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Enhanced photoluminescence caused by localized excitons observed in MgZnO alloy

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Temperature-dependent photoluminescence of MgZnO alloy film has been studied, and it is found that the emission intensity increases significantly at a certain temperature range and then decreases when increasing temperature further. The anomalous increase is resulted from the localized excitons in MgZnO alloy, as revealed by the enhanced second-order longitudinal optical phonon in the Raman spectrum of the MgZnO film. A schematic model was suggested to depict the carrier transportation process in the MgZnO film considering the existence of localized exciton states. The results reported in this paper indicate that localized excitons in MgZnO alloy can result in greatly enhanced emission efficiency, which is eagerly wanted for the application of ZnO-based materials in high-efficiency light-emitting devices. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Localized excitons, referring to the excitons that are spatially localized in a certain small area due to composition or thickness fluctuation in crystals or films, have stimulated intensive research in the past decades because they have been demonstrated to be responsible for the high emission efficiency of a variety of alloy semiconductors.[1–8] A case in point is that the emission efficiency of GaP can be greatly enhanced due to the formation of localized exciton states caused by the incorporation of nitrogen.[1,2] Another example is the defect-insensitive emission in InGaN alloy, which is widely accepted to result from strongly localized excitons formed in indium-rich clusters.[3–8] Although localized excitons have been extensively studied and utilized in GaN- and GaP-based light-emitting devices,[9,10] there are only two reports on localized excitons in MgZnO.[11,12] Ye *et al.*[11] and Kong *et al.*[12] demonstrated the formation of localized excitons in MgZnO alloy by resonant Raman spectroscopy. However, the enhancement in emission efficiency caused by localized excitons in the MgZnO was not observed in their cases. Should localized excitons be proven to be of help in enhancing the emission efficiency of ZnO-based materials just as they are in InGaN and GaP:N, it will be of great significance in realizing high-performance ZnO-based light-emitting devices. However, no report on this topic can be found to the best of our knowledge. In this paper, localized excitons in MgZnO alloy films have been studied, and a remarkable enhancement in the photoluminescence (PL) intensity of the MgZnO alloy film caused by the localized excitons has been observed.

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II. EXPERIMENTS

The MgZnO alloy films were deposited onto the basal plane of sapphire (c-Al_2O_3) using a plasma-assisted molecular beam epitaxy technique, and a thin MgO layer was used as a buffer for the growth of the MgZnO. The precursors used for the growth of the MgO buffers and MgZnO layers were elemental zinc (6*N* in purity), elemental magnesium (6*N* in purity), and radical oxygen, and the radical oxygen was achieved by activating high purity O_2 gas (5*N* in purity) using an Oxford Applied Research atomic source cell (model HD25) with radio frequency operating at 13.56 MHz. The power of the source cell was fixed at 320 W, the oxygen flow rate at 1.25 SCCM (SCCM denotes cubic centimeter per minute at STP), the substrate temperature at 700 °C, and the pressure in the growth chamber at about 2×10^{-6} mbar during the growth process. In this way, MgZnO alloy films with a thickness of about 500 nm were obtained. The Mg content in the $Mg_xZn_{1-x}O$ films was determined by x-ray photoelectron spectroscopy (XPS). A Rigaku D/max-RA x-ray diffractometer (XRD) with Cu $K\alpha$ radiation ($\lambda=0.154$ nm) was used to evaluate the crystalline properties of the films. The PL signals of the MgZnO films were collected using a SPEX 1404 monochromator. Resonant Raman measurements on the MgZnO films were carried out in a JY-630 micro-Raman spectrometer under backscattering configuration. Note that the excitation sources for the PL and Raman measurements are both the 325 nm line of a He–Cd laser.

III. RESULTS AND DISCUSSION

Figure 1 shows the XPS spectrum of the $Mg_xZn_{1-x}O$ film. Note that the intensity of the Mg 2*p* peak has been magnified by 100 times for comparison. The Mg content in the $Mg_xZn_{1-x}O$ film was determined to be 0.12 from the XPS spectrum. The XRD pattern of the MgZnO film is shown in the inset of Fig. 1. Besides the diffraction from the Al_2O_3

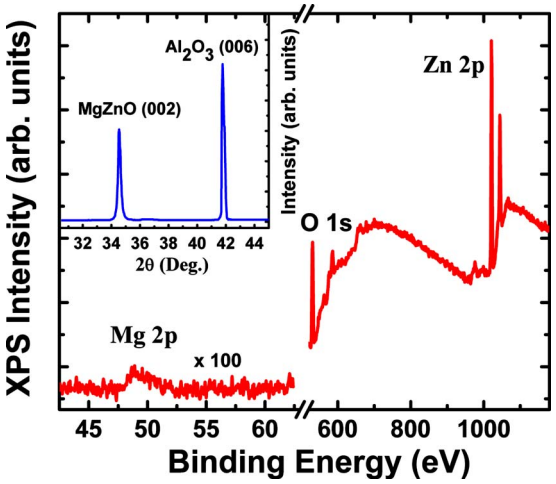

FIG. 1. (Color online) XPS spectrum of the $Mg_xZn_{1-x}O$ alloy. Note that the Mg 2*p* signal has been magnified by 100 times for clarity. The inset shows the XRD pattern of the MgZnO film.

substrate, only one peak corresponding to the diffraction from MgZnO (002) facet can be observed, indicating that the MgZnO film is crystallized in hexagonal structure with preferred *c*-axis orientation.

Shown in Fig. 2 are the PL spectra of the $Mg_{0.12}Zn_{0.88}O$ alloy at different temperatures. The 12 K spectrum is dominated by three emission bands at 3.540, 3.512, and 3.400 eV, and they are labeled as P1, P2, and P3, respectively. The integrated intensity of P1 and P2 as a function of temperature is shown in Fig. 3. The emission intensity of P1 decreases monotonously with increasing temperature, and the variation trend can be well fitted using the following formula:[13]

$$I(T) = \frac{I_0}{1 + A\ \exp(-E_A/KT)}, \tag{1}$$

where $I(T)$ and I_0 are the integrated intensity of the emission band, A is constant, and E_A is the activation energy. The best fitting yields an activation energy of about 58 meV, which is

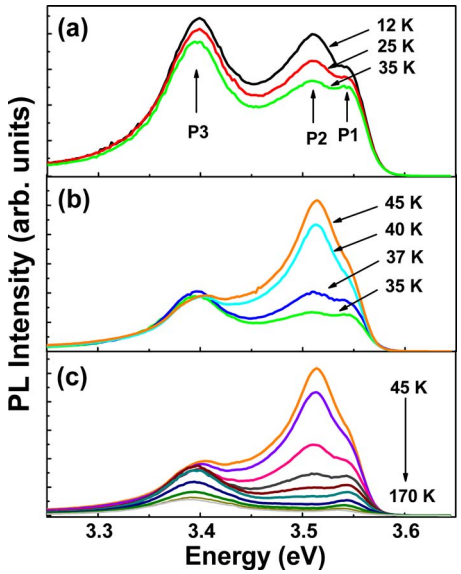

FIG. 2. (Color online) PL spectra of the $Mg_{0.12}Zn_{0.88}O$ layer in different temperature ranges: (a) 12–35 K, (b) 35–45 K, and (c) 45–170 K.

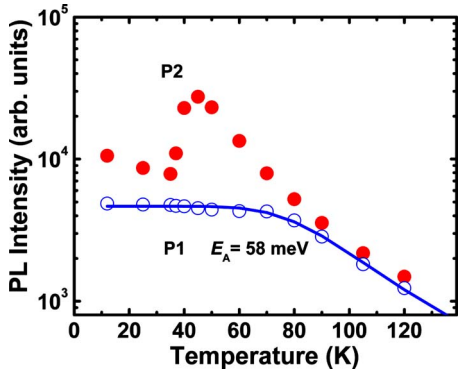

FIG. 3. (Color online) Temperature-dependent emission intensity of P1 and P2, where scattered symbols are experimental data, while the solid curve gives the fitting result.

almost identical to the exciton binding energy of ZnO (60 meV).[14] Therefore, the peak located at 3.540 eV can be attributed to the free exciton (FX) emission of the MgZnO alloy by neglecting the influence of Mg incorporation on the exciton binding energy of ZnO. The emission intensity of P2 decreases when the temperature increases from 12 to 35 K then increases anomalous by nearly three times when the temperature increases further to 45 K. Then by increasing the temperature further, it decreases gradually just as what is observed in the normal case. We note that the above anomalous variation is not occasional because four measurements were carried out on two samples grown under the same conditions, and very similar phenomena have been observed.

This anomalous enhanced emission in a certain temperature range is a symbol of localized excitons.[15,16] The formation of localized excitons in our MgZnO film is collaborated by the dependence of the full width at half maximum (FWHM) of P2 on temperature, as shown in Fig. 4. While the FWHM of the FX increases monotonously with temperature as commonly observed, an anomalous decrease in the linewidth of P2 is observed in the temperature range from 35 to 45 K. This anomalous variation can also be explained in terms of the localized excitons as follows: At relatively low temperature, the linewidth of P2 is mainly determined by the broad distribution of the localized states with different localization potentials. When temperature rises, some localized centers with weak localization will be delocalized, and the

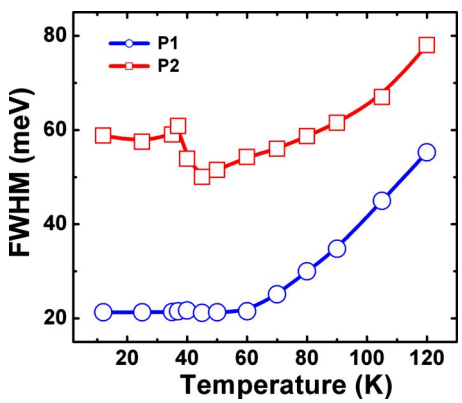

FIG. 4. (Color online) The FWHM of P1 and P2 as a function of temperature. The lines are guides to the eyes.

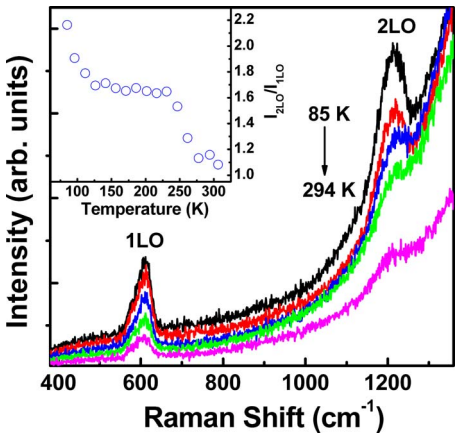

FIG. 5. (Color online) Resonant Raman spectra of the $Mg_{0.12}Zn_{0.88}O$ alloy film at different temperatures. The inset shows the intensity ratio of I_{2LO}/I_{1LO} as a function of temperature.

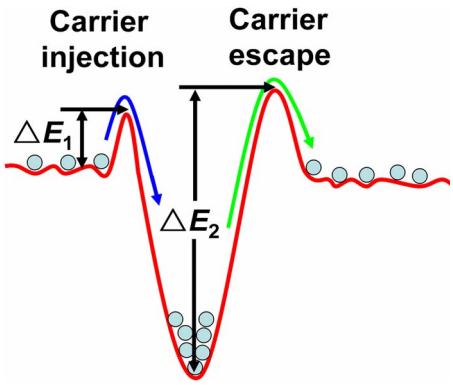

FIG. 6. (Color online) A schematic illustration showing the processes of carrier injection into and escape out of the localized centers.

delocalized carriers favor finding localized states with stronger localization, resulting in narrowing of the distribution of localized centers; thus the FWHM of the emission decreases. When the temperature increases further (above 45 K), electron-phonon scattering or ionized impurity scattering dominates the broadening. Consequently, the FWHM increases with temperature when temperature is above 45 K. Similar behaviors have been observed in quantum dots with strong localization.[17–19]

Resonant Raman scattering (RRS) spectroscopy has been proven to be a useful tool to characterize the formation of localized excitons.[20,21] In order to confirm the formation of localized exciton states in our MgZnO alloy film, temperature-dependent RRS spectra were recorded in the temperature range from 85 to 294 K, as shown in Fig. 5, in which two peaks located at around 606 and 1216 cm^{-1} can be observed superposed on a strong fluorescence background. The two peaks can be attributed to the first and second-order longitude optical (2LO) phonon modes of MgZnO alloy according to their positions.[22] A noteworthy character in the Raman spectra is that the 1LO phonon peak presents an asymmetric profile with a tail in the smaller frequency side, which suggests that the intermediate electronic states involved in resonant Raman process are strongly spatially localized.[23,24] Furthermore, another interesting phenomenon in the Raman spectra is that the intensity of 2LO is larger than that of 1LO, and the intensity ratio of I_{2LO}/I_{1LO} decreases gradually with increasing temperature, as shown in the inset of Fig. 5. Note that the intensity of the 2LO and 1LO peaks was obtained by subtracting the contribution of the background fluorescence. This anomalous enhancement of the 2LO at low temperature compared with 1LO has also been observed in MgZnO alloy by others and was attributed to the extrinsic Fröhlich interaction via the localized excitons as the intermediate electronic states.[11,12] The enhancement in the intensity of 2LO compared with 1LO is an evidence of the existence of localized excitons in our MgZnO alloy film.[11,21,25] Note that the localized excitons may be caused by the composition fluctuation in the film, in which some Zn-rich tiny areas are surrounded by MgZnO matrix. The decrease in the intensity ratio of I_{2LO}/I_{1LO} with increasing temperature may be due to the gradual delocalization of the localized excitons at elevated temperature.

The enhanced PL related to localized excitons in the MgZnO alloy film can be understood as follows: It is assumed that the effective barrier preventing carriers from entering into the localized centers is ΔE_1, while the confinement potential energy of the localized centers is ΔE_2, which are illustrated schematically in Fig. 6. Note that the shape of the barrier profile is immaterial and the carrier flow depends solely on the barrier height. At low temperature, most of the photogenerated carriers are frozen in the broad distributed localized states, and the number of carriers that can pass across the barrier is very few. Therefore, the carriers in the localized centers will be thermally quenched with increasing temperature. As a result, the emission from localized excitons (P2) decreases gradually with increasing temperature at low temperature region, as revealed in Fig. 2(a). With increasing temperature, some carriers may be thermally activated and tend to enter into the stronger localized centers by passing across the barrier ΔE_1. Then at a certain temperature range, the number of injected carriers is larger than that of quenched ones. In addition to the enhanced radiative recombination probability in the localized centers caused by confinement effect, an enhanced PL is resulted. The barrier height of ΔE_1 can then be estimated approximately to be equivalent to the thermal energy of 45 K (about 4.0 meV) based on the variation trend of the emission intensity with temperature. With further increasing temperature, the number of injected carriers becomes saturated for the relatively small barrier ΔE_1, while more and more localized excitons will escape out of the localized centers at elevated temperature. Additionally, some other quenching channels such as ionized impurity scattering and optical phonon scattering will decrease the number of carriers in the localized centers. Consequently, the number of the injected carriers becomes smaller than that of the quenched ones, and then the emission intensity of the localized excitons decreases with further increasing temperature.

IV. CONCLUSION

In conclusion, remarkable enhancement in the PL of MgZnO alloy film has been observed at a certain temperature

range, and this enhancement can be attributed to the filling effect of localized exciton states. The results reported in this paper reveal that localized excitons can enhance the emission efficiency of MgZnO just as they do in InGaN and GaP:N, thus may open up opportunities for high-efficiency light-emitting devices in ZnO-based materials by utilizing localized excitons.

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