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Ultraviolet Luminescence in $Mg_{0.12}Zn_{0.88}O$ Alloy Films *

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We investigate the origin of ultraviolet (UV) emission from $Mg_{0.12}Zn_{0.88}O$ alloy thin films with a wurtzite structure fabricated on c-plane Al_2O_3 substrates by plasma assisted molecular beam epitaxy. At room temperature, the absorption edge and UV emission band of the $Mg_{0.12}Zn_{0.88}O$ film shift to high-energy side compared with ZnO films. Temperature dependence of the photoluminescence spectra shows that the UV emission is composed of free exciton and neutral donor bound exciton emissions. Two-step dissociation processes of the UV emission are observed with the increasing temperature. The thermal quenching mechanism is attributed to the dissociation of the free exciton from the neutral donor bound exciton in the low temperature region and the dissociation of free electron and hole from the free exciton in the high temperature region.

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Recently, short wavelength lasers have been paid much attention for applications in high-density information storage. As a wide band gap semiconductor, ZnO is one of the most promising materials for producing ultraviolet (UV) laser at room temperature (RT) due to its large exciton binding energy of 60 meV.[1−3] To obtain high performance light emitting devices such as UV lasers, MgZnO alloy thin films are commonly used as a potential barrier material in ZnO-based heterostructures.[4,5] However, ZnO and MgO belong to wurtzite and cubic structures, respectively. Thus MgZnO alloy thin films exist with phase segregation in high Mg concentrations. Therefore, a large number of reports have focused on the fabrication of the wurtzite MgZnO.[6−8] So far, it has been reported that wurtzite MgZnO was grown with maximum Mg content up to 49 at.%.[6]

In our previous works,[9] we concentrated on the structure confirmation of MgZnO thin films with higher Mg content (above 20 at.%) toward the fabrication of UV light emitting devices as the barrier material. However, recent optical studies showed significantly improved optical properties for MgZnO alloy thin films with lower Mg content (below 20 at.%). As the reported highly efficient UV luminescence in MgZnO,[1] a strong UV emission having almost the same thermal activation energy with ZnO was observed even at room temperature. Compared with ZnO, a strong blue-shift was observed in the UV region for MgZnO, depending on the Mg content. The above results indicate that MgZnO alloy films have potential applications in UV light emitting devices as an active region. However, only a few works were reported on the photoluminescence properties of MgZnO films, in which was only the study of the energy position and the line width of the UV emission peak. Sharma *et al.* first observed an intense UV band edge emission related to the excitons in MgZnO films at room temperature,[7] but direct demonstration was not given. Therefore, it is necessary to understand the mechanism of UV emission for realizing the application of MgZnO-based optoelectronic devices.

In this Letter, we investigate the UV emission properties of $Mg_{0.12}Zn_{0.88}O$ alloy grown on a *c*-plane Al_2O_3 substrate by plasma assisted molecular beam epitaxy (P-MBE). We can attribute the UV emission of the $Mg_{0.12}Zn_{0.88}O$ film to the recombination of free exciton and neutral donor bound exciton. Two quenching processes with different activation energies are studied in detail.

A VG V80H MBE system with Knudsen-cells is used to grow the $Mg_{0.12}Zn_{0.88}O$ alloy thin films. The background vacuum of the growth chamber is about 1×10^{-8} Pa. The purities of Zn and Mg solid sources are 6N and 5N, respectively. Oxygen with 5N purity activated by radio-frequency plasma is served as the oxygen source. During the growth, the rf power of O-plasma is fixed at 300 W and the gas flow rate was

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kept at 2.0 sccm. The c-plane Al_2O_3 is used as the substrate. In order to obtain a clean fresh surface, the substrates are chemically etched in a hot solution of H_2SO_4:H_3PO_4=3:1 at 160°C for 15 min. Then the substrates are thermally pretreated at 700°C for 30 min and exposed to O-plasma at 650°C for another 30 min, which is expected to remove contaminant on the surface and obtain an oxygen-terminated Al_2O_3 (0001) surface.

The samples were characterized by x-ray diffraction (XRD) using a D/max-RA x-ray diffractometer with Cu K_α lines of 0.15418 nm. The content ratio of Mg:Zn (at.%) in the MgZnO films was evaluated by using x-ray photoelectron spectroscopy (XPS) and the energy dispersive spectrometer (EDS) of scanning electron microscopy (SEM).[10] The absorption spectra were measured by using a xenon lamp with a UV-360 spectrophotometer. A JY63 Micro Raman spectrometer was employed for the photoluminescence (PL) measurement. The excitation source was the 325 nm line of a He–Cd laser with 50 mW powers.

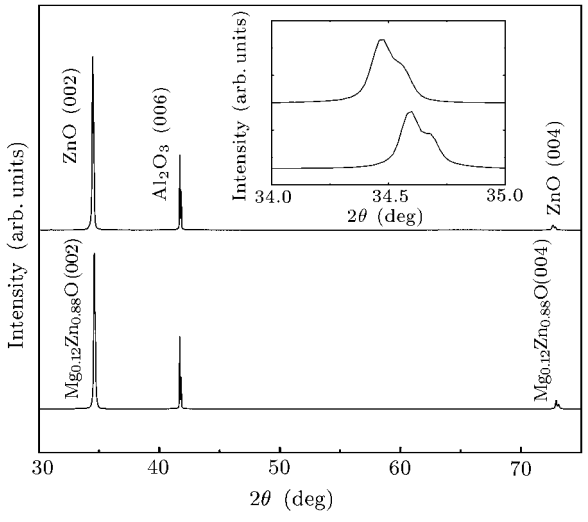

Fig. 1. X-ray diffraction spectra of ZnO and $Mg_{0.12}Zn_{0.88}O$ thin films. The inset shows the enlarged lineshape of ZnO and $Mg_{0.12}Zn_{0.88}O$ (002) diffraction peaks.

The XRD spectra of the ZnO and $Mg_{0.12}Zn_{0.88}O$ alloy thin films are shown in Fig. 1. Three peaks can be observed in the XRD spectra. The peak at 41.68° is the [006] diffraction peak of Al_2O_3, and the other two peaks are attributed to the [002] and [004] diffraction peaks for ZnO and $Mg_{0.12}Zn_{0.88}O$, respectively. It is indicated that the $Mg_{0.12}Zn_{0.88}O$ alloy film with the wurtzite structure is obtained. The inset shows the enlarged line shapes of the [002] diffraction peaks of ZnO and $Mg_{0.12}Zn_{0.88}O$. An asymmetric line shape of the [002] diffraction peaks is duo to the superposition of two diffraction peaks from $K_{\alpha 1}$ and $K_{\alpha 2}$. From the insert of Fig. 1, it can be seen clearly that the [002] peak position of $Mg_{0.12}Zn_{0.88}O$ differs from that of ZnO. This indicates that Zn^{2+} ions in the ZnO lattice are partly replaced by Mg^{2+} ions, resulting in the decrease of the lattice constant with the increasing Mg content.

Figure 2 shows the PL and absorption spectra of the ZnO and $Mg_{0.12}Zn_{0.88}O$ thin films measured at RT. For the PL spectra, both the two samples show one intense UV luminescence without deep level emission related to impurities or defects. Compared with the ZnO sample, the UV band of the $Mg_{0.12}Zn_{0.88}O$ film shifts from 3.29 to 3.44 eV. The full width at half maximum (FWHM) of the UV emission band is broadened from 61 to 72 meV, which is attributed to the disorder of Mg composition in the alloy films. Both the ZnO and $Mg_{0.12}Zn_{0.88}O$ samples are high transparent in the visible region from 400 to 800 nm and have a sharp absorption edge in the UV region. Here, the blue-shift of $Mg_{0.12}Zn_{0.88}O$ absorption edge is in agreement with the result of the PL measurements.

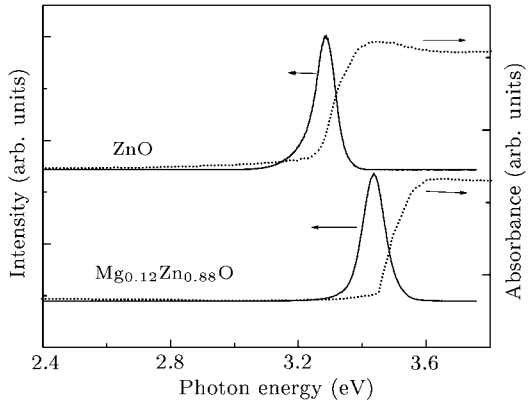

Fig. 2. Absorption spectra and PL spectra of the ZnO and $Mg_{0.12}Zn_{0.88}O$ thin films at RT.

In order to study the origin of UV emission in the $Mg_{0.12}Zn_{0.88}O$ thin film, PL spectra were measured at different temperatures from 91 to 342 K, as shown in Fig. 3(a). At temperatures lower than 162 K, there is no noticeable change for the PL peak position. In the temperature range from 162 K to RT, the UV band shifts to low energy side obviously with the increasing temperature, and a shoulder appears at high-energy side of the UV peak. Figure 4 shows the temperature dependence of the PL band FWHM for the $Mg_{0.12}Zn_{0.88}O$ film. At low temperatures, the PL band broadened significantly with the increasing temperature. At 162 K, the FWHM of the PL band reaches the maximum value of 67.5 meV. As the temperature increases further, the FWHM of the PL band shows an abnormal decrease. This indicates that the PL band is not from the same origin. In order to confirm further the UV emission mechanism, the UV band is fitted by using Gaussian line shape. Figure 3(b) shows the fitted result of the spectra at 102, 162,

246 and 294 K, respectively. As can be seen, the UV emission band with a shoulder can be fitted into two Gaussian peaks. At low temperatures, the emission peak at low energy side dominates in the PL spectra. With the increasing temperature, the contribution of the high-energy peak increases gradually.

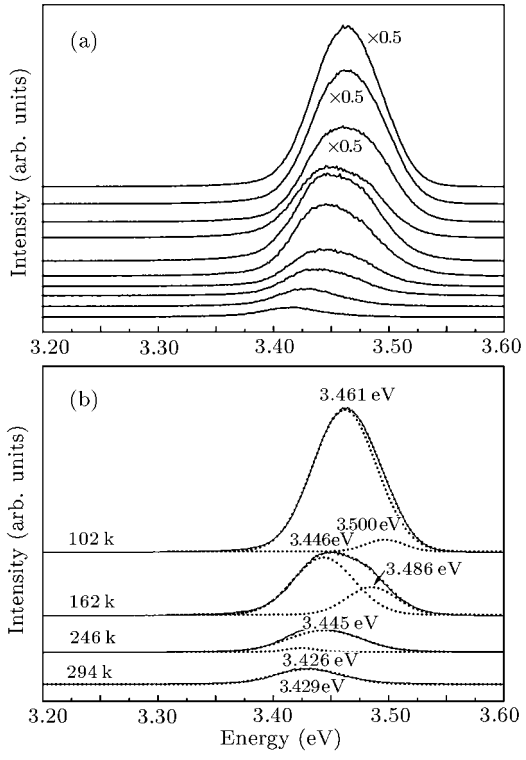

Fig. 3. (a) PL spectra measured at temperatures 91, 102, 138, 162, 186, 198, 210, 246, 294, 366 K (from top to bottom) for the $Mg_{0.12}Zn_{0.88}O$ thin film. (b) The fitting result of Gaussian lineshape of the PL peak at 102, 162, 246, and 294 K.

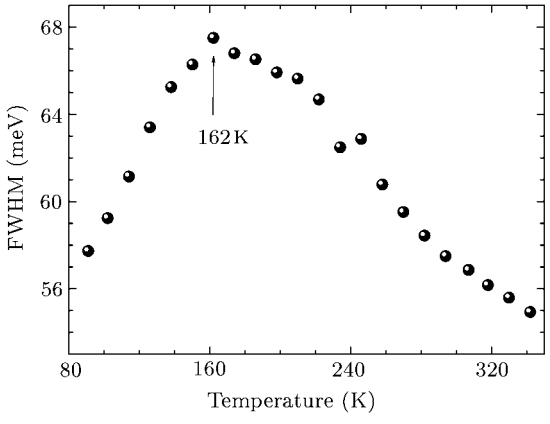

Fig. 4. FWHMs of the UV band of the $Mg_{0.12}Zn_{0.88}O$ thin film as a function of temperature ranging from 91 to 342 K.

The temperature-dependence of the PL intensity of the $Mg_{0.12}Zn_{0.88}O$ alloy film is shown in Fig. 5. Although the intensity of UV emission decreases monotonously with the increasing temperature from 81 to 366 K, two thermal quenching processes were found in different temperature ranges. Therefore, the temperature dependence of the intensity is studied by using two-step dissociation model described by

$$I(T) = \frac{I_0}{1 + A_1 \exp\left(-\dfrac{E_1}{k_B T}\right) + A_2 \exp\left(-\dfrac{E_2}{k_B T}\right)}, \tag{1}$$

where I_0, A_1 and A_2 are constants, k_B is Boltzmann's constant, and E_1 and E_2 are the activation energies. Bimberg *et al.*[11] have reported the dissociation processes of the excitons bound to acceptors or donors, where two-step dissociation processes were described well by using Eq. (1). Makino *et al.*[12] also studied the thermal quenching mechanisms of localized excitons and free excitons in ZnO/MgZnO quantum wells by using this method. In this study, curve 1 (the solid lines) in Fig. 5 expresses the results fitted with Eq. (1). The two thermal activation energies of $E_1 = 28.1$ meV and $E_2 = 57.6$ meV are obtained. With the increasing temperature, there are two different dissociation processes with two activation energies: (a) dissociation resulting in one free exciton, (b) dissociation resulting in one free electron and one free hole from the free exciton. For the two dissociation processes, the activation energies of $E_1 = 28.1$ meV and $E_2 = 57.6$ meV are attributed to the activation energies corresponding to bound exciton to free exciton (E_B), and the binding energy of the free exciton (E_x), respectively. Therefore, the observed UV PL spectra are a superposition of the free exciton emission band on the high-energy side and the bound exciton emission band on the low-energy side. In the temperature range 81–162 K, the UV emission spectra are dominated by the recombination of neutral donor-bound exciton (D_0, X), and the thermal quenching is dominated by the dissociation from the neutral (D_0, X) to free exciton. In this process, the contribution of free exciton emission becomes considerable gradually due to the increase of free exciton density, and the UV band exhibits a significant broadening, as shown in Fig. 4. This broadening includes two parts: (1) the broadening from the interaction between excitons and phonons, and (2) increase of the contribution of free exciton emission. When the temperature increases to 162 K, emission intensity of free exciton is comparable to that of bound exciton, and the FWHMs of PL band reaches the maximum value of 67.5 meV. At temperatures higher than 162 K, the bound exciton dissociates more rapidly, and the PL spectra are dominated by the recombination of the free exciton. Because the effect of this process on the FWHM is larger than that of increasing temperature, the UV band exhibits an interesting narrowing. When temperature is up to RT, the PL band is dominated by the free exciton recombination, and

the dissociation is mainly from the thermal activation from free exciton to free electron and free hole.

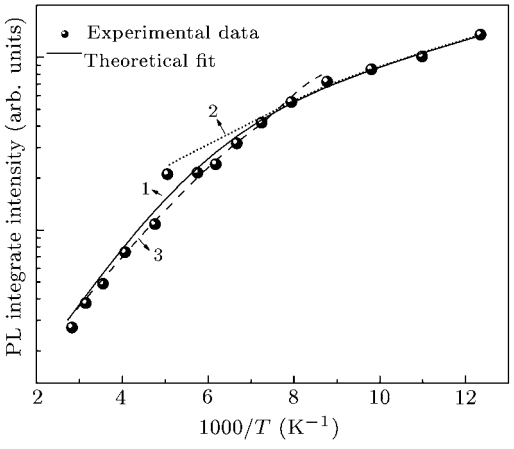

Fig. 5. The PL peak integrated intensities of $Mg_{0.12}Zn_{0.88}O$ as a function of temperature ranging from 81 to 366 K. The theoretical simulations (curve 1 by Eq. (1), curves 2 and 3 by Eq. (2)) to the experimental data points (circles).

From the results mentioned above, we have clearly suggested that the decrease of the emission intensity in the temperature range 81–162 K is due to the dissociation of bound excitons with an activation energy of 28 meV, and the quick quenching of UV emission above 162 K is due to the dissociation of free excitons with a thermal activation energy of ~58 meV. To further confirm the two steps dissociation processes of exciton complexes, the temperature dependences of the UV PL spectra in lower and higher temperature regions are fitted by Eq. (2), respectively,

$$I(T) = \frac{I_0}{1 + A\exp\left(-\dfrac{E}{k_B T}\right)}. \qquad (2)$$

As shown in Fig. 5, curves 2 and 3 (dotted and dashed lines) are the fitted results, where the activation energy of $E_1' = 29.7$ meV in lower temperature range and the activation energy of $E_2' = 58.4$ meV in higher temperature range are obtained, respectively. The values of E_1' and E_2' are close to the fitting results of $E_1 = 28.1$ meV and $E_2 = 57.6$ meV from curve 1, indicating the existence of two-step-dissociation processes. In addition, the free exciton binding energy of $E_x = 57.6$ meV is consistent with the result reported by Schmidt *et al.* in Ref. [13], in which the free exciton binding energy of MgZnO alloy films was considered to be slightly smaller than the value of ZnO bulk materials (~ 60 meV).

In summary, we have demonstrated for the first time that UV emission of the $Mg_{0.12}Zn_{0.88}O$ alloy film is originated from the recombination of bound exciton and free exciton. At low temperatures, the PL spectra of the sample are dominated by the bound exciton emission. With increasing temperature, the free exciton emission increases gradually so that the emission spectra at RT are dominated. Two thermal activation energies of 28.1 and 57.6 meV are obtained by using two-step dissociation fitting, which corresponds with the activation energy of the neutral donor bound exciton to free exciton and the binding energy of the free exciton, respectively. The results indicate that high-quality MgZnO alloy films may be used as the active region materials for the application in UV light emitting devices.

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