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Fabrication and Emission Properties of a n-ZnO/p-GaN Heterojunction Light-Emitting Diode

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Abstract: We report the fabrication and characterization of light-emitting diodes based on n-ZnO/p-GaN heterojunctions. The n-type ZnO epilayer is deposited by metalorganic chemical vapor deposition (MOCVD) on a MOCVD grown Mg-doped p-GaN layer to form a p-n heterojunction. During the etching process, the relation between the etching depth and the etching time is linear in a HF and NH_4Cl solution of a certain ratio. The etching rates of the SiO_2 and ZnO are well controlled, which are essential for device fabrication. The current-voltage relationship of this heterojunction shows a diode-like rectifying behavior. In contrast to previous reports, electroluminescence (EL) emissions are observed by the naked eye at room temperature from the n-ZnO/p-GaN heterojunction under forward- and reverse-bias. The origins of these EL emissions are discussed in comparison with the photoluminescence spectra.

Key words: ZnO/GaN heterojunction; light-emitting diode; metalorganic chemical vapor deposition; etching technology

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1 Introduction

It is well known that ZnO has several properties similar to GaN[1~3], such as a wurtzite crystal structure, a wide bandgap at room temperature, and a nearly identical in-plane lattice parameter (the lattice mismatch is about 1.8%). Compared with GaN, ZnO has some significant advantages, including a larger exciton binding energy of 60meV and the commercial availability of large area samples in bulk. Therefore, ZnO is very attractive for blue and UV optoelectronics. Furthermore, ZnO can be easily etched by wet chemical etching methods. Although p-type ZnO epitaxial growth technology has been developed during recent years, and a ZnO p-i-n homojunction light-emitting diode has been reported by Tsukazaki et al.[4], the fabrication of an effective ZnO LED still requires further development of reproducible, excellent, p-type material. There have been some reports on n-type ZnO heterojunctions, such as on p-type Cu_2O[5]. However, due to the device interface caused by a large lattice mismatch, the device performance was greatly impaired. Considering the close lattice parameters of ZnO, GaN, and SiC, there were some early reports on the fabrication of LEDs based on ZnO/GaN and ZnO/SiC heterostructures[6~8]. Some reports suggest that the 430nm emission from ZnO/GaN under forward bias originates from the deep level of p-GaN[9], and other papers have reported emissions from the ZnO/SiC heterojunction under reversed bias[10], but no emission has been observed under forward bias. Similar results have also been observed in a nanorod array n-ZnO/p-GaN heterostructure[11]. In this study, we report the fabrication and emission properties of n-ZnO/p-GaN heterojunction LEDs. The current-voltage relationship of this heterojunction shows a diode-like rectifying behavior. In contrast to previously reported results, different efficient electroluminescences (EL) are observed at room temperature from the n-ZnO/p-GaN heterojunction under

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both forward-bias and reverse-bias. Detailed results and discussion are provided to explain the above results.

2 Experiment

In this study, a Mg-doped p-GaN layer (~600nm) was first grown on sapphire (0001) substrate by the standard MOCVD growth procedure. After activation of the acceptors by rapid thermal annealing in N_2 ambient, the GaN sample was put into another low pressure MOCVD system for ZnO growth. Then, a ZnO buffer layer was grown on GaN at 400 ℃ for 5min, and an intrinsic n-ZnO film of ~600nm was deposited at 600 ℃. Hall measurements show that the hole concentration and mobility of GaN are $p = 5.8 \times 10^{17} cm^{-3}$ and $\mu_p = 25 cm^{-2}/(V \cdot s)$, and the electron concentration and mobility of ZnO are $n = 8 \times 10^{17} cm^{-3}$ and $\mu_n = 18 cm^{-2}/(V \cdot s)$, respectively.

The LED device fabrication processes are as follows. First, the n-ZnO layer was partly etched away down to the p-GaN layer with a 5% HCl solution after masking the surface. Second, after depositing a SiO_2 thin film on the surface for protection, the surface was masked for the second time. Third, 5% HF and NH_4Cl solutions were used to etch away some parts of the SiO_2 down to the n-ZnO through a 60μm × 80μm opening in the mask. Finally, Al was evaporated on the surface to be used as electrodes on the ZnO and GaN. In the third masking and etching process, unwanted Al was etched away using a certain ratio of $H_3PO_4 : CH_3COOH_4 : H_2O$ solution. It is found that the Al was etched by this solution, but SiO_2 is very resistive to it. A schematic diagram of the final heterojunction structure is shown in the inset of Fig. 1.

During the device fabrication process, the etching away of too much ZnO should be avoided when etching the SiO_2. However, ZnO is easily etched away by acid solution. The chemical characteristics of ZnO result in the etching of ZnO by HF solution during the SiO_2 etching, causing damage to the device. Thus it is critical to control the HF solution etching rate of SiO_2 and ZnO for ZnO device fabrication. By varying the ratio of HF, NH_4F, and H_2O, the etching rates of both SiO_2 and ZnO were well controlled in this work.

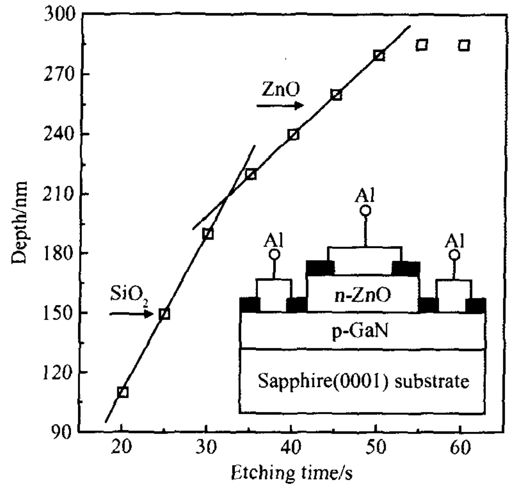

Fig. 1 Etching depth of SiO_2/ZnO as a function of etching time at room temperature Inset shows the diagram of n-ZnO/p-GaN heterojunction LED device.

Figure 1 shows the etching thickness dependence on the etching time. Both SiO_2 and ZnO etching thickness have a nearly linear relationship with the etching time when using a certain percentage of NH_4F, indicating that the H^+ ion density in the solution has been well controlled during this etching process. The etching rates were kept slow enough, with etching rates for SiO_2 and ZnO of 340 and 260nm/min respectively. Under these conditions, the etching of ZnO can be easily prevented by controlling the SiO_2 etching time during the SiO_2 etching process.

The electroluminescence of the n-ZnO/p-GaN LED was performed under both forward and reversed biased conditions at room temperature (RT). RT photoluminescence spectra were recorded as excited by a He-Cd laser (325nm).

3 Results and discussion

The current-voltage (I-V) relationship of the fabricated heterojunction at RT is presented in Fig. 2, exhibiting a diode-like rectifying behavior. The forward turn-on voltage of this n-p heterojunction is around 1.7V, which seems quite low. This may be due to the existence of interface defects[12]. The leakage current under reverse bias is $\sim 8 \times 10^{-6}$ A. It is also noticed that the current does not increase distinctly with the bias voltage. However, the forward characteristics in Fig. 2 were obtained when the n-p junctions were under reverse bias, indicating that there exists another potential barrier, which is thought to be generated by the presence of a large Schottky barrier formed by the Al contact to the p-GaN. In fact, the Al/p-GaN/Al I-V relationship does show non-ohmic contact behavior which is not shown here, and the Al/p-GaN Schottky contact is then under the forward-bias. The n-ZnO/p-GaN heterojunction shows type II band alignment, as also shown in the inset in Fig. 2. The conduction band offset is $\Delta E_C = \chi(GaN) - \chi(ZnO) = -0.15eV$, and the valance band offset ΔE_C is $\Delta E_V = E_g(GaN) - E_g(ZnO) + \Delta E_C = -0.13eV$.

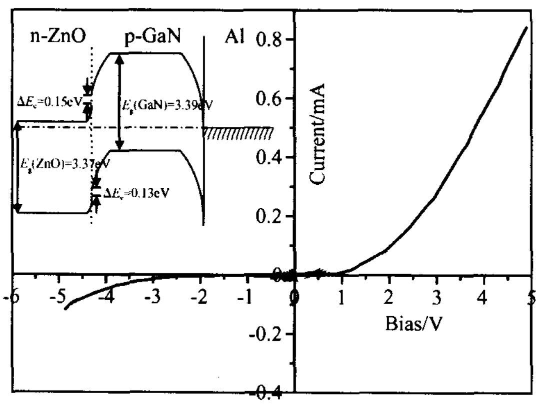

Fig. 2　Current-voltage relationship and energy-band diagram of an n-ZnO/p-GaN heterojunction device

The forward-voltage of this I-V curve was formed when voltage for the n-p junctions was under reverse-bias voltage and the Schottky contact was under forward bias. Considering the existence of Schottky contacts, the whole structure boils down to two resistors in series. One is an n-p junction, and the other results from the Schottky contact. The injection current through the junction (J_{pn}) can be derived into two branches[12]. One is the electron-injected current (J_n), the other is the hole-injected current (J_p). Under the forward bias of this LED structure, the current of the n-p junction is $J_{n-p} = J_p + J_n$. The current flows from the n-ZnO to the p-GaN, the reverse of the n-p junction direction. At the same time, the Schottky contact is under forward bias. Thus, the total forward current of this structure is $J = J_{n-p}$, which is mainly determined by the p-n junction reversed behavior with a small current. The small current may be caused by a large number of defects in the n-ZnO/p-GaN interface.

On the other hand, when the device is reverse biased, the n-p junction is then forward-biased and the Schottky contact is reverse-biased. Thus, the total reverse current of this structure is $J = J_{m-s}$, which is mainly determined by the Schottky contact junction reversed behavior. The small current may be caused by the defects in the Al/p-GaN interface, where some mixed phase structures are corrosion-resistant and remain on the p-GaN surface after the ZnO etching process.

Room temperature EL spectra of the n-ZnO/p-GaN LED were measured at both forward-bias (a) and reverse-bias (b) voltages, as shown in Fig. 3. A distinct blue EL emission at around 430nm with a tail extending to the low energy side was obtained under reverse bias voltage for the whole device, but at a forward bias for the p-n junction, as discussed above. Our results are in

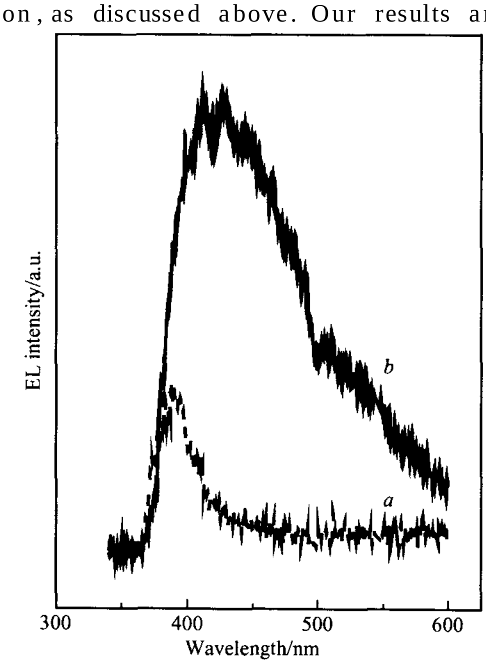

Fig. 3　Room temperature EL spectra of n-ZnO/p-GaN under forward-bias (a) and reverse-bias (b) voltages

good agreement with previous works, which attributed it to the injection of electrons from the n-ZnO side into the p-GaN side[9,13]. In order to study the origin of this emission, PL was used to characterize the p-GaN (curve c) and n-ZnO (curve a), as shown in Fig. 4. The ZnO has only a strong near band edge emission at 376nm and no deep level emissions. Compared with that of ZnO, the PL intensity of GaN is much smaller, which possibly due to a large number of nonradiative centers in the material caused by Mg incorporation. The weak emission of GaN, around 365nm, is attributed to band edge emission of the GaN. A broad emission of GaN around 390nm with a broad tail extended to the low energy side was also observed, which is related to the donor-acceptor-pair radiative transitions[14]. However, contrary to previous results, no photoluminescence peak was observed around 430nm in the p-GaN samples.

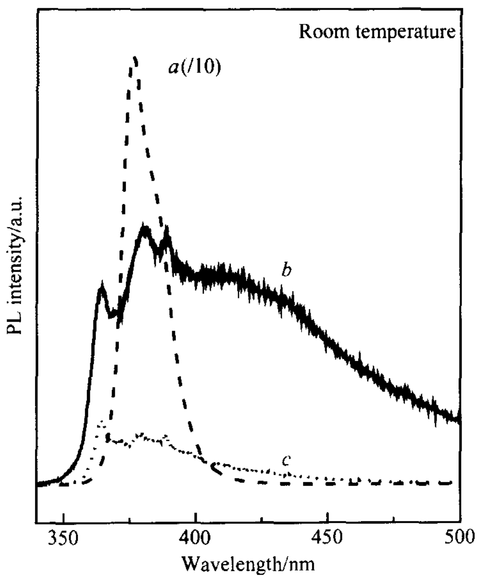

Fig. 4 Room temperature PL spectra of as-grown ZnO (curve a), GaN prior to ZnO growth (curve c), and also GaN sample (curve b) which has undergone ZnO growth and then been removed

Another p-GaN sample (curve b) was then employed for photoluminescence measurement, which had undergone ZnO growth and acid solution etching to remove the ZnO epilayer. This sample shows a distinct broad emission around 430nm apart from the near-band emission and DAP emission, as shown in Fig. 4. By comparison with the PL of p-GaN, it is believed that this broad emission comes from the interface defects which formed during the ZnO growth procedure.

Under the forward-biased condition, as shown in curve a in Fig. 3, the EL emission is centered at 3.2eV (382nm) with a relatively small peak width. The peak energy of this emission coincides well with that in the photoluminescence spectrum of p-GaN. When the device is under reverse-bias, the n-p junction shows reverse characteristics while the Schottky junction shows forward characteristics. Electrons may be injected from Al into p-GaN to recombine with holes in the GaN region to give an emission around 382nm. The absence of the near bandgap emission of the p-GaN may result from the low emission intensity and the self-absorption of the p-GaN sample surface layer formed during the ZnO growth.

4 Conclusion

In this study, both the fabrication process and wet etching technique to make n-ZnO/p-GaN heterojunction LEDs have been demonstrated. By varying the ratio of HF, NH_4F and H_2O, the etching rates of SiO_2 and ZnO were well controlled. The n-ZnO/p-GaN heterojunction exhibits a diode-like rectifying behavior with a small threshold voltage of 1.7V. Distinct EL emissions under forward and reverse biases were observed by the naked eye. The emission around 430nm under reverse-bias voltage for the device is attributed to interface defects between the ZnO and GaN, which were formed during the ZnO growth on the GaN, and the emission of 382nm that comes from the GaN under forward-bias voltage for the device is attributed to electrons injected from the Al into the p-GaN to recombine with holes in the GaN region.

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n-ZnO/p-GaN 异质结构发光二极管的制备与特性

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摘要：报道了 n-ZnO/p-GaN 异质结构发光二极管的制备及其发光特性. 采用金属有机气相外延技术在 Mg 掺杂 p 型 GaN 衬底上外延 n 型 ZnO 薄膜以形成 p-n 结. 实验发现在一定配比的 HF 酸和 NH_4Cl 溶液中，腐蚀深度和腐蚀时间呈线性关系，并且二氧化硅和 ZnO 的腐蚀速率得到很好的控制，这对器件制备的可靠性非常重要. 电流-电压(I-V)特性测试显示该器件结构具有明显的整流特性. 室温下，在正反向偏压状态下都可用肉眼观察到电致发光现象. 同时，通过与光致发光谱进行比较，对电致发光谱中发光峰的起源和发光机制进行了探讨.

关键词：ZnO/GaN 异质结构；发光二极管；金属有机气相外延；腐蚀工艺
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