Improvement of Junction Properties of ZnO Nanorod/GaN Heterojunction Using Selective Laser Processing

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We fabricated the ZnO nanorod/GaN heterojunction light emitting diode by directly-growth of the ZnO nanorods on the GaN film using the nanoparticle-assisted pulsed laser deposition. Subsequently, selective laser irradiation to the p-n junction was applied to improve the junction properties. The UV emission was strongly enhanced by the laser irradiation. The peak wavelength of the UV emission is 377 nm, which is attributed to the near-band-emission of ZnO. In addition, the forward current was increased in the I-V characteristics by a factor of 6 at a bias voltage of 30 V.

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1. Introduction

ZnO is one of the attractive semiconductors for optoelectronic application in ultraviolet (UV) region due to its wide band gap of 3.37 eV and extremely large exciton binding energy of 60 mV. Especially, one dimensional ZnO nanostructures have been paid much attention due to its unique structure [1]. The ZnO nanorods can be synthesized by several methods, such as chemical vapor deposition, hydrothermal liquid method, high pressure laser ablation, and so on [2]. We have succeeded in growing vertically-aligned ZnO nanorods without any catalyst by the nanoparticle assisted high pressure pulsed laser deposition (NAPLD) [3]. ZnO nanorods are candidate for building blocks for UV light emitting diodes. To utilize the electro-optical property of semiconductors, it is a prerequisite to obtain both n- and p-type conductivities. However, it is difficult to produce p-type conductivity in ZnO, mainly due to the low dopant solubility and self-compensation effect of intrinsic defects [4,5]. Therefore, the realization of the hetero p-n junction has been extensively studied, using already existing p-type semiconductors, for instance, like p-Si [6,7], p-GaN [8-11], p-type polymer [12,13] and so on. Among these p-type materials, GaN is often utilized because of a low lattice mismatch with ZnO of 1.9 % [14]. In this study, the ZnO nanorod/GaN heterojunction was fabricated by directly-growth of the ZnO nanorods on a p-GaN film using NAPLD. In addition, selective laser irradiation to the p-n junction was applied to improve the junction property. The electrical and emission characteristics of the ZnO nanorod/GaN heterojunction were investigated with and without laser treatment.

2. Growth of ZnO nanorods

ZnO nanorods used in this study were prepared by NAPLD method [3]. Figure 1 shows the schematic of the experimental setup of NAPLD. A sintered ZnO target (Kojundo Chemical Lab. Co., Ltd) was mounted on a rotatable holder in a quartz furnace (Kyoei-Rikaki-Ten) filled

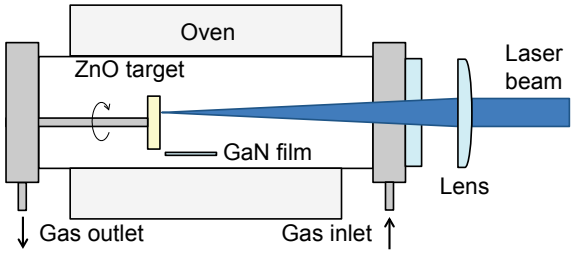

Fig. 1 Schematic of the experimental setup for synthesis of ZnO nanorods by NAPLD.

with Ar background gas of 35 kPa. A Mg-doped GaN film grown on a sapphire substrate (TDI Inc., thickness: 2 μm) was placed in front of the target. The quartz furnace was electrically heated up to 1173 K. It was confirmed that no thermal degradation of the GaN film occurred at this temperature. The target was irradiated by KrF excimer laser (Coherent Compex Pro 102 F) pulses at a fluence of 1.3 J/cm^2 and a repetition rate of 20 Hz. In NAPLD, the

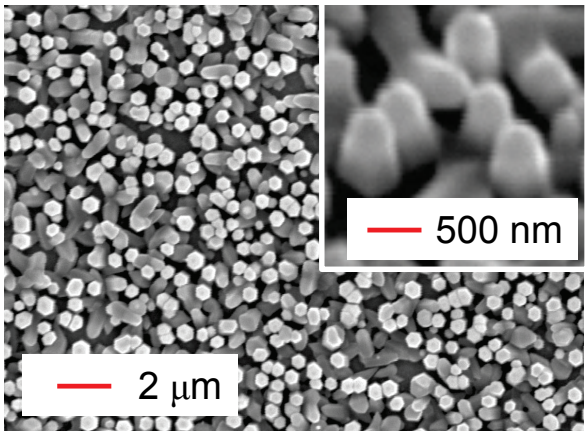

Fig. 2 SEM image of the ZnO nanorods grown on p-type GaN film. The inset is a tilted (40°) view.

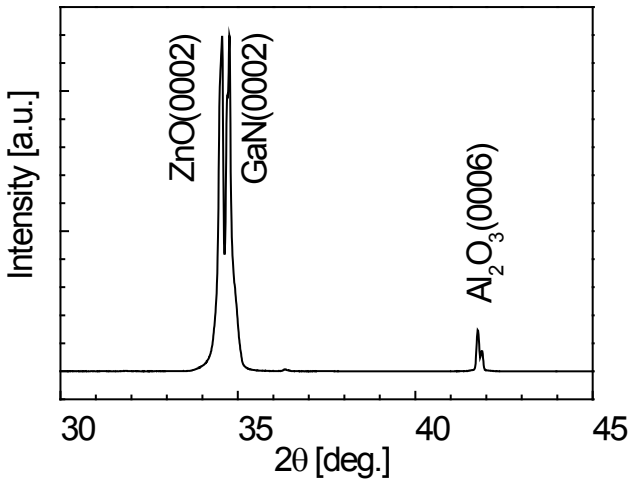

Fig. 3 XRD result of the ZnO nanorods grown on the GaN film.

ablated species are formed ZnO nanoparticles in the high pressure phase due to aggregation [15], and those nanoparticles play a very important role in nanocrystal growth [16,17]. When the nanoparticles were transported on a heated substrate, they melted and migrated on the substrate. During the migration, the size of the particles increased due to aggregation of the melted nanoparticles. And then, the aggregated particles precipitated at a place on the substrate as crystal nuclei because of increase of the melting temperature with the size of aggregated particles. In this experiment, with the increase of ablation time, many hexagonal ZnO nanorods were vertically grown from the nuclei and some nanorods were grown randomly, as shown in Fig. 2. More than the half of the nanorods were vertically-aligned, and the diameter and the length of the nanorods were about 300-500 nm and 1 μm, respectively. Only three characteristic peaks of ZnO(0002), GaN(0002), and Al_2O_3(0006) were observed from the structure in the X-ray diffraction measurement, as shown in Fig. 3.

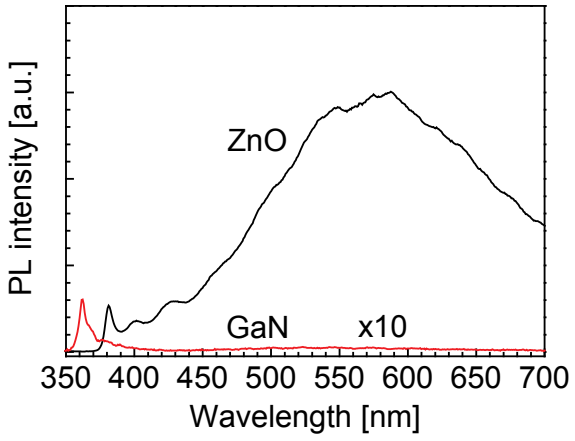

Fig. 4 The room temperature PL of the ZnO nanowires and the GaN film. The PL of GaN film has been magnified by a factor of 10.

Fig. 4 shows the photoluminescence (PL) spectra of the ZnO nanorods and the GaN film using a He-Cd laser at room-temperature. Since the PL intensity of the GaN film is very weak compared to that of the ZnO nanorods, the intensity of GaN film has been magnified by a factor of 10. The PL from the ZnO nanorods shows a weak near-band-edge (NBE) UV emission and a visible broad emission, which was related to transition by ZnO defect state [18-21]. On the other hand, a NBE emission peaked at 361 nm was observed from the GaN film [22].

3. Fabrication of n-ZnO nanorod/p-GaN heterojunction LED

Structural diagram of the n-ZnO nanorods/p-GaN heterojunction LED is shown in Fig. 5. A spin-on-glass (SOG) layer was spin-coated among the gap of ZnO nanorods for separating the electrode and GaN. A rotation rate of the spin-coating was 600 rpm for 20 seconds to be exposed the top of ZnO nanorods. Subsequently, Ni/Au was deposited on the surface of the exposed GaN by vapor deposition as the anode in order to achieve an ohmic contact. Ag paste was deposited to the top of ZnO nanorods as the cathode. I-V curve of the heterojunction shows the nonlinear increase of the current under a forward bias, and threshold voltage is about 5 V. The rectifying property was caused by ZnO nanorod/GaN heterojunction, so the thermal degradation of the GaN has not occurred during growth of ZnO nanorods by NAPLD. Figure 6 shows the electroluminescence (EL) spectrum from the heterojunction. The EL spectrum was very similar to the PL spectrum of the ZnO nanorods, which corresponds the defect-related visible emission. This result strongly suggested that the EL spectra of the heterojunction are originated from the radiative electron-hole recombination in the ZnO nanorods. The broad visible

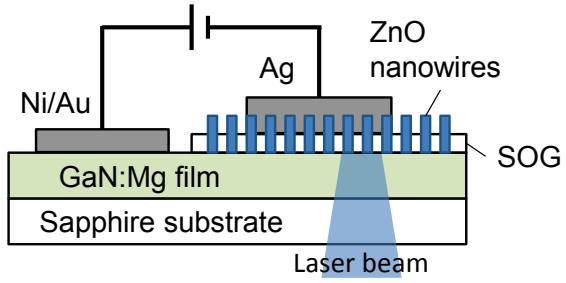

Fig. 5 Schematic of ZnO nanorod/GaN heterojunction LED, and the selective laser irradiation.

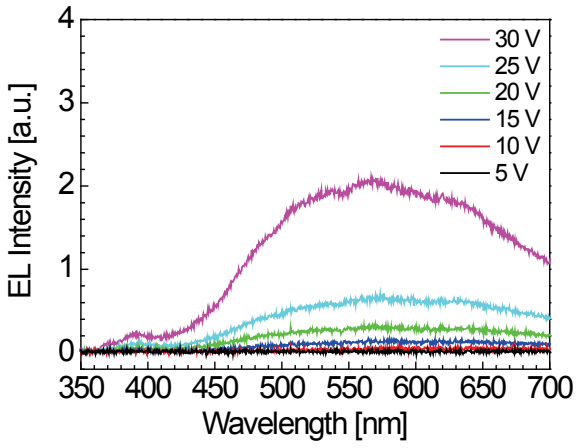

Fig. 6 EL spectra of ZnO nanowire/GaN film heterojunction LED with different forward biases of 5 to 30 V.

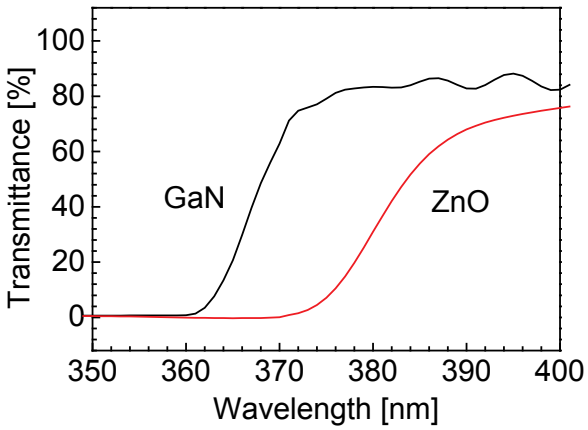

Fig. 7 Transmission spectra of ZnO film and GaN film with the thicknesses of 400 nm and 2 μm, respectively.

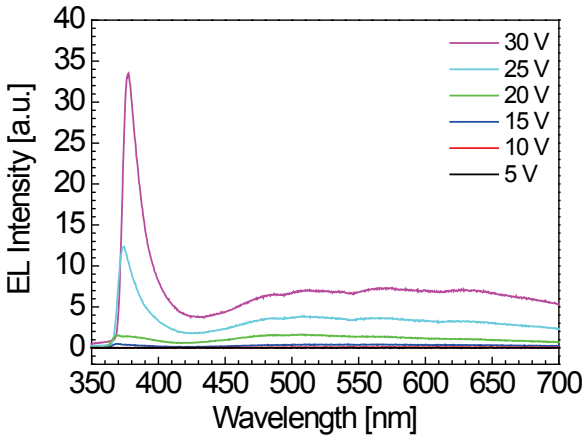

Fig. 8 EL spectra of ZnO nanowire/GaN film heterojunction LED after selective laser irradiation with different forward biases of 5 to 30 V..

emission was enhanced with the increasing applied voltage up to 30 V. When the applied voltage is more than 10 V, the emission was observed by naked eyes.

4. Laser irradiation to the p-n heterojunction

In order to improve the junction property, the pulse laser irradiation was performed to the ZnO nanorod/GaN heterojunction. In this treatment, the selection of the laser wavelength is very important. Figure 7 shows the

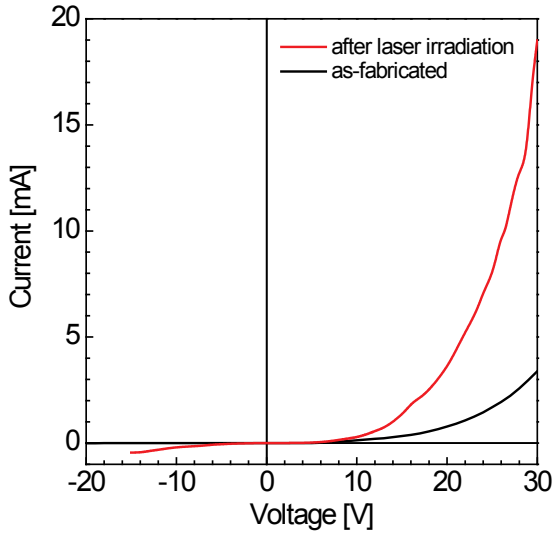

Fig. 10 I-V characteristics of the heterojunction before and after laser irradiation.

absorption spectra of the GaN film and a ZnO film measured by an absorption spectrophotometer, where the thicknesses of two films were 2 μm and 400 nm, respectively. The GaN film has absorption below 360 nm. On the other hand, the ZnO have absorption below 375nm. Therefore, when the laser beam at a wavelength of 375nm is irradiated through the GaN film, the laser beam can be absorbed at the interface between the ZnO nanorods and the GaN film. The laser beam at a wavelength of 375 nm for the laser treatment, that was generated by the second harmonic of a Q-switched Ti:sapphire laser, was irradiated to the interface. The irradiation fluence was estimated about 280 mJ/cm^2, which corresponds to melting and recrystallization fluence of a ZnO film [23]. In the experiment, 10 laser pulses with a spot size of about 1 mm were irradiated at the same point due to the non-uniform spatial distribution and 10 % stability of the pulse energy. Figure 8 shows the EL spectrum from the laser-irradiated heterojunction under various forward biases, where the EL intensities can be compared with that shown in Fig. 6. The UV emission was strongly enhanced by the laser irradiation. The peak wavelength of the UV emission is 377 nm, which is attributed to the NBE of ZnO. The visible emission was also increased, which is 3.5 times at the intensity of 550 nm under a bias of 30 V. Figure 9 (a) shows the photograph of the heterojunction LED

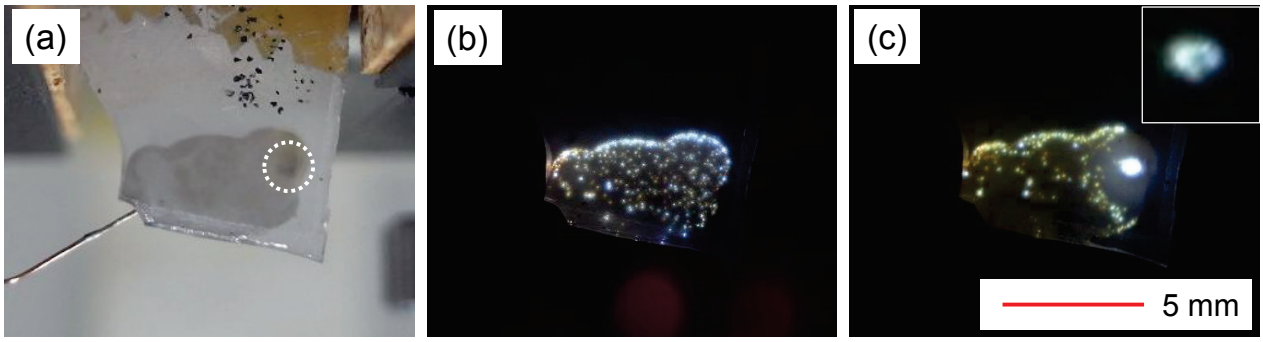

Fig. 9 (a) Photographs of the heterojunction LED, where the white dot circle shows the laser-irradiated area, and emission from the LED (b) before and (c) after laser irradiation under a forward bias of 30 V. Inset is enlarged image of the irradiated part under a forward bias of 15 V.

captured from the sapphire substrate side, where the white dot circle shows the laser-irradiated area. Figure 9 (b) and (c) show the emission from the LED before and after laser irradiation under a forward bias of 30 V, respectively. A high-bright emission was observed from the irradiated area. Although the captured image has low spatial resolution, several bright spots were found in the irradiated area under a bias of 15 V, as shown inset in figure 9 (c), indicating that local rapid-heating is achieved at each bottom of nanorod and the ZnO nanorod/GaN heterojunction structure is maintained. The I-V characteristic of the heterojunction after the laser irradiation was measured. Figure 8 shows the I-V characteristic of the heterojunction after laser irradiation. I-V curve before laser irradiation is also shown for comparison in Fig. 10. In both cases, rectification characteristics were observed. After the laser irradiation, the threshold voltage was almost the same, but the forward current was increased by a factor of 6 at a bias voltage of 30 V. Unfortunately, the leakage current was also increased under a reverse bias. Although optimization of the laser-irradiation intensity is needed, we demonstrated the improvement of the junction properties of the ZnO nanorod/GaN film heterojunction LED. The selective laser irradiation can be one of the effective techniques to improve the electrical and emission characteristics of the ZnO nanorod/GaN heterojunction LED.

5. Conclusion

We achieved improvement of the electrical and optical characteristics of the ZnO nanorod/GaN heterojunction LED. The NBE UV emission peaking at 377 nm was strongly enhanced by the laser irradiation, and the visible emission was also increased, which is 3.5 times at the intensity of 550 nm under a forward bias of 30 V. In addition, the forward current was increased in the I-V characteristics by a factor of 6. Therefore, the selective laser irradiation can be one of the effective techniques to improve the electrical and emission characteristics of the ZnO nanorod/GaN heterojunction LED as a post-treatment technique.

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