

[Article]

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## ZnO 荧光粉中的紫外发射和绿色发射之间的关系

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**摘要** 通过在低氧分压和真空中热处理 ZnO 粉末, 获得了 ZnO 荧光粉. ZnO 荧光粉有两个发射谱带, 分别位于 380 nm(紫外)和 510 nm(绿色). 紫外谱带对应于 ZnO 中的激子发射, 是一个单中心发光过程; 绿色谱带是一个复合发光过程, 与 ZnO 中的本征缺陷相关, 如氧空位、锌空位等. 实验表明, 高密度的激发条件有利于紫外发射, 而低氧分压下的热处理有利于提高绿色发射谱带的强度. 研究结果还表明, 与紫外发射相联系的激子可向与本征缺陷相联系的绿色发光中心传递能量, 这种传递可能是通过激子扩散实现的.

**关键词:** ZnO, 发光, 激子发射, 本征缺陷发射, 能量传递

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## The Relationships between UV Emission and Green Emission in ZnO Phosphor

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**Abstract** ZnO phosphor was synthesized by annealing ZnO powder at low O<sub>2</sub> partial pressure and in vacuum. ZnO has two emissions, which are located at about 380 nm (UV emission) and 510 nm (green emission). The UV emission can be attributed to the exciton emission, which is a single-center process, whereas the green emission is related to native defects, such as V<sub>O</sub><sup>•</sup> and V<sub>Zn</sub><sup>'</sup>, which is a two-center (donor-acceptor) recombination process. The high-density excitation favors the UV emission, whereas the green emission likely appears in the samples annealed at low O<sub>2</sub> partial pressure. It was shown that the energy transfer may occur from the UV emission center to the green emission center, and the exciton diffusion mechanism for the transfer was proposed.

**Keywords:** ZnO, Luminescence, Exciton emission, Native defect emission, Energy transfer

ZnO is a multifunctional material and has several applications, particularly the green emission of ZnO for field emission display (FED)<sup>[1-3]</sup>. Besides this, it was found other applications including solar cells<sup>[4]</sup>, UV blocking<sup>[5]</sup>, as light-emitting materials<sup>[6-8]</sup>, and so on. In recent times, the preparation of nanostructure ZnO<sup>[9-11]</sup> and thin films<sup>[12-14]</sup> of ZnO has generated considerable

research interest.

Considerable research studies have been carried out to investigate the luminescent properties of ZnO<sup>[15-18]</sup>. ZnO phosphor has two emissions, which are located at about 380 nm (UV emission) and 510 nm (green emission). It is well known that the UV emission is due to exciton transitions<sup>[9]</sup>. Although the mecha-

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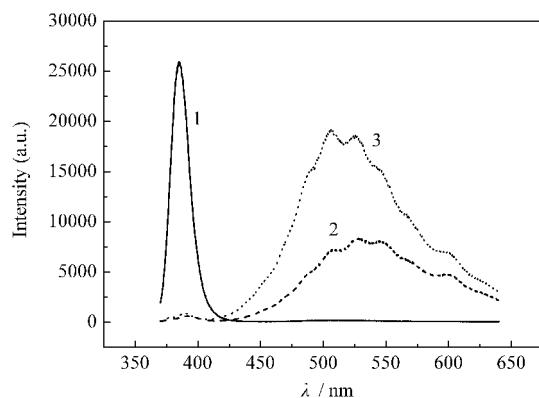
nism of luminescence of the green emission is still under debate<sup>[16, 17, 20-23]</sup>, it is widely accepted that this emission is correlated to the transition between native defects, such as  $V_{\text{O}}^{\bullet}$  and  $V_{\text{Zn}}^{\prime}$ <sup>[2, 16, 18]</sup>. However, the relationships between the two emissions were barely studied.

In this study, ZnO phosphors were prepared under different conditions and their luminescent properties were measured under excitation using Xe lamp, 325 nm laser, or cathode ray. On the basis of the measured data, the luminescent characters of the UV emission and the green emission as well as their relationships were discussed.

## 1 Experimental

The purity of ZnO used as the starting material was more than 99.9%. The luminescent samples were prepared by thermal treatments of ZnO powders using the following two procedures: high temperature annealing at low  $O_2$  partial pressure (such as  $N_2$ ,  $Ar+5\% H_2$ ) and high temperature annealing in vacuum, i. e. in vacuumed quartz tubes ( $\sim 1$  Pa). The annealing temperature varied from 400 °C to 1000 °C, and the annealing time was 2 h.

The photoluminescence (PL) was measured using a Hitachi F4500 fluorimeter and energy calibration was applied. In this fluorimeter, a 150-W Xe lamp was used as the excitation source. Cathodoluminescent (CL) measurements were conducted using YFC-2 cathodoluminescentometer with an accelerating voltage of 10 kV and a current density of  $1 \mu A \cdot cm^{-2}$  for the electron beam. PL emission spectra were also measured under excitation using He-Cd laser (325 nm) and the monochromator and the detector on a LabRam Raman Spectrometer (Jobin-Yvon company) were used. FLS920 Combined Steady State and Life-



**Fig.1 Emission spectra of ZnO phosphors excited by 325 nm He-Ge laser**

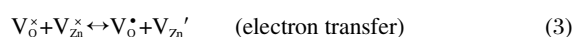
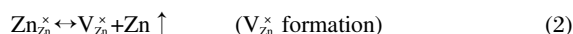
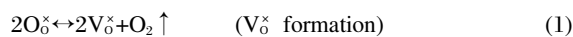
(1) as-obtained material; (2) vacuum annealed at 900 °C; (3) annealed in  $Ar+5\% H_2$  atmosphere at 900 °C

time Spectrometer (Edinburgh Instrument Ltd.) was used for measuring the temperature dependence of the emission spectra (Oxford Instrument ITC601 temperature controller was used for temperature control) and the decay curve of the green emission. The decay curve of the UV emission was measured using an FL920 Fluorescence Lifetime Spectrometer (Edinburgh Instrument Ltd.) equipped with a 372 nm laser (a diode laser) as an excitation source.

## 2 Results and discussion

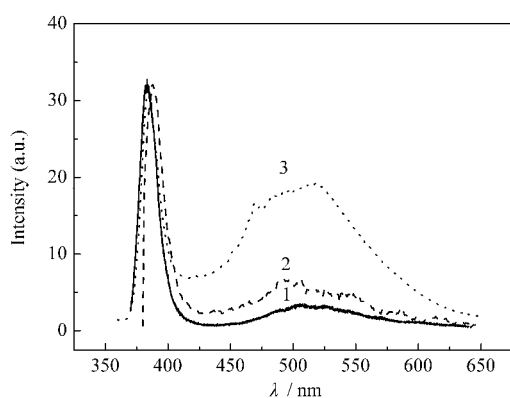
### 2.1 Appearance of UV and green emissions

Fig.1 shows the emission spectra for the samples of ZnO that were excited by 325 nm He-Ge laser. Two emissions appeared for the samples annealed at 900 °C for 2 h at low  $O_2$  partial pressure and in vacuum. The UV emission is a narrow peak with a peak wavelength of 380 nm and a FWHM (full width at half maximum) of 18 nm; the green emission is a broad peak with a peak wavelength of 510 nm and a FWHM of 95 nm. This emission character is in agreement with that reported in previous studies<sup>[16, 17, 20]</sup>. For as-obtained ZnO, only the UV emission was observed. It is well known that the UV peak is attributed to the exciton emission<sup>[19]</sup>, which is an intrinsic property of ZnO; thus, irrespective of whether the samples were annealed at low  $O_2$  partial pressure, this emission can be observed in all the three samples. Regarding the green emissions, several mechanisms were proposed<sup>[15, 16, 20]</sup>. It was believed that the emission is related to  $V_{\text{O}}^{\bullet}$  and this is a more generally accepted hypothesis. Guo's study<sup>[14]</sup> indicated that the green peak could be attributed to a recombination emission between  $V_{\text{O}}^{\bullet}$  and  $V_{\text{Zn}}^{\prime}$ . Although this mechanism was not well proved, it was thought to be reasonable and acceptable. Thus, the contents of native defects ( $V_{\text{O}}^{\bullet}$  and  $V_{\text{Zn}}^{\prime}$ ) increased when ZnO was annealed in  $Ar + 5\% H_2$  or in vacuum and the intensity of green emission was enhanced. The defect equilibria may be represented as follows:



The above results indicate that annealing ZnO at low  $O_2$  partial pressure or in vacuum was an essential condition to improve the intensity of the green luminescence.

Fig.2 shows the emission spectra of ZnO phosphor excited under different excitation conditions (normalized). The sample was prepared by vacuum annealing at 900 °C. Both the UV and



**Fig.2 Emission spectra of ZnO phosphor excited by laser (1), cathode ray (2), and xenon lamp (3)**

The sample was prepared by vacuum annealing at 900 °C.

the green emissions appear for all excitations; however, the intensity ratio of the UV emission to the green emission varied. The areas of the UV emission peak and the green emission peak were calculated to represent the emission intensities, denoted as  $I_{UV}$  and  $I_{green}$ . The ratio  $I_{UV}/I_{green}$  was 1.70, 0.45, and 0.30 for excitations using laser, cathode ray, and Xe lamp, respectively. The cathode ray and laser beam have high excitation density. Under these excitation conditions, the UV emission is relatively strong. However, under the excitation of Xe lamp, because its excitation density is lower, the intensity of the exciton emission is reduced. Actually, the content of excitons depends on the excitation density, thus high-density excitation favors UV emission.

## 2.2 Decay curves of the UV emission and the green emission

The decay curves for both UV emission and green emission were measured at room temperature for the sample prepared by vacuum annealing at 900 °C, which are shown in Fig.3. The decay curve for the UV emission can be fitted by a single exponential function:

$$I = I_0 e^{-at} \quad (4)$$

where  $a$  is a constant and  $t$  represents the time;  $I_0$  and  $I_t$  are the initial luminescent intensity and intensity at  $t$  time. Curve fitting data showed that  $a = 3.44 \text{ ns}^{-1}$ ; thus, the lifetime  $\tau = 1/a = 0.29 \text{ ns}$  (the lifetime is normally defined for the single exponential decay curve as the time spent when  $I_t$  decays to  $I_0/e$ ). The results are in accordance with those of Reynolds<sup>[19]</sup> and also indicate that the exciton emission is a single-center process<sup>[24]</sup>.

The decay curve for the green emission follows the hyperbolic function:

$$I = I_0(1+bt)^{-\alpha} \quad (5)$$

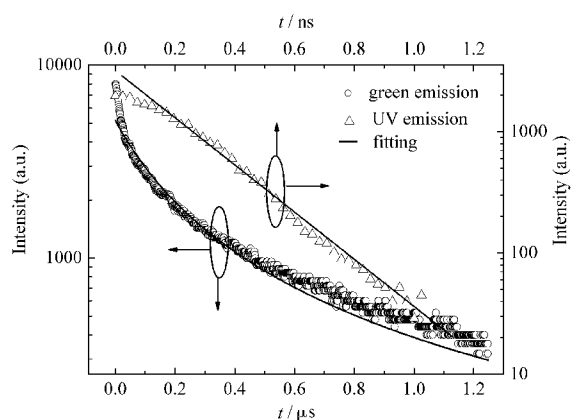
where  $b$  and  $\alpha$  are constants, the values of which are  $26.8 \text{ ns}^{-1}$

and 1.64, respectively, as shown by curve fitting data. The fitted value of  $\alpha$  deviates from the theoretical value of 2. For the hyperbolic decay curve, under normal circumstances, the lifetime  $\tau$  is also defined as the time required for  $I_t$  to decay to  $I_0/e$ . In this case, the lifetime  $\tau$  for the green emission is 90 ns. The above-mentioned result shows that the green emission is produced by a two-center (donor-acceptor) recombination process<sup>[24]</sup>. Although the mechanism of the green emission is still under debate<sup>[16,17,20,23]</sup>, it is generally accepted that  $V_o^\bullet$  is the donor in this process. However, certain authors<sup>[21, 23]</sup> believed that  $V_{Zn}'$  was the acceptor in this process. There was not enough evidence, but this hypothesis seemed reasonable. To better understand the mechanism of the green emission, further study is necessary. Although the decay curves of the UV emission and the green emission follow different criteria, from Fig.3, it is still clear that the decay of the UV emission is much faster than that of the green emission.

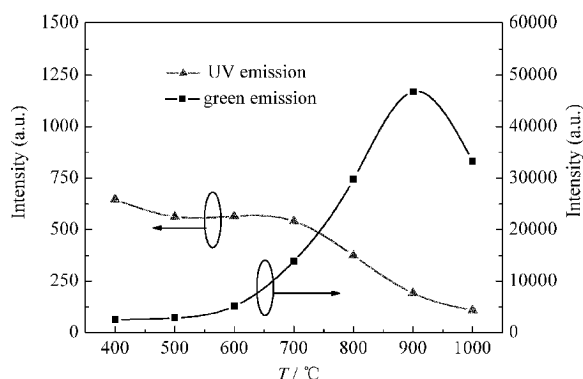
For the UV decay curve, Reynolds *et al.*<sup>[19]</sup> reported the results that are similar to those reported in this study. Ozawa's book<sup>[25]</sup> also describes the decay curves for both the UV emission and the green emission, which show reasonable agreement with those described in this study; however, in contrast to the curves described in this study, the curves described in Ozawa's book are schematic.

## 2.3 Energy transfer from the UV emission center to the green emission center

When ZnO samples were placed in vacuumed quartz tubes and annealed at temperatures ranging from 400 °C to 900 °C, because the contents of the native defects (e. g.  $V_o^\bullet$  and  $V_{Zn}'$ ) increased with temperature, the intensity of the green emission increased dramatically, whereas the intensity of the UV emission decreased, which is shown in Fig.4. A similar result, that is, the



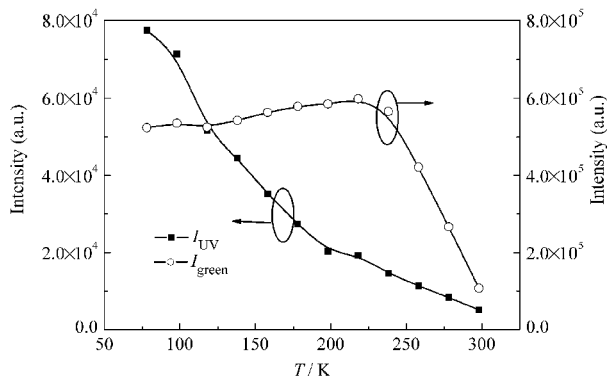
**Fig.3 Decay curves of the UV and the green emissions for the sample prepared by vacuum annealed at 900 °C**



**Fig.4** Variations of the UV emission intensity and the green emission intensity of ZnO phosphors with annealing temperature

increase of the green emission corresponding to the decrease of the UV emission was also reported by Studenikin *et al.*<sup>[26]</sup> on ZnO films, but the relationships between the UV and the green emissions were not well analyzed. The data in Fig.4 shows that an energy transfer process may occur from the UV emission center to the green emission center.

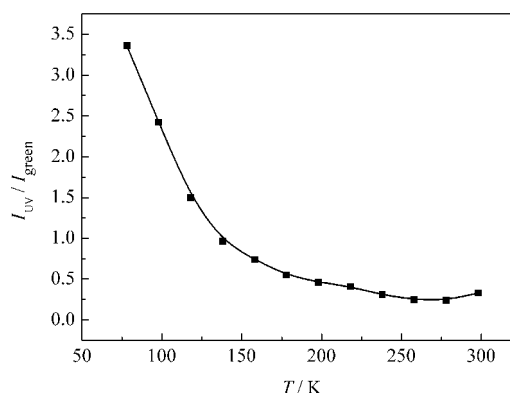
In addition, the variations of the UV emission intensity ( $I_{UV}$ ) and the green emission intensity ( $I_{green}$ ) with temperature were measured for the sample that was vacuum annealed at 1073 K (Fig.5). When the temperature varied from 78 to 218 K, the green emission intensity increased and at temperatures above 218 K, the green emission intensity decreased, whereas the UV emission intensity decreased in the whole temperature range measured (from 78 to 298 K). The correlation between the increase of the green emission and the decrease of the UV emission also suggests that the energy transfer may occur from the UV emission center to the green emission center. In addition, the intensity increment of the green emission from 78 K to 218



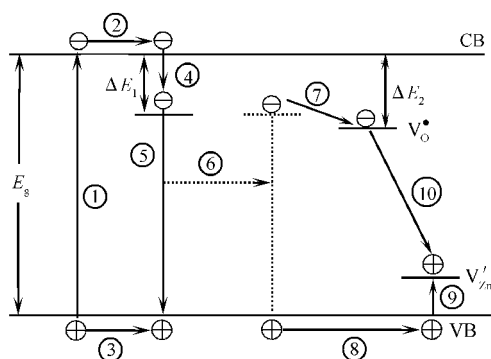
**Fig.5** Variations of the intensities of the UV emission and the green emission with measuring temperature for the sample prepared by vacuum annealing at 1073 K

K is about  $7.4 \times 10^4$  units, and the intensity decrement of the UV emission in the same temperature range is about  $5.8 \times 10^4$  units. Approximate equivalence between the increment of the green emission and the decrement of the UV emission further supports the occurrence of the energy transfer. Furthermore, the data shown in Fig.5 also indicate that the temperature increase assists in the energy transfer process; thus, it may be considered that the possible mechanism for the energy transfer is exciton diffusion<sup>[27]</sup>. From the excitation and the emission spectra of ZnO phosphor described in Aleksandra's study<sup>[28]</sup>, it is found that the UV emission peak almost did not overlap the green excitation band; thus, resonance and reabsorption are not the main energy transfer processes<sup>[27]</sup>. Above 218 K, the green emission decreases, and this could be attributed to the thermal quenching effect. Fig.6 shows the variation in the intensity ratio of  $I_{UV}/I_{green}$ . At a low temperature range, i. e., below 158 K, the ratio  $I_{UV}/I_{green}$  decreases dramatically with temperature increases, indicating that in this temperature range, the energy transfer efficiency is increased because the exciton diffusion is faster at higher temperatures<sup>[27]</sup>. Above 158 K, the ratio  $I_{UV}/I_{green}$  is almost constant, which implies that the transfer efficiency was saturated because for the selected sample, the contents of the defects  $V_o^\bullet$  and  $V_{Zn}'$  were fixed and there were no more luminescent centers to capture the energy transferred from the excitons.

From Fig.4, it can be seen that the intensity of the UV emission decreases by about 540 units in the temperature range studied, whereas the intensity of the green emission increased about  $3.1 \times 10^4$  units, which is much larger than the decrement of the UV emission. This nonequivalence implied that the intensity enhancement of the green emission was not only due to the energy transfer from the excitons but also due to the contents of defects



**Fig.6** Variation of the intensity ratio  $I_{UV}/I_{green}$  with measuring temperature for the sample prepared by vacuum annealing at 1073 K



**Fig.7 Schematic diagram representing the energy transfer mechanism**

$E_g=3.25$  eV,  $\Delta E_1=59$  meV,  $\Delta E_2=190$  meV; 1) excitation, 2) electron shift in CB, 3) hole shift in VB, 4) formation of exciton, 5) UV emission, 6) exciton diffusion, 7) energy (electron) transfer, 8) shift of the hole from the exciton, 9) hole trapping by acceptor ( $V_{Zn}'$ ), 10) green emission.

$V_O$  and  $V_{Zn}'$  increasing with the increase of the annealing temperature.

The mechanism of energy transfer from UV center (exciton) to green center in ZnO is schematically illustrated in Fig.7. The values of the energy levels are quoted from previous studies<sup>[17, 19]</sup>. The processes of excitation, exciton diffusion, and energy transfer as well as the emission are described in caption of Fig.7. Additional investigations are necessary to provide strong evidence in favor of this model.

### 3 Conclusions

The characters of the UV emission and the green emission of ZnO phosphor were investigated and the relationships between the two emissions were discussed. The UV emission is attributed to the exciton emission and it appeared in all ZnO samples when the excitation density was relatively high. Because the green emission is related to the native defects, such as  $V_O$  and  $V_{Zn}'$ , it only occurred in the samples annealed at low  $O_2$  partial pressure. The decay curve measurements indicated that the UV emission could be attributed to the single-center process and the green emission to the two-center (donor-acceptor) recombination process. It was shown that the energy transfer may occur from the exciton to the green emission center and the exciton diffusion mechanism was proposed.

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