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Recombination dynamics of excitons in $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ alloy films grown using the high-temperature-annealed self-buffer layer by laser-assisted molecular-beam epitaxy

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Recombination dynamics of excitons in $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ epilayers grown by laser-assisted molecular-beam epitaxy on a ScAlMgO_4 substrate were investigated. By using the MgZnO high-temperature-annealed self-buffer layer (HITAB), the value of full width at half maximum of the near-band-edge (NBE) photoluminescence (PL) peak at 3.6 eV was decreased from 133 to 94 meV at 293 K, and the intensity ratio of the NBE emission to the deep emission band centered around 2.2 eV was increased by a factor of 3. Also, the PL lifetime of the NBE peak at 293 K under the excitation density of $1 \mu\text{J}/\text{cm}^2$ was increased from 49 to 60 ps. These results suggest that HITAB gave rise to improved alloy compositional homogeneity and reduced concentration of point defects. © 2007 American Institute of Physics. [DOI: 10.1063/1.2719168]

ZnO and related (Be, Mg, Zn, Cd)O alloys are an excellent candidate for the use in ultraviolet (UV) and visible light emitters, according to their wide bandgap energy.¹ To fabricate high-performance devices, formation of $\text{Mg}_x\text{Zn}_{1-x}\text{O}/\text{ZnO}$ heterostructures and quantum wells (QWs) is essential. A $\text{Mg}_{0.3}\text{Zn}_{0.7}\text{O}/\text{ZnO}$ heterostructure field-effect transistor has been demonstrated,² and the enhancement of exciton binding energy has been shown in $\text{Mg}_{0.27}\text{Zn}_{0.73}\text{O}/\text{ZnO}$ multiple QWs (Ref. 3) [59 meV for ZnO (Ref. 4) and 115 meV for the QWs].

Recently, a reproducible fabrication of p -type⁵⁻⁷ ZnO has been realized, and ZnO p - i - n homojunction light-emitting diodes (LEDs) emitting near UV to blue color electroluminescence were demonstrated.⁸ Prior to that, overall quality of undoped ZnO epilayers grown by laser-assisted molecular-beam epitaxy (L-MBE) has been significantly improved by reducing structural and point defects: crystallographic perfection and lattice coherency were improved by the use of (i) a nearly lattice-matched ScAlMgO_4 (SCAM) substrate⁹ and (ii) the ZnO high-temperature-annealed self-buffer layer (HITAB).¹⁰ Densities of Zn vacancies (V_{Zn}) and nonradiative recombination centers (NRCs) were decreased by (iii) a high-temperature growth with subsequent slow cooling (the cooling rate, R_c , being $-10^\circ\text{C}/\text{min}$) under

minimum O_2 pressure (P_{O_2}).¹¹ Among these, the concept of HITAB is to serve as a perfectly strain-free, atomically smooth, high crystallinity quasihomoepitaxial template for the overlayer growth.¹⁰ However, the effectiveness of using HITAB has not yet been examined for the MgZnO hetero-epitaxy.

In this letter, roles of MgZnO HITAB in improving optical qualities are discussed for L-MBE of $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ by means of steady-state and time-resolved photoluminescence (PL) measurements. Issues on residual NRCs in the state-of-the-art MgZnO epilayers are also discussed.

An approximately 600-nm-thick $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ epilayer was grown by temperature-variable combinatorial L-MBE, by which the growth temperature (T_g) was distributed from 840°C at one of the sample edges to 980°C at another sample edge, on an 100-nm-thick $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ HITAB prepared on SCAM substrate ($\text{MgZnO}/\text{HITAB}$). After the growth, the epilayer was cooled down slowly ($R_c = -10^\circ\text{C}/\text{min}$) under P_{O_2} of 10^{-9} Torr.¹¹ The MgZnO HITAB preparation was initiated with the growth of $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}$ at 650°C ($P_{\text{O}_2} = 10^{-6}$ Torr) followed by an annealing at 1000°C for 1 h ($P_{\text{O}_2} = 10^{-3}$ Torr). For comparison, an approximately 400-nm-thick $\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}$ epilayer was grown directly on SCAM substrate (MgZnO/SCAM). We note that the control sample thickness is not ideal, since the increased thickness (total of 700 nm for $\text{MgZnO}/\text{HITAB}$) would result in better material quality. However, judging from our experience, the quality variations due to the thickness difference are not large in this study.

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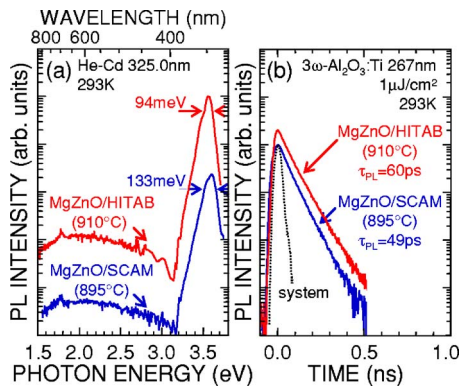


FIG. 1. (Color online) (a) PL spectra and (b) TRPL signals of $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}/\text{HITAB}$ and $\text{Mg}_{0.12}\text{Zn}_{0.88}\text{O}/\text{SCAM}$ at 293 K. The excitation density for the TRPL measurements was $1 \mu\text{J}/\text{cm}^2$. The trace denoted by “system” shows the system response.

Steady-state PL spectra were excited using the 325.0 nm line of a cw He–Cd laser ($6 \text{ W}/\text{cm}^2$). Time-resolved photoluminescence (TRPL) measurements on the near-band-edge (NBE) PL peak were carried out using an ~ 100 fs pulse of a frequency-tripled mode-locked $\text{Al}_2\text{O}_3:\text{Ti}$ laser (267 nm, $120 \sim 1000 \text{ nJ}/\text{cm}^2$ per pulse). The TRPL signal was collected using a standard streak camera acquisition technique.

PL spectra measured at 293 K of $\text{MgZnO}/\text{HITAB}$ and MgZnO/SCAM grown at around 900°C are shown in Fig. 1(a). Both the epilayers exhibited a predominant NBE emission peak at approximately 3.6 eV and a deep emission band centered around 2.2 eV. The value of full width at half maximum (FWHM) of the NBE peak was decreased from 133 to 94 meV by the use of HITAB. The result indicates the improved compositional homogeneity and is consistent with the results of x-ray diffraction measurements: the FWHM value of (0002) MgZnO diffraction peak, which reflects the broadening of out-of-plane (c) lattice parameter, was also decreased from 80 to 65 arcsec. These improvements are attributed to the accommodation of the lattice mismatch to SCAM substrate, and are not originated from the difference in the alloy compositions, because the MgO molar fractions x estimated from the c lattice parameters⁹ are quite similar (0.11 for $\text{MgZnO}/\text{HITAB}$ and 0.12 for MgZnO/SCAM). Here we note that the value of x in $\text{MgZnO}/\text{HITAB}$ grown at 910°C was lower than that in MgZnO/SCAM grown at 895°C . This result is opposite to the trend^{12,13} that x increases with increasing T_g due to the higher vapor pressure of Zn species compared to that of Mg ones. Because x decreased with the increase in T_g for the MgZnO films grown on both HITAB and SCAM (data not shown) and T_g was only up to 650°C in Refs. 12 and 13, different Mg/Zn incorporation mechanisms may exist for high T_g regions.

Together with the improvement in the compositional homogeneity, the ratio of integrated NBE emission intensity to that of the deep emission band for $\text{MgZnO}/\text{HITAB}$ was 3 times higher than that for MgZnO/SCAM . The broad deep emission band seen in Fig. 1(a) may be a convolution of the luminescence bands similar to the green band at 2.4 eV and the red one at 2.0 eV in ZnO , and the emission can be related to the native point defects.¹ The result suggests the decrease in the point defect concentration by the use of HITAB. The TRPL signals of the NBE peak measured at the peak energy at 293 K exhibited a single-exponential decay shape, as shown in Fig. 1(b). The PL lifetimes (τ_{PL}) were 49 ps for

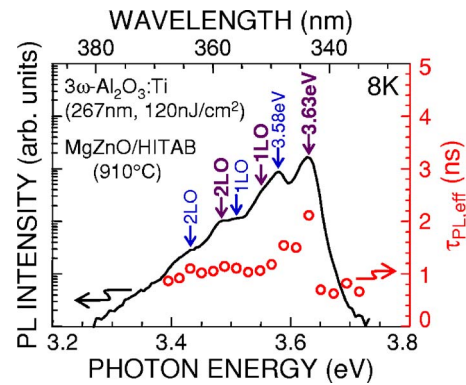


FIG. 2. (Color online) PL spectra and effective PL lifetimes (open circles) of $\text{Mg}_{0.11}\text{Zn}_{0.89}\text{O}/\text{HITAB}$ at particular photon energies at 8 K. The excitation density for the TRPL measurements was $120 \text{ nJ}/\text{cm}^2$.

MgZnO/SCAM and 60 ps for $\text{MgZnO}/\text{HITAB}$ when the excitation density was $1 \mu\text{J}/\text{cm}^2$. Because τ_{PL} at room temperature is generally dominated by the nonradiative lifetime (τ_{NR}), which will be discussed later, the slight increase in τ_{PL} also suggests the slight decrease in the concentration of NRCs by the use of HITAB.

The PL spectrum of $\text{MgZnO}/\text{HITAB}$ at 8 K is shown in Fig. 2. The spectrum exhibited emission peaks at 3.63 and 3.58 eV and shoulders in their lower energy side. The shoulders are assigned as being due to the longitudinal optical (LO) phonon replicas of the main peaks, since their energy separation (~ 70 meV) nearly agreed with the LO phonon energy of ZnO : energies of $A_1(\text{LO})$ and $E_1(\text{LO})$ modes are 71 and 72 meV, respectively.¹⁴ The TRPL signal measured at the NBE peak energy at 8 K of $\text{MgZnO}/\text{HITAB}$ [uppermost trace in Fig. 3(a)] can be fitted by a biexponential function $I(t) = I_1 \exp(-t/\tau_1) + I_2 \exp(-t/\tau_2)$, where $I(t)$ is the PL intensity at time t , I_i represents the initial intensity of the i th component, and τ_i represents the lifetime. The effective PL lifetimes defined by $\tau_{PL,eff} = (I_1\tau_1 + I_2\tau_2)/(I_1 + I_2)$ are plotted as a function of monitored photon energy in Fig. 2. Representative $\tau_{PL,eff}$ was approximately 1 ns and the maxima were found at the main NBE peak energies at 3.63 and 3.58 eV. Since the radiative lifetime (τ_R) of free excitons in ZnO at low temperature is approximately 100 ps,¹¹ the long $\tau_{PL,eff}$ values suggest the contribution of certain bound/localized states. As a matter of fact, the NBE peak energy exhibited the “S-shape” behavior in response to a temperature rise, which is a decrease in the energy at the lowest-temperature range followed by an increase and the second decrease at middle- and high-temperature ranges, respectively. In addition, the NBE peak energy at 300 K was lower only by 51 meV than that at 8 K, which is much smaller than that for free excitons in ZnO being 97 meV.¹¹ Since the polarization induced internal electric fields are negligible in our strain-free MgZnO films, the weak redshift with the increase in temperature (T) is not due to the strain effect.

The TRPL signals measured at the NBE peak energy of $\text{MgZnO}/\text{HITAB}$ are shown as a function of T in Fig. 3(a). The signals exhibited a biexponential decay shape below 75 K. However, the decay shape turned out to be single exponential and the decay constant decreased rapidly above 100 K. We note that the spectral diffusion (peak redshift after the pulsed laser excitation) also disappeared above 100 K. In order to analyze the role of radiative and nonradiative processes in MgZnO as a function of T , values of τ_R and τ_{NR}

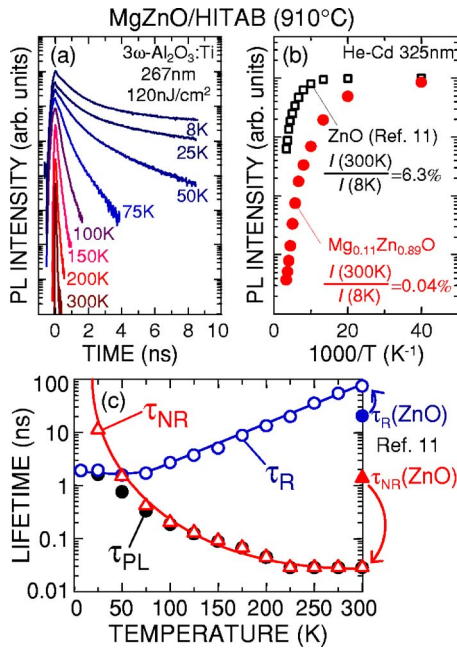


FIG. 3. (Color online) (a) TRPL signals measured at the NBE PL peak energy of Mg_{0.11}Zn_{0.89}O/HITAB as a function of T . (b) Spectrally integrated PL intensity as a function of $1/T$. At 300 K, η_{int}^{eq} was 0.04%, which was more than two orders of magnitude lower than that of ZnO being 6.3% (Ref. 11). (c) Effective PL lifetime $\tau_{PL,eff}$ (closed circles) of Mg_{0.11}Zn_{0.89}O/HITAB as a function of T . Values of τ_R (open circles) and τ_{NR} (open triangles) derived from $\tau_{PL,eff}$ and η_{int}^{eq} are also plotted. The solid lines are drawn as guide for the eyes. At 300 K, τ_R and τ_{NR} were 75.4 ns and 30 ps, respectively, under the excitation density of 120 nJ/cm². Note that τ_R and τ_{NR} of the ZnO epilayer grown on ZnO HITAB were 20.6 and 1.4 ns, respectively (Ref. 11).

of the NBE peak were deduced from the experimental values of τ_{PL} and the equivalent internal quantum efficiency (η_{int}^{eq}) using the relations $1/\tau_{PL} = 1/\tau_R + 1/\tau_{NR}$ and $\eta_{int}^{eq} = 1/(1 + \tau_R/\tau_{NR})$, where $\tau_{PL,eff}$ values were used for τ_{PL} . In this letter, η_{int}^{eq} is substituted by the spectrally integrated PL intensity at particular T divided by the value at 8 K and is plotted as a function of $1/T$ in Fig. 3(b). The obtained values of τ_R and τ_{NR} are plotted by open circles and triangles, respectively, in Fig. 3(c). As shown, τ_R is nearly temperature independent below 75 K, which is characteristics of excitons bound or localized at nearly zero-dimensional spaces.¹⁵ Above 75 K, τ_R increases according to approximately $T^{1.5}$, since the excitons become free in three-dimensional space.¹⁵ The τ_R value at 300 K (75.4 ns) is more than 3 times longer than that of ZnO on HITAB (20.6 ns) (Ref. 11) under the same excitation conditions (120 nJ/cm²). The result suggests the decrease in oscillator strength in MgZnO alloys. Conversely, τ_{NR} decreases rapidly in response to a temperature rise and dominates the recombination process above 100 K. The temperature at which τ_R and τ_{NR} crossover is approximately 50 K, which is lower than that of ZnO (~ 160 K).¹¹ Accordingly, τ_{NR} at 300 K is as short as 30 ps and η_{int}^{eq} is 0.04%. These values are approximately 2 orders of magnitude smaller than ZnO (1.4 ns and 6.3%).¹¹ These results reflect the presence of high density NRCs in the present MgZnO films, even when grown on HITAB. As a matter of fact, τ_{NR} increased from 30 ps for the excitation density of

120 nJ/cm² to 60 ps for 1 μ J/cm² [Fig. 1(b)]. The result is a fingerprint that NRCs are not saturated under our excitation conditions. Because the improvement in τ_{NR} is not so remarkable although appropriate high T_g growth and slow cooling¹¹ were already carried out on MgZnO/HITAB, the synthesized MgZnO target must contain certain impurities responsible for the short τ_{NR} . Therefore, purification of the starting material (target) is an essential way to improve τ_{NR} .

In summary, recombination dynamics of excitons in Mg_{0.11}Zn_{0.89}O alloy films grown by L-MBE were studied. The use of MgZnO HITAB was shown to improve the alloy compositional homogeneity and decrease the concentration of point defects responsible for the deep luminescence band. These achievements may be due to the accommodation of lattice mismatch to the SCAM substrates. Because the improvement in τ_{NR} was not so remarkable and η_{int}^{eq} of the NBE peak at 300 K was still as low as 0.04%, further reduction in the NRC concentration is mandatory.

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- ¹For a review, see for example, Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, *J. Appl. Phys.* **98**, 041301 (2005).
- ²K. Koike, I. Nakashima, K. Hashimoto, S. Sasa, M. Inoue, and M. Yano, *Appl. Phys. Lett.* **87**, 112106 (2005).
- ³H. D. Sun, T. Makino, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, *J. Appl. Phys.* **91**, 1993 (2002).
- ⁴D. G. Thomas, *J. Phys. Chem. Solids* **15**, 86 (1960).
- ⁵K. Minegishi, Y. Koiwai, Y. Kikuchi, K. Yano, M. Kasuga, and A. Shimizu, *Jpn. J. Appl. Phys., Part 2* **36**, L1453 (1997).
- ⁶M. Joseph, H. Tabata, and T. Kawai, *Jpn. J. Appl. Phys., Part 2* **38**, L1205 (1999).
- ⁷D. C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, *Appl. Phys. Lett.* **81**, 1830 (2002).
- ⁸A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, *Nat. Mater.* **4**, 42 (2005); A. Tsukazaki, M. Kubota, A. Ohtomo, T. Onuma, K. Ohtani, H. Ohno, S. F. Chichibu, and M. Kawasaki, *Jpn. J. Appl. Phys., Part 2* **44**, L643 (2005).
- ⁹A. Ohtomo, K. Tamura, K. Saikusa, K. Takahashi, T. Makino, Y. Segawa, H. Koinuma, and M. Kawasaki, *Appl. Phys. Lett.* **75**, 2635 (1999); A. Ohtomo and A. Tsukazaki, *Semicond. Sci. Technol.* **20**, S1 (2005).
- ¹⁰A. Tsukazaki, A. Ohtomo, S. Yoshida, M. Kawasaki, C. H. Chia, T. Makino, Y. Segawa, T. Koida, S. F. Chichibu, and H. Koinuma, *Appl. Phys. Lett.* **83**, 2784 (2003).
- ¹¹S. F. Chichibu, A. Uedono, A. Tsukazaki, T. Onuma, M. Zamfirescu, A. Ohtomo, A. Kavokin, G. Cantwell, C. W. Litton, T. Sota, and M. Kawasaki, *Semicond. Sci. Technol.* **20**, S67 (2005); S. F. Chichibu, T. Onuma, M. Kubota, A. Uedono, T. Sota, A. Tsukazaki, A. Ohtomo, and M. Kawasaki, *J. Appl. Phys.* **99**, 093505 (2006).
- ¹²A. Ohtomo, M. Kawasaki, T. Koida, K. Masubuchi, H. Koinuma, Y. Sakurai, Y. Yoshida, T. Yasuda, and Y. Segawa, *Appl. Phys. Lett.* **72**, 2466 (1998).
- ¹³T. Koyama, T. Ohmori, N. Shibata, T. Onuma, and S. F. Chichibu, *J. Vac. Sci. Technol. B* **22**, 2220 (2004).
- ¹⁴T. C. Damen, S. P. S. Porto, and B. Tell, *Phys. Rev.* **142**, 570 (1966).
- ¹⁵J. Feldmann, G. Peter, E. O. Göbel, P. Dawson, K. Moore, C. Foxon, and R. J. Elliot, *Phys. Rev. Lett.* **59**, 2337 (1987); H. Akiyama, S. Koshida, T. Someya, K. Wada, H. Noge, Y. Nakamura, T. Inoshita, A. Shimizu, and H. Sakai, *ibid.* **72**, 924 (1994).