A Ga-doped ZnO transparent conduct layer for GaN-based LEDs

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Abstract: An 8 μm thick Ga-doped ZnO (GZO) film grown by metal-source vapor phase epitaxy was deposited on a GaN-based light-emitting diode (LED) to substitute for the conventional ITO as a transparent conduct layer (TCL). Electroluminescence spectra exhibited that the intensity value of LED emission with a GZO TCL is markedly improved by 23.6% as compared to an LED with an ITO TCL at 20 mA. In addition, the forward voltage of the LED with a GZO TCL at 20 mA is higher than that of the conventional LED. To investigate the reason for the increase of the forward voltage, X-ray photoelectron spectroscopy was performed to analyze the interface properties of the GZO/p-GaN heterojunction. The large valence band offset (2.24 $\pm$ 0.21 eV) resulting from the formation of Ga_2O_3 in the GZO/p-GaN interface was attributed to the increase of the forward voltage.

Key words: Ga-doped ZnO film; light-emitting diode; electroluminescence spectra; X-ray photoelectron spectroscopy
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1. Introduction

Recently, ZnO has received considerable attention as a transparent conduct layer (TCL) of GaN-based light-emitting diodes (LEDs) due to its outstanding properties. ZnO has a band gap of 3.37 eV, corresponding to an ultraviolet region located at 368 nm, which means that ZnO is almost transparent to visible light. It also has high temperature stability, high refractive index around 2.0, and low cost. As a result, ZnO is considered to be an alternative to indium tin oxide (ITO) as a TCL[1, 2].

Serving as a TCL, ZnO always needs to be doped by n-type dopants such as Al, In and Ga, to decrease its resistivity. Among these metal dopants, Ga is considered the most promising one because of its lower reactivity to oxidation and similar atomic radius compared to Zn[3, 4]. There are many methods to deposit Ga-doped ZnO (GZO) films[5–7]. However, the growth rate of these methods is quite low. Moreover, the interface properties of the GZO/p-GaN heterojunction are still not very clear[2, 8].

In this article, a novel growth method called metal-source vapor phase epitaxy (MVPE) was used to deposit a thick GZO film on a GaN-based LED as a TCL. This method exhibits high growth rate, good crystallinity and uniform thickness, and costs less to manufacture. For the details of this method, the reader is referred to Ref. [9]. The electrical and optical properties of the LED, as well as the interface properties of the GZO/p-GaN heterojunction, were also investigated.

2. Experiment

The InGaN/GaN multiple quantum well (MQWs LED wafer used in this study was grown on c-plane (0001) sapphire substrates by MOCVD. The wafer consisted of a 30 nm-thick GaN nucleation layer followed by a 4 μm n-type GaN layer doped with Si, followed by five periods of InGaN/GaN MQWs, then followed by a AlGaN electron blocking layer and a 0.2 μm p-type GaN layer doped with Mg. Finally, a GZO film was deposited on p-GaN by MVPE. Highly pure metal Zn (5N), metal Ga (6N) and deionized water (H_2O) were used as the precursors for Zn, Ga and O, respectively. A highly pure mixture of nitrogen and hydrogen gas (5N) was employed as the carrier gas. The growth temperature is 790 ℃, the growth time is 10 min, and the growth rate is about 0.8 μm/min. Hall measurements showed that our as-grown GZO films have a resistivity of (5–8) $\times$ 10^{-3} Ω·cm

After GZO deposition, the LED wafer was fabricated to a mesa structure through inductively coupled plasma etching, as shown in Fig. 1. Ti/Au pads were deposited on the n-side, and Ti/Al pads were deposited on the p-side by electron-beam evaporation for wire bonding. For comparison, an LED with ITO as a TCL was also prepared.

The electrical and optical properties of the LED with a GZO TCL were measured by electroluminescence (EL) spectra. The interface properties of the GZO/p-GaN heterojunction were also investigated by X-ray photoelectron spectroscopy (XPS)

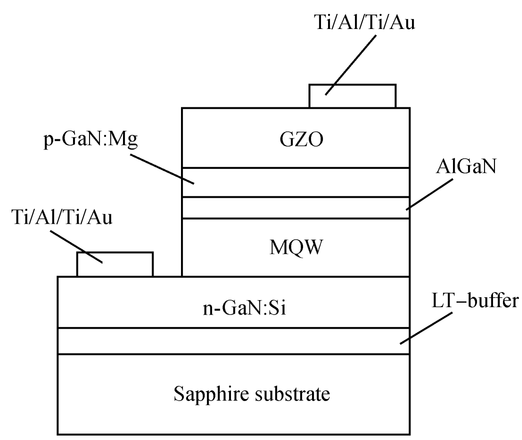

Fig. 1. Schematic structure of the InGaN/GaN multiple quantum well LED with GZO as a transparent conduct layer.

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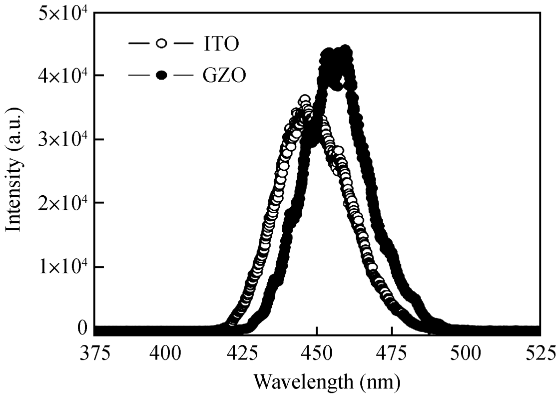

Fig. 2. EL spectra of the LED with a GZO TCL and the LED with an ITO TCL.

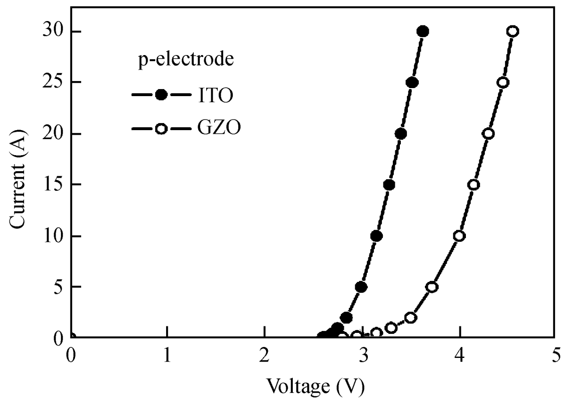

Fig. 3. Current–voltage curve of the LED with a GZO TCL and the LED with an ITO TCL.

measurements, which was performed on a VG MK II XPS instrument with AlKα ($h\upsilon$ = 1486.6 eV) as the X-ray radiation source.

3. Results and discussion

Figure 2 shows the EL spectra of the LED with a GZO TCL and of the LED with an ITO TCL. The EL intensity value of the LED with a GZO TCL is dramatically improved by 23.6% as compared to that of the LED with an ITO TCL at 20 mA. It was thought that the enhancement of the EL intensity is because the thick GZO film has a high light transmission rate in the visible light region and a higher refractive index than ITO. It can not only act as a transparent electrode, but also a current spreading layer and light extraction layer. Moreover, a thick GZO film can also enhance the light extraction efficiency by extracting light from the side face of the GZO film into free space. From Fig. 2, we also notice that the main emission peak of the LED with a GZO TCL shifts toward long wavelength about 10 nm compared to that of the LED with an ITO TCL. This might be attributed to the high growth temperature of the GZO film, which leads to indium diffusion in the InGaN/GaN multiple quantum well.

Figure 3 exhibits the current–voltage (I–V) properties of the LED with a GZO TCL and the LED with an ITO TCL. The forward voltage of the LED with a GZO TCL at 20 mA is 4.2 V, which is higher than that of the LED with an ITO TCL (3.4 V). This might be attributed to the higher resistance of GZO films as compared to ITO films. Besides, the oxidative environment during the GZO deposition period may also result in the high forward voltage. When the GZO film is deposited by MVPE, formation of Ga_2O_3 may happen in the GZO/p-GaN interface.

In order to investigate the existence of Ga_2O_3 in the interface of the GZO/p-GaN heterojunction, as well as research the band offset, XPS measurements were used to analyze the interface properties[10, 11].

Three samples were used in this XPS experiment, namely, an 8 μm thick GZO film grown on p-GaN, a 200 nm thick p-GaN film, and a 200 nm thick GZO grown on p-GaN, where the 200 nm GZO film was reduced to a few nanometers by HCl etching and Ar^+ bombardment until the Zn2p and Ga2p core levels (CLs) could both be detected.

The formula of calculating the valence band offset (ΔE_V) is $\Delta E_V = \Delta E_{CL} + (E_{Ga2p}^{GaN} - E_{VBM}^{GaN}) - (E_{Zn2p}^{ZnO} - E_{VBM}^{ZnO})$, where $E_{Zn2p}^{ZnO} - E_{VBM}^{ZnO}$ and $E_{Ga2p}^{GaN} - E_{VBM}^{GaN}$ are determined by ZnO and GaN bulk constants. $\Delta E_{CL} = E_{Zn2p}^{ZnO} - E_{Ga2p}^{GaN}$ is the energy difference between Zn2p and Ga2p CLs measured by ZnO/GaN heterojunction sample. The CL spectra were fitted to a Voigt line shape by employing a Shirley background, and the valence band maximum (VBM) position was determined by linear extrapolation of the leading edges of the VB spectra to the base lines. The uncertainty of the CL position is lower than 0.03 eV and the inaccuracy of the VBM is lower than 0.1 eV.

Table 1. XPS CL spectra fitting results and VBM positions obtained from the spectra. Energies are referenced to the Fermi level (0 eV).

Sample	State	Relative binding energy (eV)
ZnO	Zn2p	1021.41 ± 0.03 (Zn–O in GZO)
		1022.35 ± 0.03 (pure Zn–O)
	VBM	2.40 ± 0.1
GaN	Ga2p	1117.06 ± 0.03
	VBM	0.97 ± 0.1
GZO/GaN	Zn2p	1021.35 ± 0.03
	Ga2p	1116.19 ± 0.03 (Ga–N)
		1117.39 ± 0.03 (Ga–O)

Figure 4(a) is the Zn2p CL, and Figure 4(b) is the VBM spectra of ZnO measured by the ZnO sample. The Zn2p CL consists of two components by Voigt fitting. The first peak located at 1021.41 eV is attributed to the Zn–O bonds in Ga-doped ZnO, while the second peak at 1022.35 eV is attributed to the pure Zn–O bonds. Ga doping lowered the binding energy of Zn–O bonds[12]. Figure 4(c) is the Ga2p CL spectra, and Figure 4(d) is the VBM spectra of GaN for the GaN sample. The Zn2p and Ga2p CL spectra for the ZnO/GaN sample are shown in Figs. 4(e) and 4(f). Ga2p CL also consists of two components. The one at 1116.19 eV corresponds to Ga–N bonds, while the one at 1117.39 eV is attributed to Ga–O bonds[13]. This proves the existence of Ga_2O_3 at the interface of GZO/p-GaN because it is the most stable Ga oxide[14]. All parameters are summarized in Table 1.

According to these parameters, the ΔE_V value is calculated to be 2.24 ± 0.21 eV, and the conduction band offset (ΔE_C) is 2.26 ± 0.21 eV, which is larger than those reported (~1.0eV)[10]. This demonstrates that the existence of Ga_2O_3 surely enhanced the band offset of the GZO/p-GaN heterojunc-

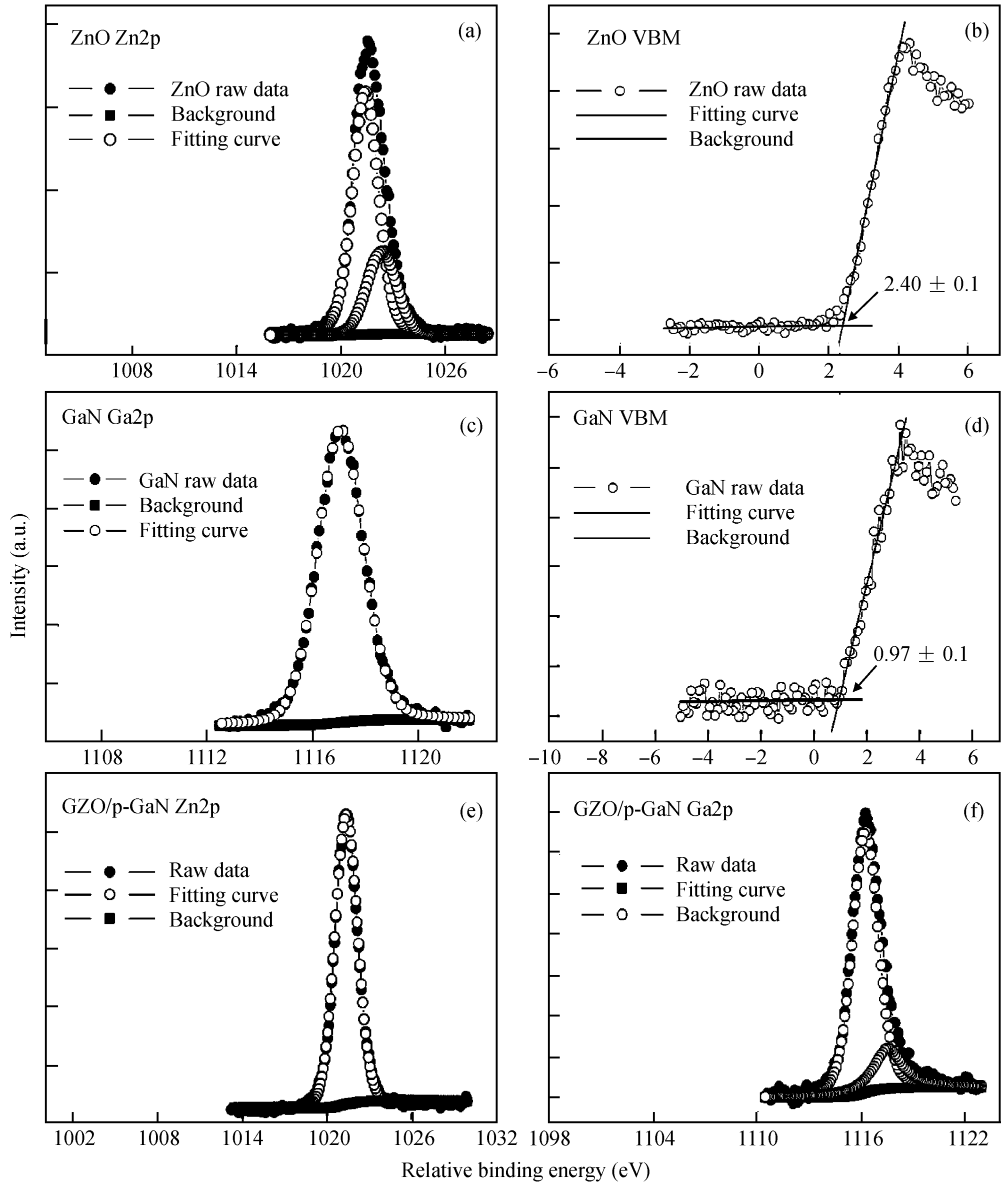

Fig. 4. Zn2p CL peaks for the (a) ZnO and (e) ZnO/GaN samples, Ga2p spectra on (c) GaN and (f) ZnO/GaN samples, and VB spectra for (b) ZnO and (d) GaN samples. All peaks have been fitted using a Shirley background and Voigt (mixed Lorentzian–Gaussian) line shapes.

tion. The energy gap of Ga_2O_3 is 4.9 eV, which is much higher than that of GaN. This might lead to the increase of band offset at the interface of GZO/p-GaN. The high band offset indicates that there is contact resistance at the interface and will definitely block the current transmission, which will cause the enhancement of the series resistor of the LED. Consequently, it leads to the LED with a GZO TCL having a higher forward voltage at 20 mA than the LED with an ITO TCL. Figure 5 shows the energy band diagram of GZO/p-GaN, which is a type-Ⅱ heterojunction.

4. Conclusion

A GaN-based LED with an 8 μm thick GZO film serving as a TCL was demonstrated. The GZO film was deposited by a home-made MVPE system without the post-deposition annealing process. EL spectra showed that the intensity value of the LED with a GZO TCL is dramatically improved by 23.6% as

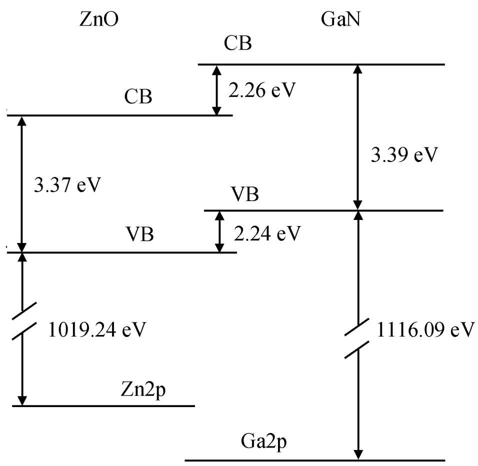

Fig. 5. Energy band diagram of GZO/p-GaN heterojunction.

compared to that of the LED with an ITO TCL at 20 mA, while the forward voltage is much higher.

XPS was used to analyze the interface properties of the GZO/p-GaN interface. The valence band offset is calculated as being 2.24 ± 0.21 eV, and the conduction band offset is 2.26 ± 0.21 eV. The higher band offset may be attributed to the existence of Ga_2O_3 in the interface of the GZO/p-GaN heterojunction, which caused the higher contact resistance, and then enhanced the series resistor of the LED. As a result, the forward voltage of the LED with a GZO TCL rose. To decrease the forward voltage, optimization of the MVPE growth parameters is needed to avoid the formation of Ga_2O_3 in the interface of the GZO/p-GaN heterojunction. The performance of the LED with a GZO TCL can also be improved by enhancing the carrier concentration in the GZO film and introducing a heavily-doped interlayer between the p-GaN layer and the GZO film.

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