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Authors	T. Makino,C. H. Chia,N. T. Tuan,Y. Segawa,M. Kawasaki,A. Ohtomo,K. Tamura,H. Koinuma
Citation	Applied Physics Letters, Vol. 77, No. 11,
Pub. date	2000, 9
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Radiative and nonradiative recombination processes in lattice-matched (Cd,Zn)O/(Mg,Zn)O multiquantum wells

T. Makino,[a] C. H. Chia,[b] Nguen T. Tuan, and Y. Segawa
Photodynamics Research Center, RIKEN (Institute of Physical and Chemical Research), Sendai 980-0845, Japan

M. Kawasaki, A. Ohtomo, and K. Tamura
Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama 226-8502, Japan

H. Koinuma[c]
Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan

(Received 19 May 2000; accepted for publication 12 July 2000)

Time-resolved photoluminescence studies have been performed on (Cd,Zn)O/(Mg,Zn)O multiquantum wells, which are almost perfectly lattice matched (0.034%), grown by laser molecular-beam epitaxy on a $ScAlMgO_4$ substrate. Radiative recombination of excitons in the wells exhibits a significant spectral distribution of times. This distribution was interpreted in terms of localization of excitons by potential fluctuations due to alloy disorder and to well width and depth variations. The temperature dependence of the radiative lifetime of excitons was deduced from the measurement of both the photoluminescence decay time and intensity. We found that the radiative lifetime increases linearly with temperature, showing a two-dimensional feature of excitons in the quantum wells. © *2000 American Institute of Physics.* [S0003-6951(00)01837-4]

Recently, as an oxide wide-band-gap semiconductor, ZnO is expected to be one of the main candidates for ultraviolet optical applications such as light-emitting diodes or laser diodes. The large exciton binding energy (EBE) of 59 meV[1] allows us to observe the excitonic absorption and recombination even at room temperature (RT), which makes this material appealing. Excitonic laser oscillation with a very low threshold ($24\,kW/cm^2$) at RT was confirmed in 50 nm thin films on sapphire(0001) substrates.[2–4] Such observations indicate that an exciton-related recombination process can be utilized as an optoelectronic device operatable at RT. A lower pumping threshold can be expected, in principle, if an exciton-related recombination, rather than a recombination of an electron–hole plasma, is used. Fabrication and characterization of alloyed semiconductors such as (Mg,Zn)O or (Cd,Zn)O are important from the viewpoint of band-gap engineering as well as a $p-n$ junction. The alloyed oxide
(Mg,Zn)O has been found to be a suitable material for the barrier layers of ZnO/(Mg,Zn)O multiquantum wells (MQWs) owing to its larger band-gap energy as revealed in previous studies.[5,6] On the other hand, a (Cd,Zn)O mixed crystal is expected to expand the wavelength tunability by virtue of its narrower band gap. A (Cd,Zn)O/(Mg,Zn)O (CZM) quantum well having a perfect (in-plane) lattice match can be achieved by choosing an appropriate combination of cadmium and magnesium concentrations.[7] This is one of the advantages compared to (In,Ga)N/(Al,Ga)N quantum wells. In the latter case, an internal electric field induced by lattice strain makes the excitonic properties complicated. There have been few experimental studies on the optical properties of this alloyed epitaxial film.[8] In this letter, we report on a combined analysis and the deduced results of temperature dependences of the photoluminescence (PL) decay time and the integrated PL intensity. The relevant analysis was performed in order to separate the radiative and nonradiative recombination times in CZM MQWs on $ScAlMgO_4$ substrates grown by laser molecular-beam epitaxy (LMBE).

MQW of ten periods, $[Cd_{0.004}Zn_{0.996}O/Mg_{0.12}Zn_{0.88}O]_{10}$, was grown by the LMBE under high vacuum condition[9] on a $ScAlMgO_4(0001)$ substrate, the lattice constant of which matches that of ZnO with 0.09%. The buffer, composed of a 360-Å-thick ZnO epilayer, was used for the flat heterointerface if the Cd is incorporated. The well layer thickness (L_w) was ≈ 22 Å. The thickness of the barrier layer was approximately 50 Å. Thickness was precisely determined from x-ray diffraction analysis. The thicknesses indicated below in units of angstrom are the averaged ones of ten well layers. Excimer laser pulses (248 nm) were impinged onto a (Cd,Zn)O or (Mg,Zn)O ceramic target (99.999%) located 5 cm away from substrate surface. The films having c-axis orientation were grown at 500 °C in 1×10^{-5} Torr of pure oxygen (99.9995%). The mismatch of the lattice constants between (Cd,Zn)O and (Mg,Zn)O was estimated to be 0.034%. The sample was kept in a cryostat under strain-free conditions for the temperature-dependent measurements. The time-integrated PL (TIPL) was measured by using a cw He–Cd laser (325 nm), and the PL from the sample was monitored using a 0.3-m monochromator with a charge coupled device. The time-resolved PL (TRPL) measurements were performed with a streak camera in conjunction with a monochromator. Pulsed excitation was provided by the frequency doubled beam of a mode-locked Ti:sapphire laser, which was pumped by an Ar-ion laser. The

[a]Electronic mail: tmakino@postman.riken.go.jp
[b]Also at: Department of Physics, Tohoku University, Japan.
[c]Also a member of CREST, Japan Science and Technology Corporation.

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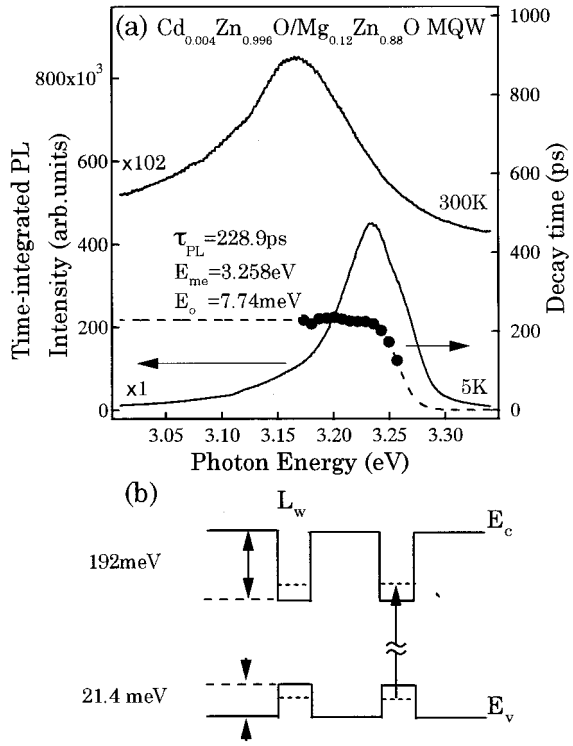

FIG. 1. (a) Temperature dependence of time-integrated photoluminescence in a $[Cd_{0.004}Zn_{0.996}O(22\,Å)/Mg_{0.12}Zn_{0.88}O(50\,Å)]_{10}$ MQW on a lattice-matched $ScAlMgO_4$ substrate, under standard cw conditions. Measured bath temperatures are shown on the right-hand side. The uppermost spectrum was normalized by multiplying the values shown on the left-hand side (i.e., $\times 102$). PL decay times as a function of monitored photon energy at 5 K. The broken curve is the theoretical one fitted by Eq. (1). (b) Band diagram of conduction and valence bands between barrier and well layers (Ref. 10). The upward arrow shows the lowest interband transition.

power of excitation was about $90\,kW/cm^2$. No subtractions for reflected or transmitted lights were made in our calculation. No temperature dependence of the peak energies or shape of the PL spectra was observed. The spectral resolution of all measurements was less than 0.3 nm. The energy of the photoexcitation was 3.397 eV, which is resonant to the *B*-exciton state in the ZnO buffer layer at 5 K.

Figure 1(a) shows the temperature dependence of the TIPL spectra. It should be noted that room temperature luminescence of excitons in this sample could be clearly observed. When the measured temperature is 5 K, the main PL peak is located at 3.235 eV. The resonance energy of the free excitons in the wells at 5 K was determined in the following way. The peak energy of the absorption spectrum in (Cd,Zn)O epilayers without a buffer layer was estimated to be 3.337 eV. The lowest transition energy of excitons formed with the confined electrons and holes was calculated on the basis of the assumption that the EBE is 59 meV. The discontinuities of the conduction band ($\Delta_e = 192\,meV$) and the valence band ($\Delta_h = 21.4\,meV$)[10] were used in the calculation. Effective masses[1] of an electron ($m_e^* = 0.28\,m_0$) and a hole ($m_h^* = 1.8\,m_0$) were used. Here, m_0 is the free electron mass. These band offsets (214 meV) and the optical transition process on this MQW are shown in Fig. 1(b). The resonant energy of the quantized excitons is estimated to be 3.408 eV. We could not directly measure the absorption spectrum due to the presence of the 36 nm ZnO buffer layer. No resonant structure could be observed in the reflection spectra in the MQWs measured at 5 K. The Stokes shift between the main PL peak and the exciton energy of the quantum wells was estimated to be 173 meV. It was suggested that the main peak is due to excitons localized at energy minima induced by well width and depth fluctuations and by the concentration fluctuations.

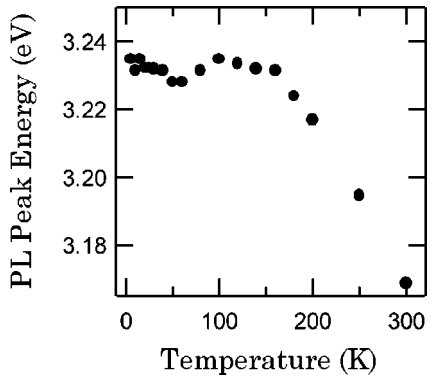

FIG. 2. Temperature dependence of peak energy in time-integrated photoluminescence spectra.

Figure 2 shows the temperature dependence of the TIPL peak energy. The peak energy decreases from 5 to 60 K, increases between 60 and 100 K, and then decreases for higher temperatures. This ''S-shaped'' PL shift is caused by a change in the exciton dynamics along with the temperature due to the exciton localization as was proposed by Cho *et al.*[11] The blueshift from 60 to 100 K indicates that the localized excitons are delocalized above 100 K, the thermal energy of which was estimated to be 8.63 meV. The redshift for the higher temperatures is due to the temperature-induced narrowing of the band-gap energy.

In the lower part of Fig. 1(a), the PL decay times as a function of monitored photon energy at 5 K in the CZM MQW are shown. The decay time was shorter than the temporal resolution of our setup above 200 K. The PL decay time is a monotonically decreasing function of the monitored photon energy. This is because the decay of the localized excitons is not only due to radiative recombination but also due to the transfer process to the tail state. If the density of the tail state is approximated as $\exp(E/E_0)$, and if the effective recombination lifetime (τ_{PL}) does not change with emission energy, the observed lifetime $\tau(E)$ can be expressed by the following equation:[12]

$$\tau(E) = \frac{\tau_{PL}}{\exp[(E - E_{me})/E_0]}, \tag{1}$$

where E_0 shows the degree of the depth in the tail state and E_{me} is the characteristic energy representing the absorption edge. The best fit could be obtained using $\tau_{PL} = 228.9\,ps$, $E_0 = 7.74\,meV$, and $E_{me} = 3.258\,eV$. The estimated value of E_0 is comparable to the thermal energy shown above. Therefore, the depth of localization is estimated to be about 8 meV in this sample. The spectrally integrated PL intensity decreases with increasing T, which indicates an enhancement of nonradiative processes. The normalized variation of PL intensity versus T nicely follows an $\exp(T/T_0)$ law with $T_0 \sim 36\,K$. Since the measured PL decay time is simply given

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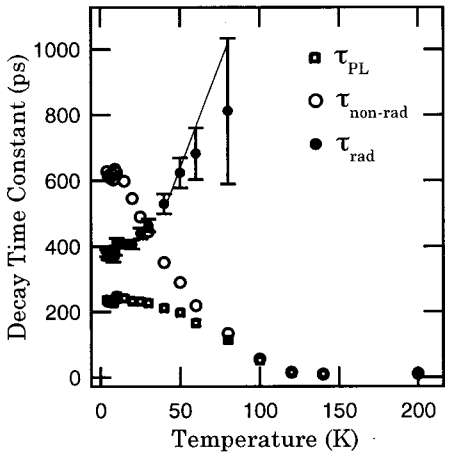

FIG. 3. Temperature dependence of recombination lifetimes, τ_{PL}, τ_{rad}, and τ_{nonrad}. The solid line is the theoretical one fitted by Eq. (2).

by $\tau_{PL}^{-1}=\tau_{nonrad}^{-1}+\tau_{rad}^{-1}$, we obtain a lower bound to the radiative lifetime $\tau_{rad}=\tau_{PL}/\eta$ by assuming that η equals 1 at $T=0$ K and follows the abovementioned exponential law.

Figure 3 shows the temperature dependences of effective, radiative, and nonradiative recombination times (τ_{PL}, τ_{rad}, and τ_{nonrad}) obtained by the temperature dependence of the TIPL intensity and PL decay time. The τ_{rad} values were almost constant at values of T below 25 K because of the localization of excitons, and the τ_{rad} increases proportionally to $T^{1.16}$ between 40 and 80 K. The nonradiative lifetimes are almost identical to that of PL above $T=100$ K. Since the radiative lifetimes have giant error bars in this T range, we did not plot that of radiative lifetime in this range. It is likely that excitons are delocalized and become nearly free two-dimensional (2D) excitons above 40 K because the theoretical calculation[13] for the oscillator strength predicts the relation of $\tau_{rad}\propto T^{1.0}$ for 2D excitons,[13,14] in which the wave vector selection rule is taken into account between the radiation field and the exciton center-of-mass motion. This is also consistent with the fact that the thickness of this MQW is narrower than the exciton Bohr diameter of 36 Å. On the other hand, τ_{nonrad} is a monotonically decreasing function of measured T, and the nonradiative recombination process becomes dominant above 100 K. We can now estimate the radiative lifetime of the free exciton at the low-T limit from the temperature dependence of the radiative lifetime in the T range of 40–80 K. According to Lefebvre *et al.*,[14] the approximate expression for the temperature dependence of the lifetime is

$$\frac{\partial\tau_{rad}}{\partial T}=\frac{2Mk_B}{\hbar^2k_0^2}\tau_0, \tag{2}$$

where τ_0 is the reciprocal value of the exciton radiative rate at the low-temperature limit, T is temperature, M is the exciton effective mass, k_B is a Boltzmann constant, and k_0 is the wave vector of light in vacuum at the excitonic resonance. This formula is valid under the condition that the thermalization time of excitons is very short compared to radiative recombination times. The term τ_0 can be obtained from the temperature dependence of τ_{rad} via Eq. (2). We obtain $\tau_0\approx 0.5$ ps from $\partial\tau_{rad}/\partial T=7.32\ \mathrm{ps\,K^{-1}}$, $k_0=1.80\times10^7\ \mathrm{m^{-1}}$, and $M=2.08m_0$.

Let us now comment on the very small radiative lifetime of 0.5 ps, which is one or two orders of magnitude smaller than the values obtained for GaAs MQW (25 ps),[13] which simply means that the oscillator strength in CdZnO MQW is larger by one and a half orders of magnitude. This is not really surprising, if one considers the value for longitudinal-transverse splitting of the exciton energy,[1] which could be deduced from reflection spectra.

In summary, radiative and nonradiative recombination processes were assessed in perfectly lattice-matched (Cd,Zn)O/(Mg,Zn)O MQWs deposited by LMBE by means of TRPL spectroscopy. We have determined the variation of the radiative lifetime of QW excitons versus T to be linear, attributed principally to the excitons from which we deduce a radiative lifetime of 0.5 ps in the low-temperature limit. Enhancement of nonradiative processes was observed with increasing T. The nonradiative process became dominant above 100 K.

This work was partially supported by the Proposal Based Program of NEDO (Grant No. 99S12010) and by the Special Postdoctoral Research Program of RIKEN, Japan.

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