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Electroluminescence from ZnO nanowire-based *p*-GaN/*n*-ZnO heterojunction light-emitting diodes

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Abstract Vertically aligned ZnO nanowires were successfully grown on the sapphire substrate by nanoparticle-assisted pulsed laser deposition (NAPLD), which were employed in fabricating the ZnO nanowire-based heterojunction structures. *p*-GaN/*n*-ZnO heterojunction light-emitting diodes (LEDs) with embedded ZnO nanowires were obtained by fabricating *p*-GaN:Mg film/ZnO nanowire/*n*-ZnO film structures. The current–voltage measurements showed a typical diode characteristic with a threshold voltage of about 2.5 V. Electroluminescence (EL) emission having the wavelength of about 380 nm was observed under forward bias in the heterojunction diodes and was intensified by increasing the applied voltage up to 30 V.

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1 Introduction

ZnO is one of the most promising materials for short-wavelength light-emitting diode (LED) and laser diode applications. However, the application of ZnO to homojunction diodes has been limited due to the difficulties of high-quality ZnO fabrication and *p*-doping on ZnO [1–3]. As an alternative approach to utilize ZnO for optoelectronic applications, a ZnO film/GaN film heterojunction structure has been suggested [2–4]. However, the heterojunction diodes have the low efficiency because of the high energy barrier at the junction interface. This limitation of current thin-film technology can be surmounted by employing ZnO nanowires in the heterojunction structure, which can exploit their simple fabrication processes and superior properties, such as high crystalline quality, large surface area, and quantum confinement effect [5, 6]. The high injection current and light emission with quantum effect at nanosized junctions could demonstrate development potential for high-performance devices [7–9]. Although much progress has been made in these areas [10–12], there have been few publications reporting EL and even fewer with a dominant UV emission.

In this study, vertically aligned ZnO nanowires were successfully grown on the sapphire substrate by nanoparticle-assisted pulsed laser deposition (NAPLD), which were employed in the heterojunction structures. The fabrication of ZnO buffer layer/ZnO nanowire array/*p*-GaN film heterojunction LEDs and their EL characteristics are introduced. The nanosized heterojunctions for LED applications were formed by covering the hybrid structures consisted of ZnO buffer layer and ZnO nanowire arrays on the *p*-GaN films. EL emission in the UV–violet region was observed from the LEDs under forward bias. In addition, *p*-GaN/*n*-ZnO heterojunction LEDs with embedded ZnO nanowires were also obtained by dispersing ZnO nanowires on a *p*-GaN film, which was then covered by an *n*-type ZnO film and their EL characteristics were studied by comparing with those of the *n*-ZnO film/*p*-GaN film heterojunction diodes.

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2 Synthesis and characterization of ZnO nanowires

A sintered ZnO target with 99.99% purity was used as source material in synthesizing ZnO nanowires. This material was ablated with a KrF excimer laser at a fluence of $4\ \mathrm{J/cm^2}$ in a chamber filled with argon background gas for 120 min, which operated at a repetition rate of 20 Hz. The substrate–target distance was fixed to 15 mm and the typical values of temperature and chamber pressure in the furnace were 1000°C and 260 Torr, respectively. In the case of the conventional PLD, ZnO thin films have been deposited in an oxygen background gas at a relatively low pressure of approximately 0.1 Torr or less. In NAPLD, however, ZnO nanoparticles are synthesized at a higher background gas pressure. In this case, the ablated species are perfectly confined in a small volume with a stoichiometric composition of ZnO, and then ZnO nanoparticles are formed in the gas phase during the transport of the ablated species to the substrate. When the nanoparticles were formed in the gas phase, they were deposited on the (0001) sapphire substrate (1 cm × 1 cm) then melted and migrated on the substrate. During the migration, nanoparticles aggregated each other. As a result of the melting temperature getting higher with the size of aggregated particles, they precipitated at a place on the substrate. With the increasing ablation time, most of the ZnO nanocrystals merged together into a continuous network and larger clusters, among which some isolated nanocrystals also existed and served as nucleation centers to initiate the growth of ZnO nanowires [13–15].

The morphology of the as-deposited products was analyzed by scanning electron microscopy (SEM). The optical properties of ZnO nanowires were investigated by observing the photoluminescence (PL) under excitation at 355 nm using a frequency-tripled Q-switched Nd:YAG laser. Their current–voltage (I–V) characteristics were also measured.

As shown in Fig. 1a, this synthesis method could produce the hybrid structures consisting of ZnO buffer layer and vertically-aligned ZnO nanowires which had an average diameter of about 200 nm and length in the micrometer range. The room temperature PL spectrum in Fig. 1b shows a strong UV peak at around 390 nm, which is the contribution of the near-band-edge emission of the wide band gap ZnO. The surface I–V curve of the as-deposited ZnO products in contact with Al was shown in Fig. 1c which shows ohmic contact characteristics.

3 Fabrication of ZnO-based LEDs and their electroluminescence

Three different ZnO-based heterojunction structures for LED applications were simply fabricated by the following processes:

1. Covering of the as-deposited hybrid structures consisting of ZnO buffer layer and ZnO nanowire arrays on a p-GaN film.
2. Removal of the as-deposited ZnO nanowires from the growth substrate into alcoholic solution by sonication, and then dropping the solution containing ZnO nanowires onto a p-GaN thin film, and finally covering an n-ZnO film on them.
3. Simple covering an n-ZnO film on a p-GaN film.

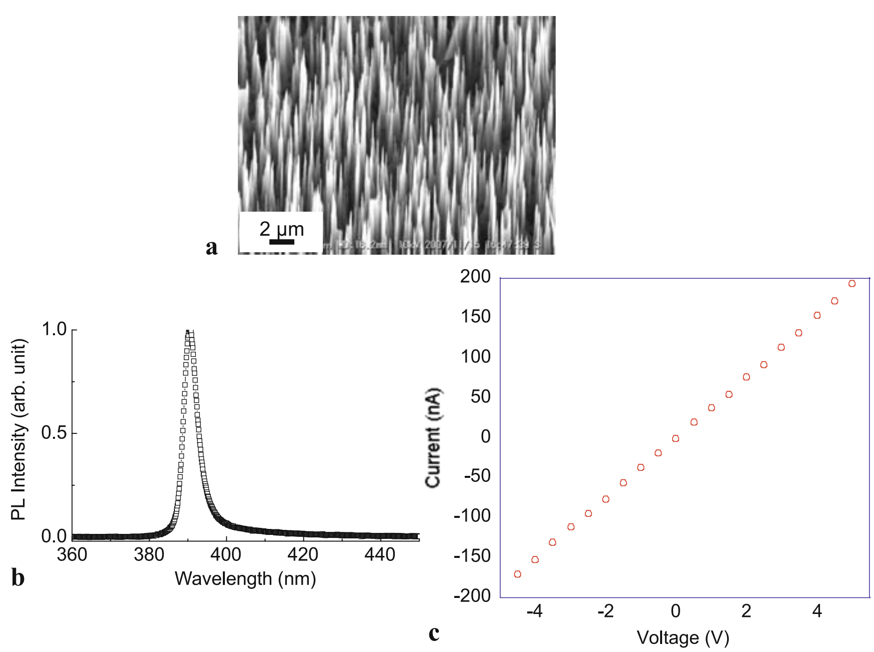

Fig. 1 (**a**) SEM image, (**b**) PL spectrum of vertically aligned ZnO nanowires grown by NAPLD, and (**c**) I–V characteristics of Al metal contacts on the as-deposited ZnO products

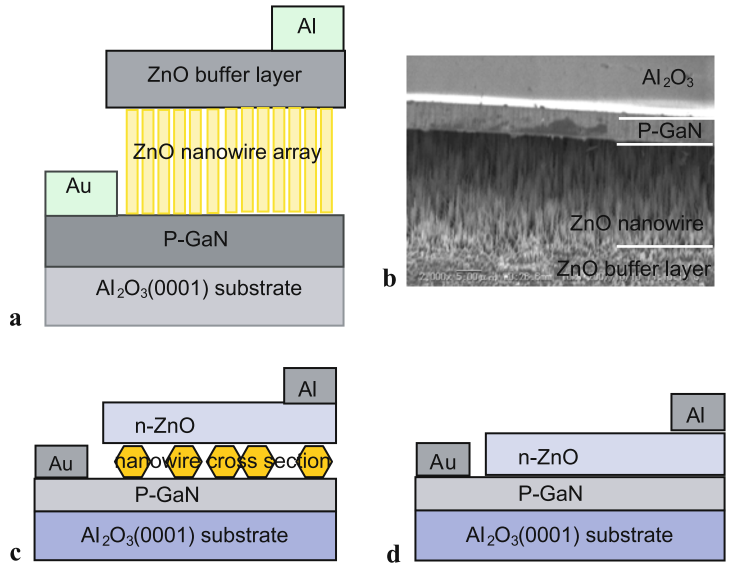

Fig. 2 Schematics of three heterojunction structures: (**a**) ZnO buffer layer/ZnO nanowire array/p-GaN film, (**b**) SEM image of heterojunction (**a**), (**c**) ZnO nanowire-embedded p-GaN/n-ZnO, and (**d**) film-based p-GaN/n-ZnO

Figure 2 shows the schematics of the above three heterojunction structures.

3.1 ZnO buffer layer/ZnO nanowire array/p-GaN film heterojunction LEDs

Scanning electron microscopy (SEM) image of the first heterojunction LED structure was also shown in Fig. 2b, in which the distinctive layers of the p-GaN film, the ZnO nanowire array, and the ZnO buffer layer were observed. The average diameter and length of ZnO nanowires which formed nanosized junctions on the surface of the p-GaN film were about 200 nm and 8 μm, respectively. The top ZnO buffer layer having the thickness of about 4 μm exhibited n-type conductivity due to the defects, such as grain boundaries in the polycrystalline structures, and formed seamless interface contacts with the ZnO nanowires. The resulting polycrystalline ZnO buffer layer/ZnO nanowire array/p-GaN film heterojunction structure can be defined as n^+–n–p^+ junction, because the polycrystalline ZnO buffer layer has higher carrier concentrations than the single crystalline ZnO nanowires [16]. EL emission of the first heterojunction diode (ZnO buffer layer/ZnO nanowire array/p-GaN film) was observed under various forward-bias voltages. Ohmic contacts were formed on the top ZnO buffer layer in contact with Al and the p-GaN film by depositing Au using an evaporation system. As shown in Fig. 3a, the EL spectra of the ZnO buffer layer/ZnO nanowire array/p-GaN film heterojunction diode showed broad UV–violet emission peaks. The UV–violet peaks centered at 380 nm were intensified by increasing the applied voltage up to 30 V. Even though the UV–violet light emission from the diode was not detected in the EL spectrum at the applied voltage of 5 V, the violet light emission was observed by the naked eye. Figure 3b shows the light emission photograph of the heterojunction diode. The origin of the EL emission of the heterojunction diodes was investigated by comparing the EL and PL spectra. As shown in Fig. 1b, PL spectrum of the ZnO nanowire array exhibits intense near-band-edge UV emission with a wavelength maximum at 390 nm and an absent deep-level emission due to the defects. The PL observations strongly suggest that the UV–violet emissions at about 380 nm in the EL spectra of the heterojunction diode originate from the radiative electron–hole recombination in the ZnO nanowires. The EL emission in the ZnO nanowires is also supported by the energy band diagram built using Anderson model [17] which shows a smaller energy barrier for the holes compared to that for the electrons at the heterojunction interface between the ZnO nanowires and the p-GaN film. Therefore, it is expected that the injected holes from the p-GaN films into the ZnO nanowires recombine with electrons in the ZnO nanowires. Figure 3c shows the peak intensities in Fig. 3a as a function of the forward current. It can be seen that the peak intensity is almost proportional to the current.

The I–V characteristics of the ZnO buffer layer/ZnO nanowire array/p-GaN film heterojunction diode were observed as shown in Fig. 4. The I–V curves of the heterojunction diode in Fig. 4a clearly show the nonlinear increase of the current under forward bias. Rectifying characteristics with a threshold voltage of 2.5 V was obtained. The I–V characteristics of the heterojunction diode were further considered by plotting the current in log scale as shown in Fig. 4b which shows the leakage currents are as small as $\sim 10^{-6}$ A. The current in log scale had a linear relationship with the applied voltage and the slope changed when the applied voltage excessed 6 V, which probably originated from the excessive carrier injections [12].

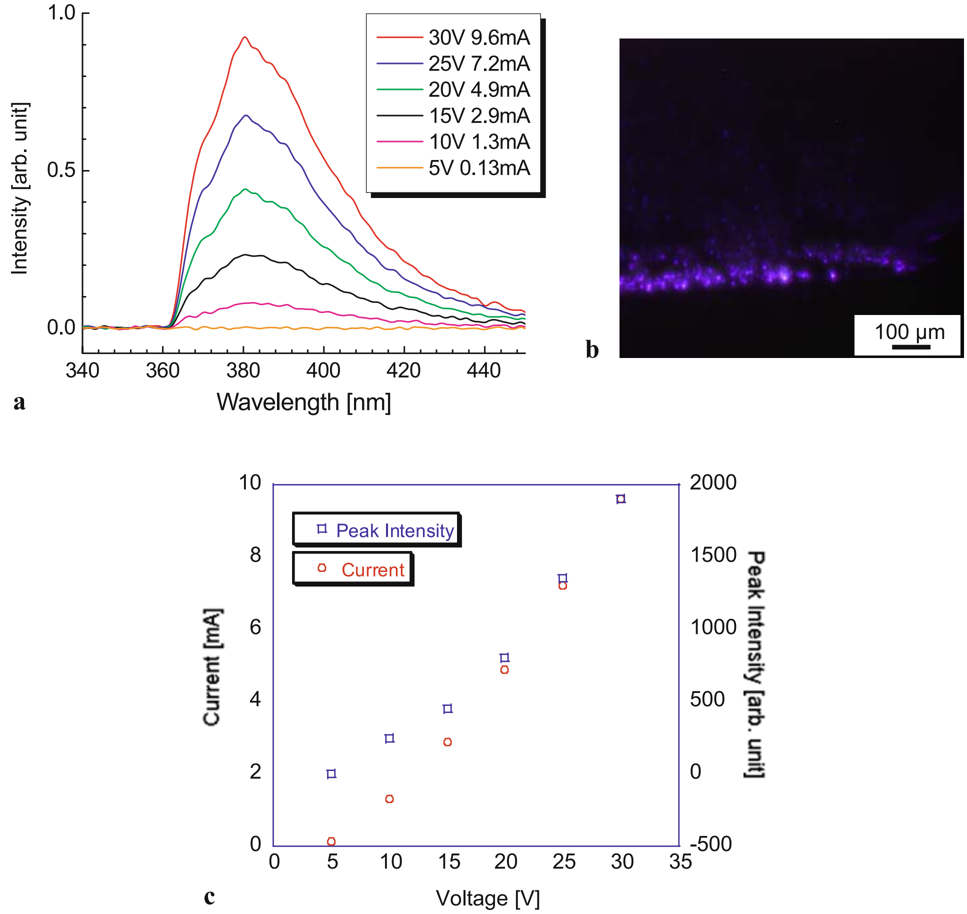

Fig. 3 (**a**) EL spectra, (**b**) light emission photograph of the ZnO buffer layer/ZnO nanowire array/*p*-GaN film heterojunction diode, and (**c**) dependence of EL peak intensities on the forward current

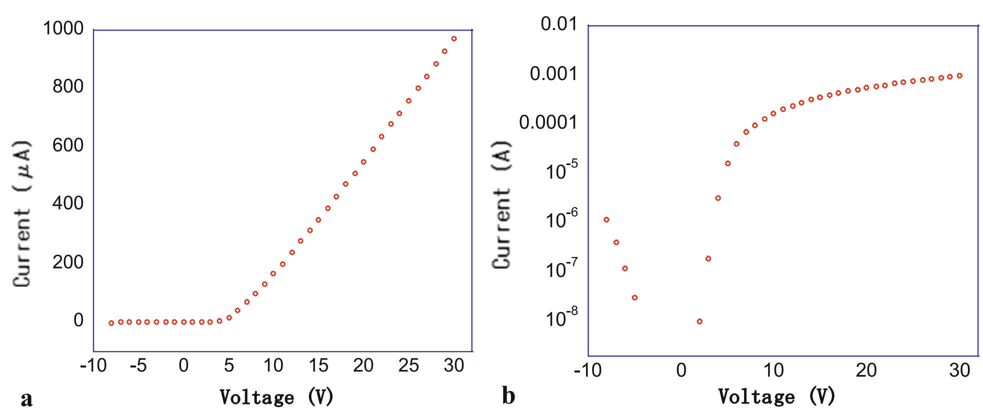

Fig. 4 *I*–*V* characteristics of the ZnO buffer layer/ZnO nanowire array/*p*-GaN film heterojunction diode: (**a**) *I*–*V* curves, (**b**) log(*I*–*V*) curves

3.2 *p*-GaN/*n*-ZnO heterojunction LEDs with embedded ZnO nanowires

As mentioned before, the second *p*-GaN/*n*-ZnO heterojunction structure with embedded ZnO nanowires was obtained by dispersing the as-deposited ZnO nanowires horizontally on a *p*-GaN thin film and then covering by an *n*-ZnO thin film. For comparison, the third film-based *p*-GaN/*n*-ZnO heterojunction structure was also simply fabricated. EL emissions were observed from the above two heterojunction diodes under various forward biases. As shown in Fig. 5a, the EL spectra of the film-based heterojunction diodes showed broad UV–violet emission peaks centered at about 380 nm, which was intensified by increasing the forward current to 5 mA. Even though the light emission from the film-based heterojunction diodes was too weak to be detected in the EL spectra at a forward current of 1 mA, the light emission was observed by the naked eye. Comparison of Figs. 5a and 5b showed that the EL emission from the heterojunction diodes with embedded nanowires was stronger than that of the film-based heterojunction diodes.

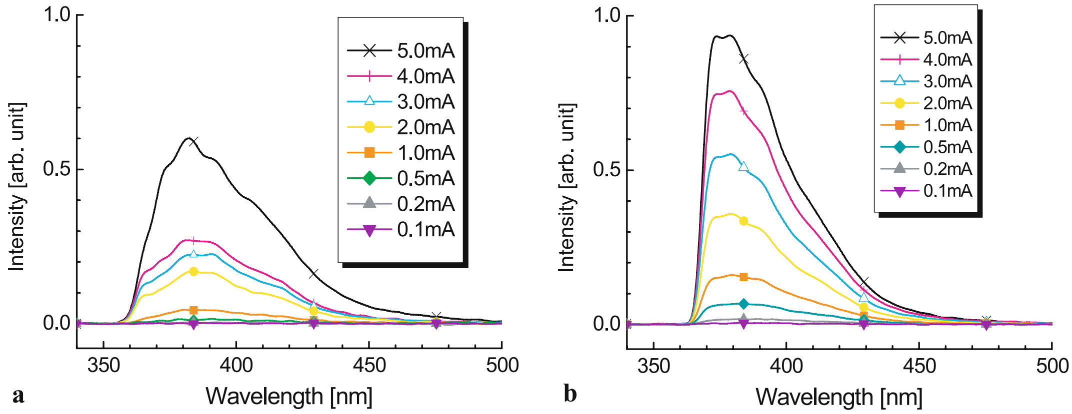

Fig. 5 EL spectra of (**a**) film-based GaN/ZnO heterojunction diodes and (**b**) *p*-GaN/*n*-ZnO heterojunction diodes with embedded ZnO nanowires

The heterojunction diodes with embedded nanowires also emitted UV–violet light, at a wavelength of about 380 nm even at the low forward current of 0.2 mA. An increased intensity of the EL peak was observed by increasing the forward current to 5.0 mA. It is expected that the relatively strong intensity of the EL peak of the nanosized heterojunction diodes compared to those of the film-based diodes is due to the low density of the interfacial defects which interrupt the electron injection from ZnO to GaN films. At the low injection current from the Al-doped ZnO films and the ZnO nanowires to the Mg-doped GaN films, the light emission was produced from the conduction band to deep acceptor-level transitions in the Mg-doped GaN films. However, the high injection current enhanced a fast, radiative electron–hole recombination which increased the strength of the luminescence from the shallow Mg acceptor levels compared to the deep Mg-related levels [18]. Therefore, it is concluded that the EL characteristics of the heterojunction diodes with embedded ZnO nanowires, that is, the intensification of the light emission peaks on the increase of the forward current, were due to the electron injection from the ZnO nanowires to the GaN films for radiative electron–hole recombination in the GaN films.

The current–voltage (I–V) characteristics of the film-based diodes and the *p*-GaN/*n*-ZnO heterojunction diodes with embedded ZnO nanowires were observed (see Fig. 6). The I–V curves clearly showed the nonlinear increase of current under the forward bias, and the leakage current of the heterojunctions with embedded nanowires was about 10^{-6} A, which was much smaller than that of the film-based heterojunctions at the reverse bias of 10 V. In addition, in the case of the heterojunction diodes with embedded nanowires, the current abruptly increased when the applied voltage exceeded 2.5 V, which was smaller than the turn-on voltage of 3.0 V of the film-based heterojunctions. These different I–V characteristics of the heterojunction diodes with embedded nanowires compared to the film-based heterojunction diodes can be explained by energy-band structures at the heterojunction interfaces, that is, the interface between the *n*-ZnO nanowires and the *p*-GaN films for the heterojunctions with embedded nanowires and the interface between the *n*-ZnO films and *p*-GaN films for the film-based heterojunctions. The Fermi energy level of the *n*-ZnO films in the film-based heterojunctions was closer to the conduction band compared to that of the ZnO nanowire in the nanowire-based heterojunctions thus resulting in a decrease of the energy barrier at the junction interfaces of the heterojunction diodes with embedded nanowires [11]. In addition, the heterojunction interface of the *p*-GaN/*n*-ZnO diodes with embedded nanowires, which has a lower density of interfacial defects and nanosized contacts, could enhance the electron injection from the ZnO nanowires to the *p*-GaN films and boost the electron–hole recombination when the forward bias is applied. Therefore, the turn-on voltage and the leakage current under the reverse bias of the heterojunctions with embedded nanowires should be smaller compared to that of the film-based heterojunctions.

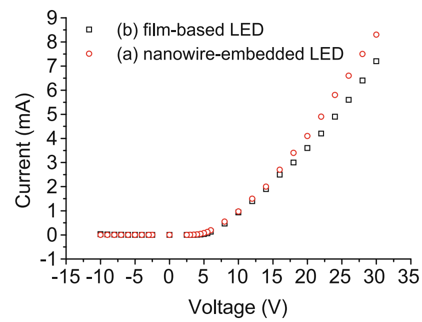

Fig. 6 I–V curves of (**a**) *p*-GaN/*n*-ZnO heterojunction diodes with embedded ZnO nanowires and (**b**) film-based GaN/ZnO heterojunction diodes

4 Conclusions

To summarize, vertically aligned ZnO nanowires were successfully synthesized by nanoparticle-assisted pulsed laser deposition (NAPLD), which were employed in the fabrication of the nanosized heterojunctions for LED applications. Three different heterojunction diodes were fabricated and their electroluminescence (EL) characteristics were investigated. The radiative electron–hole recombination was taken in the ZnO nanowires due to the small energy barrier for holes. The p-GaN/n-ZnO heterojunction diodes with embedded nanowires exhibited improved EL emission and electrical characteristics compared to those of the film-based GaN/ZnO heterojunction diodes. As the UV–violet light was emitted by a high injection current through the nanosized heterojunction interface, it is proposed that the development of efficient GaN/ZnO heterojunction LEDs using ZnO nanowires would be possible.

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