# Tunable electroluminescence from n-ZnCdO/p-GaN heterojunction

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## ARTICLE INFO

## ABSTRACT

By cadmium allowing of zinc oxide, a phosphor-free single-chip white light emission diode based on n-ZnCdO/p-GaN heterostructure has been realized. The white light electroluminescence was produced by the superposition of two intense emission bands, a blue band and a yellow band. The origins of the blue band was contributed by both GaN and ZnCdO, while the yellow band was from the recombination of the holes and the electrons in the interface of GaN and ZnCdO.

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## 1. Introduction

White light emitting diodes (LEDs) have a great potential in solid-state lighting to replace the traditional lamps for their characteristics of long lifetimes, energy saving [1]. To obtain white LEDs, phosphors coating on GaN-based blue or ultraviolet LED are usually used [2]. But due to the performance and the lifetime of white LEDs are limited by the degradation of phosphors, phosphor-free single-chip white LED has drawn great attention. A few methods have been proposed to fabricate white LEDs without using phosphors. For example the LED emission band could be adjusted by codoping Si and Zn into the active region of a InGaN/GaN multiquantum well (MQW) active region, [3] by stacking quantum dots or quantum wells with different sizes or compositions, [4–7] or by applying Indium phase-separated active layers of InGaN active layers [8]. Another idea is to combine two emission layers into one chip, such as the cascade single-chip phosphor-free white LEDs [9].

As a wide bandgap semiconductor, ZnO is a promising candidate for short wavelength LEDs and laser diodes [10–12]. The bandgap and the emission bands of ZnO could be adjusted by Cu, Mg or Cd alloying [12–16]. ZnO is also a multifunctional material.

For example, ZnO is a green phosphor with potential use in low-voltage fluorescence application. Considering that the physical properties of ZnO and GaN are similar, ZnO thin film could be used as a buffer layer to grow GaN wafers. According to the above characteristics of ZnO, a phosphor-free single-chip white LED was designed based on a n-ZnCdO/p-GaN heterojunction. Because of the lack of reproducible and high quality p-ZnO, ZnO/GaN heterojunction has already been fabricated to achieve blue–violet electroluminescence [17–19].

Usually for ZnO there are two emission bands [20]. One is a near band gap ultraviolet emission, and the other is a green band related to defects [21]. It was thought by properly modulating the band gap of ZnO with Cd alloying, the visible emission from the ZnCdO alloy may redshift to long wavelength [22]. Combining this emission band with blue emission from GaN a single-chip phosphor-free heterojunction could be realized. In our study, a ZnCdO thin film was deposited on p-GaN wafer by metal-organic chemical deposition. A white electroluminescence was observed on the ZnCdO/GaN heterojunction.

## 2. Experimental details

A $Zn_{1-x}Cd_xO$ thin film was grown by a metalorganic chemical vapor deposition on $Al_2O_3$. The growth temperature of the $Zn_{1-x}Cd_xO$ was fixed at 450 °C with the pressure of $2 \times 10^4$ Pa in order to achieve reasonable cadmium incorporation. Diethylzinc (DEZn), dimethylcadmium (DMCd) and oxygen were employed as the precursors using high purity nitrogen as a carrier

gas. To fabricate the heterojunction, a commercial p-GaN/Al$_2$O$_3$ wafer was used as the substrate. Using the same growth condition as the Zn$_{0.95}$Cd$_{0.05}$O film on Al$_2$O$_3$ wafer, n-Zn$_{0.95}$Cd$_{0.05}$O/p-GaN structure was obtained. The Ohmic contacts are realized by thermally evaporating Ni/Au on p-GaN film and Al on n-Zn$_{0.95}$Cd$_{0.05}$O film, respectively. Pure ZnO thin film was also fabricated by the same method for comparison.

The x-ray diffraction (XRD) patterns of the as-synthesized ZnO and Zn$_{1-x}$Cd$_x$O thin films were measured with an x-ray diffractometer with the Cu Ka radiation. Optical absorption spectra were recorded using a Shimadzu UV-3101PC scanning spectrophotometer. The room temperature (RT) photoluminescence (PL) was performed using a He–Cd laser line of 325 nm as the excitation source. The current–voltage (I–V) characteristic of this device was measured using a Hall measurement system. The EL spectra of the diode were performed at RT in a F4500 spectrometer.

## 3. Results and discussion

Fig. 1 shows the XRD spectra. Both ZnO and ZnCdO films (grown on p-GaN/Al$_2$O$_3$ wafer) reveal that only (002) diffractive peak dominates the spectra. Compared with ZnO, the (002) diffractive peak of ZnCdO shifts to the lower angle side (ZnO-$2\theta=34.638°$, ZnCdO-$2\theta=34.417°$), which was observed in the enlarged views of the ZnO(002)/GaN(002) and the ZnCdO(002)/GaN(002) regions (insets of the Fig. 1). Considering the ionic radius of Cd$^{2+}$ ions is larger than Zn$^{2+}$ ions, the shift indicated that the Cd$^{2+}$ ions replace the Zn$^{2+}$ ions in the lattice and an alloy was formed [16]. The content of Cd in the alloy was established as 0.05 by the analysis of energy dispersive spectrum (EDS).

Optical absorption spectra of the ZnO and ZnCdO films are presented in Fig. 2. Even though these spectra were taken at room temperature, the samples exhibit salient exciton absorption features due to the relatively large binding energy of the exciton (~60 meV) [23]. Compared with pure ZnO films, a clear redshift and broadening of the absorption edge is discernible in ZnCdO films. The gently increased absorption edge implies there are some localized electron and/or hole states in ZnCdO alloy thin film [24–28]. Just these localized states lead to the broadening of the absorption edges. The optical band gap can be derived by the following equation: [29]

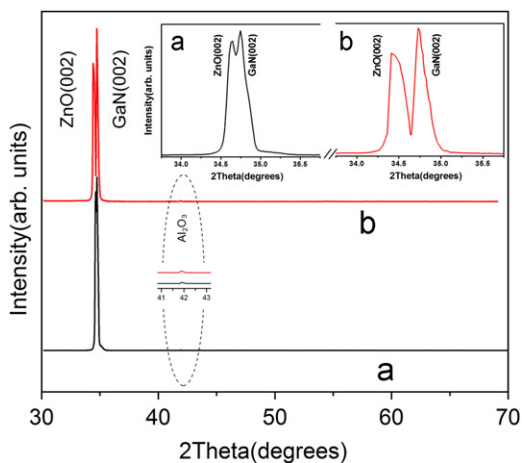$$\alpha = \frac{A(h\upsilon - E)^{1/2}}{h\upsilon}$$



**Fig. 1.** XRD results of: (a) pure ZnO films/GaN; and (b) ZnCdO films/GaN. The insets are enlarged views.
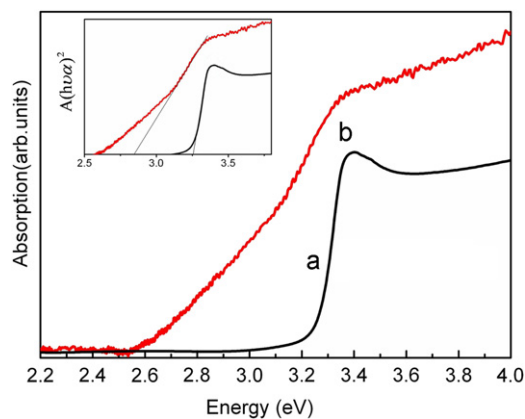


**Fig. 2.** Absorption spectra of: (a) pure ZnO film, and (b) ZnCdO film. The inset shows a plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (see text for details).
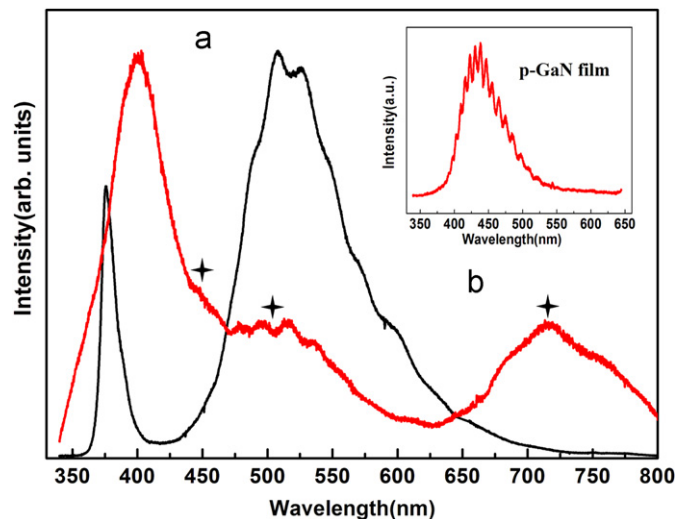


**Fig. 3.** Room temperature PL spectra of: (a) pure ZnO film, and (b) ZnCdO film. The inset shows the PL spectrum of p-GaN.

where $\alpha$ is the absorption coefficient, $E$ is the band gap, and $A$ is a constant. Band gap values were obtained by extrapolating the linear region near the onset in a plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$ (shown in the inset of Fig. 2). Due to the existence of free exciton absorption, 60 meV should be added. So the optical band gap falls to 2.9 eV for ZnCdO thin film.

Fig. 3 shows the room temperature PL spectra of pure ZnO film and Zn$_{0.95}$Cd$_{0.05}$O film, respectively. The emission from the pure ZnO films is composed of two main parts. The origin of the observed near-UV lines (375 nm) is attributed to the near band gap excitonic emission [30]. The visible PL band is mainly attributed to defects such as oxygen vacancies, which are related to deep level emissions [31,32]. For Zn$_{0.95}$Cd$_{0.05}$O film the UV emission peak is broadened and redshifts to 400 nm, which could be expected from the changes of the optical band gap derived from the absorption spectrum. In addition, the PL spectrum of Zn$_{0.95}$Cd$_{0.05}$O encompassed three new emission peaks in the visible region: a blue emission on the right shoulder of UV emission peak; a broad green emission band centered at around 500 nm and a red light emission located at 716 nm. In contrast to the visible emission band of ZnO, the green emission band of Zn$_{0.95}$Cd$_{0.05}$O is deduced originated from the radiative recombination related to the oxygen vacancies. The blue emission in this study could be attributed to the interstitial zinc in Zn$_{0.95}$Cd$_{0.05}$O

film [33]. Since the XRD result has confirmed $Cd^{2+}$ ions replace $Zn^{2+}$ ions in the lattice, it is reasonable that interstitial zinc exists in the present study. The substituted $Zn^{2+}$ ions occupied the interstice and the positions of oxygen. The depression of the green emission peak is the evidence. Although, the exact nature of the new red light emission remains unclear from our current results, we suggest that some new defect could be formed with the $Cd^{2+}$ alloying process. The PL emission from p-GaN is shown in the inset of Fig. 3. The emission from the p-GaN thin film is redshifted from the bandgap to around 430 nm, which is commonly observed in Mg-doped GaN due to the band to acceptor transitions [34].

According to the *I–V* results shown in Fig. 4, the turn-on voltage was 3.9 V from the n-ZnCdO/p-GaN heterostructure. The n-ZnCdO/p-GaN heterostructure was used to fabricate a light emitting diode device as illustrated in the schematic of Fig. 4(inset). The top of the n-$Zn_{0.95}Cd_{0.05}$O film was contacted by Al and the p-GaN film was contacted with thermally evaporating Ni/Au. Fig. 5(a) shows EL spectra with different forward bias
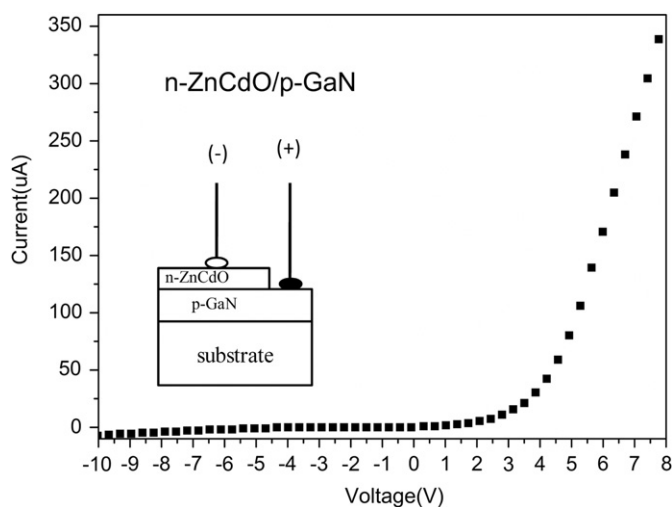


**Fig. 4.** Room temperature *I–V* characteristic of the as-grown n-ZnCdO/p-GaN heterostructure used to fabricate a light emitting diode LED. The inset shows the schematic configuration of the heterojunction LED structure.

(4 V–16 V). Under the driven voltage of 4 V, two emission bands could be observed centered at 500 nm (green band) and 585 nm (yellow band). With the increase of driven voltage, the peak position of yellow band is quite stable. However in the other emission band, the peak position shifts to the short wavelength side with increasing the voltage (from 500 nm to around 455 nm, denoted as the blue band). And the EL intensity of the blue band enhances faster than the yellow band. Under high driven voltage a new emission centered at 360 nm could be observed. The chromatic coordinates responding to different drive voltage are also given in Fig. 5(b). It should be noted that the chromatic coordinate is (0.31, 0.32) when the applied voltage is 12 V, which is close to the standard value of pure white. Fig. 5(c) illustrates that the emission occurs from the n-ZnCdO/p-GaN heterojunction and that there is no short circuit in the constructed device.

The EL emission band is considered as a combination of the various transitions from both p-GaN and $Zn_{0.95}Cd_{0.05}$O. According to the two semiconductors are contacted, the energetic barrier $\Delta E_C$ for electrons is [11]

$$\Delta E_C = \chi_{ZnCdO} - \chi_{GaN} = 4.4 - 4.2 = 0.2 \text{eV},$$

(In the case of ZnCdO, the electron affinity is also assumed to lie between 4.3 eV (ZnO) and 4.5 eV (CdO), [35], here 4.4 eV was used) while the energetic barrier $\Delta E_V$ for holes is:

$$\Delta E_V = Eg_{ZnCdO} + \Delta E_C - Eg_{GaN} = 2.9 + 0.2 - 3.4 = -0.3 \text{eV}.$$

Under forward bias, the energy relationship is in favor of holes transfers from GaN to ZnCdO. As shown in the EL spectra, the green EL emission band observed under low applied voltage is deduced originated from the defect related emission in $Zn_{0.95}Cd_{0.05}$O layer (according to the PL spectrum). With increasing the applied voltage, the energetic barrier for electrons further reduced. The ultraviolet (UV) emission peak located at 360 nm under high applied voltage is observed, which can be attributed to the near band gap emission from GaN (the peak position is close to the band gap of GaN). Then, it could be observed that both GaN and $Zn_{0.95}Cd_{0.05}$O have a blue emission band in the PL spectra. In the EL spectra, the peak position of the blue band shifts to the short wavelength side with the increasing of forward bias. Therefore, the blue EL band is considered as a complex contributed by both GaN and $Zn_{0.95}Cd_{0.05}$O. For the yellow emission band, it was not observed in the PL spectra of GaN and $Zn_{0.95}Cd_{0.05}$O, but kept a stable peak position in EL spectra.
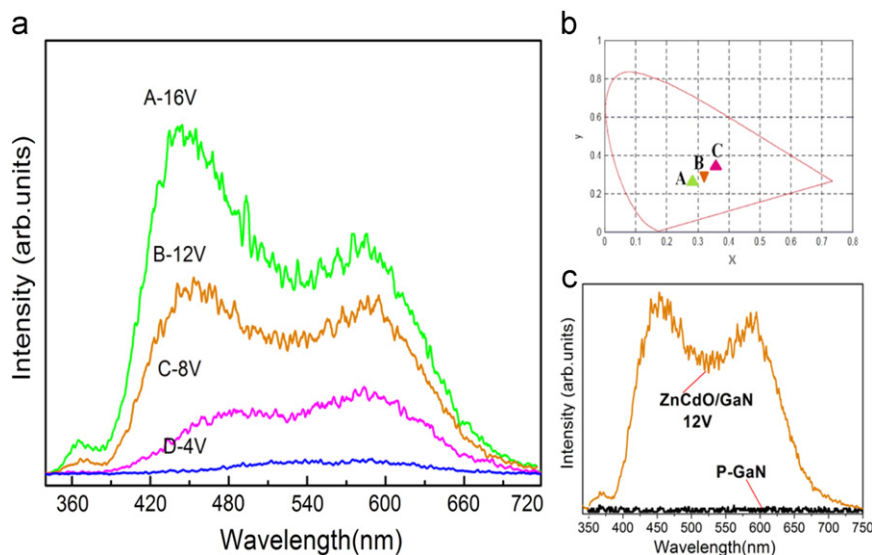


**Fig. 5.** (a) Room temperature EL spectra for the as-grown n-ZnCdO/p-GaN heterojunction LED with different forward drive voltages (4–16 V); (b) is the chromaticity coordinates *x, y* in CIE (Commission Internationale de'Eclairage) for the white LED at different forward driven voltages (A-16 V (0.29, 0.29); B-12 V (0.31, 0.32); C-8 V (0.36, 0.38)); (c) the comparison of EL spectra from the heterojunction LED structure and an Ni/Au/p-GaN/Ni/Au structure.

The red emission band in $Zn_{0.95}Cd_{0.05}O$ PL spectra disappeared in the EL spectra. It is assumed that the yellow emission is originated from the interface of GaN and $Zn_{0.95}Cd_{0.05}O$, because the yellow emission band is just between red and blue emissions. Based on the above analysis, a movement of emission layer is clearly observed. Under a relative low driven voltage, the recombination-region of injected holes and electrons are mainly in the $Zn_{0.95}Cd_{0.05}O$ layer and the interface. Under this status, the green band from $Zn_{0.95}Cd_{0.05}O$ could be detected. With increasing the applied bias the recombination zone moves towards the GaN layer. So the UV emission from GaN was observed and the blue emission band shifted. Because the interface took part in the recombination process all the time, the peak position of the yellow emission band was quite fixed.

## 4. Conclusions

In summary, the n-ZnCdO/p-GaN heterostructure was used to fabricate a light emitting diode device as demonstrated in EL measurement. Using band gap engineering, the XRD result have confirmed $Cd^{2+}$ ions replace $Zn^{2+}$ ions in the lattice and the band gap of the alloy $Zn_{1-x}Cd_xO$ films was tuned to the lower energy side to 2.9 eV compared with that of pure ZnO film when $x$ equals to 0.05, compared with that of pure ZnO film. Correspondingly, the UV emission peak of the alloy ZnCdO films is broadened and redshifts to 400 nm, and a new red light emission related to the alloy was observed in the PL spectrum. After the proper voltage regulation, the white emission was obtained. Under the driven voltage of 12 V, the chromatic coordinate is located (0.31, 0.32), which is close to the standard value of pure white. The yellow EL band was attributed to the recombination of the holes and electrons in the interface of GaN and ZnCdO.

## Acknowledgments

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