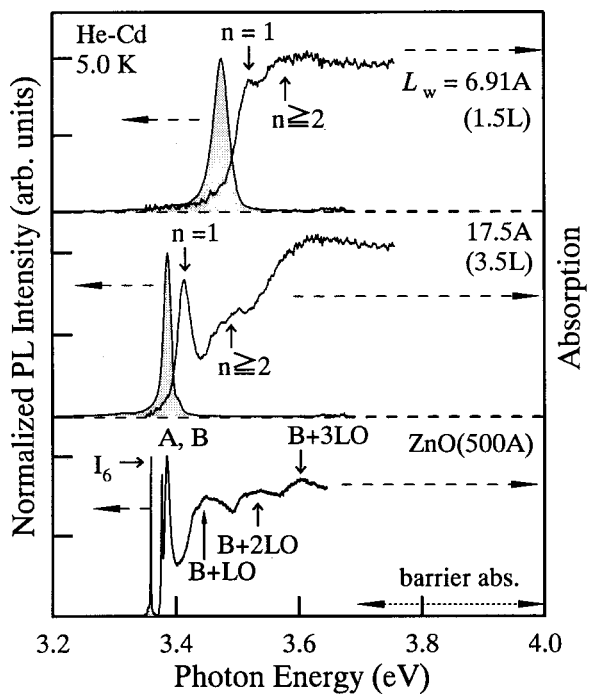

FIG. 1. PL and absorption spectra in $[ZnO(L_w)/Mg_{0.12}Zn_{0.88}O]_{10}$ MQWs measured at 5 K for well widths ($L_w = 17.5$ and 6.91 Å). Absorption energy of barrier layers is shown by a horizontal arrow. Spectra in a 500-Å-thick ZnO film are also shown. ''A, B'' indicates A- and B-exciton absorption bands, ''I_6'' shows PL of a bound exciton state, ''B+LO, B+2LO, and B+3LO'' correspond to exciton-phonon complex transitions, ''$n=1$'' show the lowest excitonic absorption of the well layers, and ''$n \geqslant 2$'' means the excited states of the exciton or higher interband (subband) transitions.

$ZnO/Mg_{0.12}Zn_{0.88}O$ MQWs on SCAM substrates measured at 5 K with L_w of 17.5 and 6.91 Å. The PL and absorption spectra in a 500-Å-thick ZnO epilayer on SCAM were included for comparison.[8] Both the PL and absorption peaks shifted towards the higher energy side as L_w decreased. This shift was due to the quantum confinement effect. The exciton Bohr radius is ≈ 18 Å.[1] The absorption peaks ($n=1$) arise from the lowest excitonic states of well layers. The peak energies of PL were constantly located on the lower energy side of those of absorption peaks.

Figures 2(b)–2(c) show the well width dependence of the peak energies of PL (closed circles) and absorption (open squares), respectively, in $[ZnO/Mg_{0.12}Zn_{0.88}O]_{10}$ and $[ZnO/Mg_{0.27}Zn_{0.73}O]_{10}$ on SCAM substrates. The lowest transition energy of excitons (open triangles) formed with confined electrons and holes was calculated by adopting the model of one-dimensional, finite periodic suquare-well potential, proposed by Gol'dman and Krivchnokov.[12] The EBE (59 meV) is assumed to be independent of L_w. The band discontinuity determined in Ref. 6 and the effective masses[1] of an electron ($0.28\,m_0$) and a hole ($1.8\,m_0$) were used. Here, m_0 is the free electron mass. These offsets and optical transition process on $[ZnO/Mg_{0.12}Zn_{0.88}O]_{10}$ are shown in Fig. 2(a). Figure 2(d) shows peak energies of PL excitation spectra (squares) plotted against L_w on sapphire substrates.

Since the energies of absorption maxima are relatively close to calculated values, these correspond to the lowest excitonic transition related to the lowest interband (subband) transition. The exciton absorption energy shifted to a higher energy as the barrier height increased. This result can be explained by considering the fact that confined potential is deeper for a higher barrier. This tendency was qualitatively reproduced by the calculation. In the case of MQWs on sapphire substrates, it was reported that the concentration of $x = 0.20$ is close to the limit to obtain clear electronic structures at the heterointerfaces. However, MQWs having $x = 0.27$ barrier layers on SCAM can still show clear struc-

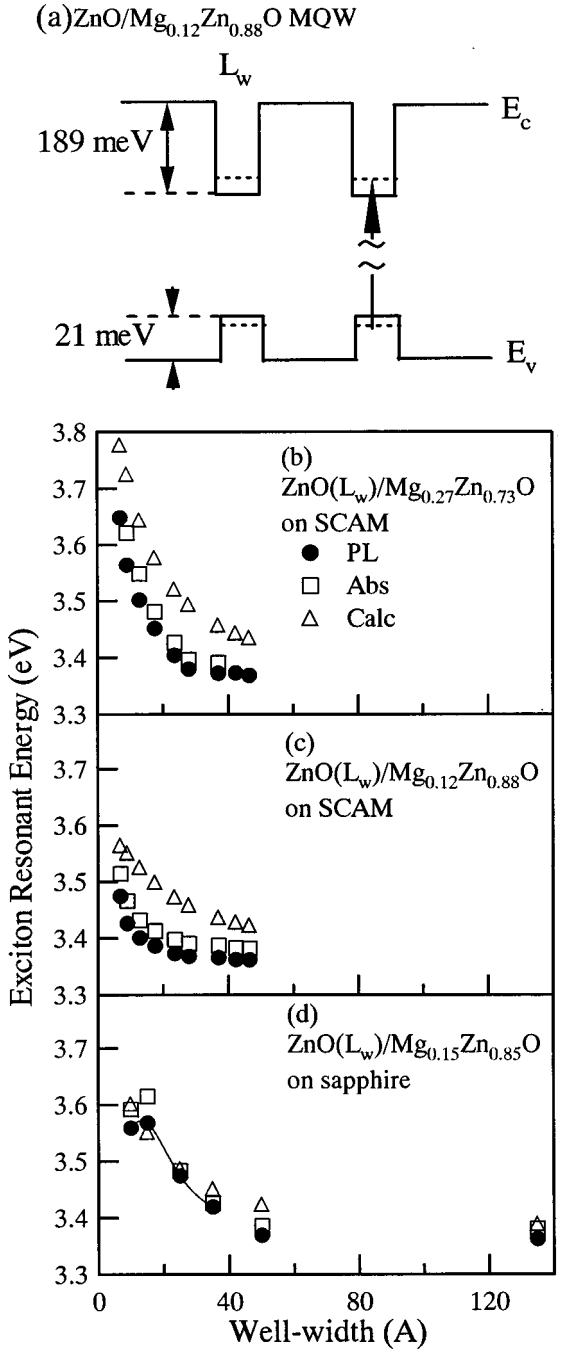

FIG. 2. (a) Diagram of conduction and valence bands between barrier and well layers in $[ZnO/Mg_{0.12}Zn_{0.88}O]$ MQW (see Ref. 6). The upward arrow shows the lowest interband transition. (b) Peak energies of PL (circles) and absorption (squares) are plotted against L_w in $[ZnO/Mg_{0.27}Zn_{0.73}O]_{10}$ on SCAM substrates. Calculated results (triangles) of the interband transition energy including the excitonic effect are also shown. (c) Similar except that the Mg content was $\approx 12\%$. (d) Similar except that the substrate was sapphire. The Mg content was $\approx 15\%$. Energies of PL excitation spectra (squares) are plotted instead of those of absorption, due to the presence of the 100-nm-thick ZnO buffer layers. Note, the peak energies of PL excitation spectra coincide with those of absorption. A solid curve is shown as a visual guide.

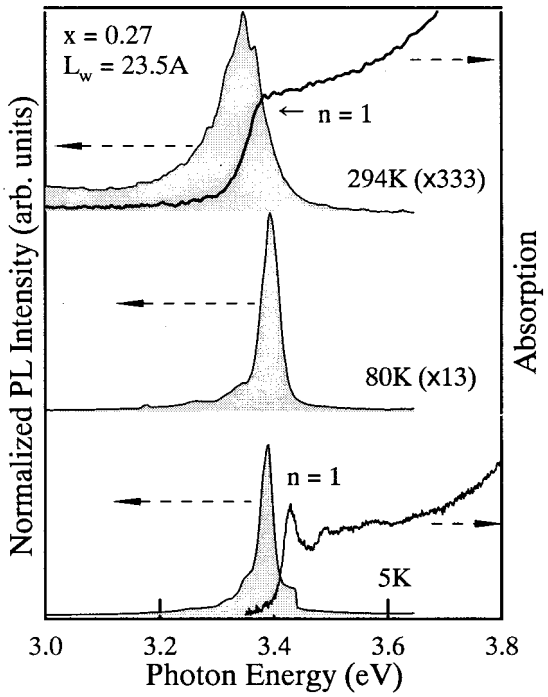

FIG. 3. Temperature dependence of PL and absorption spectra in $[ZnO(23.5\,Å)/Mg_{0.27}Zn_{0.73}O]_{10}$ on SCAM substrates. The upper two spectra were multiplied by the indicated values for normalization.

tures. The PL peaks showed a Stokes shift, as seen in the figures. The amount of the shift is a monotonically decreasing function of L_w. We can safely conclude that the dominant excitonic PL originates from excitons localized at the potentials induced by spatial fluctuations on the relevant heterostructure size, because such fluctuation has a more sensitive effect for a very thin well. However, the Stokes shift as well as the width of the PL band in the case of $x=0.27$ barrier layers are larger than those of an $x=0.12$ barrier with the same L_w. The depth fluctuation of the potential well is thought to be a reason for this enhancement. Since the $x=0.27$ is above the solubility limit, microscopic composition fluctuation is much larger than that in the barrier with $x=0.12$. The inhomogeneiety of the band gaps in the barrier layers induces the depth fluctuation and the enhancement of the exciton localization energy.

As seen in Fig. 2(d), both the peak energies have the maximum at L_w of 15 Å when sapphire substrates were used. This is a critical L_w that prevents the quantum confinement with respect to the exciton energy from having the proper effect, i.e., the confinement effect cannot be properly realized unless the L_w is more than the critical thickness of 15 Å. This is because of the poor controllability of L_w due to the lattice mismatching. On the contrary, in the case of the lattice-matched substrates, both the peak energies are monotonically decreasing functions of L_w. This tendency is in an agreement with the calculation. Therefore, it is concluded that there is no limitation with respect to the L_w if SCAM is used as a substrate, which is due to the improved surface flatness at the heterointerfaces.

Figure 3 shows the temperature dependence of PL and absorption spectra in the $[ZnO/Mg_{0.27}Zn_{0.73}O]_{10}$ on SCAM substrates with L_w of 23.5 Å. Since the PL peak at RT is located in the proximity of the exciton absorption band, it can be concluded that excitonic PL definitely persists up to RT. We confirmed such PL at RT for all 27 samples having various barrier heights and L_w. Excitonic PL in MQWs on sapphire is thermally quenched at 150 K. This is another improvement made possible by the lattice- matching condition. Time-resolved PL measurements showed that the nonradiative decay rates of excitons in MQWs on SCAM substrates are less than those in samples on sapphire, which is due to the high crystallinity.

In summary, the adoption of lattice-matched SCAM substrates significantly improved the optical properties of ZnO MQWs. First, such a matching condition enables us to attain high controllability of layer thickness. As a result, the quantum-confinement effect for the exciton energy could be confirmed experimentally if the well width is equal to 1.5 unit cells or more. Second, a bright excitonic PL was confirmed at RT. Such high-quality MQWs opens up numerous possibilities for UV optoelectric devices.

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