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Electroluminescence of ZnO nanorods/ZnMgO films/p-SiC structure heterojunction LED

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HIGHLIGHTS

- ZnMgO films were grown on SiC substrate by sol–gel.
- ZnMgO films between n-ZnO nanorods and p-SiC works as barrier layer which controls the movement of holes and electrons.
- Using ZnMgO films, electroluminescence from ZnO nanorods could be obtained.

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ABSTRACT

Through a facile low-temperature hydrothermal process, ZnO nanorod arrays were grown on ZnMgO films/p-SiC to form a heterojunction LED. ZnMgO films were grown on p-SiC by a simple sol–gel method. In this heterojunction structure, ZnMgO films works as the seeds film for the growth of ZnO nanorods. In particular, ZnMgO films can work as barrier layer between n-ZnO nanorods and p-SiC, which controls the movement of holes and electrons. Thus, with this introduced ZnMgO films, the electroluminescence (EL) from ZnO can be observed in ZnO/SiC heterojunction. Under a forward bias larger than 18 V, the emission band in electroluminescence (EL) spectrum is considered as a combination of a peak centered at 388 nm and a yellow band emission peak around 450 nm. As the injection current increased, the intensity of ultraviolet emission was also increased. At last, the function of ZnMgO films in the heterojunction structure was discussed.

1. Introduction

ZnO with excellent optical and photoelectronic properties has draw a great attention in light emission diodes (LEDs), laser diodes (LD), and photodetectors especially for its nanostructure [1–4]. Yang's group realized ZnO nanowire nanolasers in room temperature [1], which can used as the ideal miniaturized laser light sources. Nonetheless, obtainment of p-type ZnO is still a major challenge, which has impeded the development of ZnO p–n homojunction devices [5,6]. Therefore, many research groups focus their works on ZnO heterojunction devices. Commercially available p-SiC and p-Si are stable p-type substrates for ZnO-based heterojunction LEDs [7–10]. Lupan synthesized ZnO nanowires on p-Si (1 1 1), and obtained the visible-light emission [7]. Shih utilized undoped ZnO as insulator layer to obtain p-SiC EL in ZnO/SiC heterojunction [9]. But due to difference of the band gap position, the light emission from ZnO/SiC heterojunction were usually origined from SiC or Si [7,9]. Therefore, many works introduced barrier layer, such as MgO, SiO_2, to control the movement of carriers and obtain the EL emission from ZnO in heterojunction [8,9,11,12]. But it was not suitable for the growth of ZnO nanostructure due to the large lattice mismatch. ZnMgO as an important part of ZnO, is considered as ideal barrier layer material [8], which band gap can be adjusted by controlling Mg content. In Ma's report [8], electrically pumped ultraviolet random lasing was realized by using ZnMgO as barrier layer, the potential barrier for electrons can also be adjusted by changing Mg content which was meaningful for the optoelectronic device.

In this paper, we report on the fabrication and electroluminescence of a ZnO nanorods/ZnMgO films/p-SiC heterojunction LED. By introducing ZnMgO films, the injection of electron from ZnO and hole from SiC were restricted in ZnMgO films. Meanwhile, the electroluminescence originated from ZnO nanorods was detected.

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In particular, ZnMgO films can also worked as the seed layer for the growth of ZnO nanorods.

2. Experimental

2.1. Synthesis of ZnMgO films

The detail of experiment can reference to our previous work [13]. The sol was composed of $Zn(NO_3)_2$, $Mg(NO_3)_2$, and polyvinylpyrrolidone (PVP) in ethanol solution. The total concentration of metal ions was controlled at 0.1 mol/L, the concentration of Mg^{2+} was 0.02 mol/L, the concentration of Zn^{2+} was 0.08 mol/L, and the quality of PVP was 80 mg/mL. The sols were spin coated on SiC at 4500 r/min. After the spin coating, the substrate was heated to 400 °C in air for 30 min to eliminate the organic component in the films, then to 500 °C in air for 1 h to improve crystal quality of ZnMgO films. The thickness of ZnMgO films was about 400 nm.

2.2. Preparation ZnO nanorods heterojunctions

The heterojunctions were prepared by growing ZnO nanorods on the ZnMgO films/SiC substrate under hydrothermal condition. The growth solution was composed of 0.01 M zinc acetate, 0.01 M hexamethylenetetramine in 50.0 mL deionized water. The solution was heated up to 90 °C on a hotplate in an electric oven for 6 h. After reaction, the sample was washed by deionized water and dried in air at 60 °C for several hours [14]. In order to form ohmic contacts, In and Ni–Au/In electrode were fabricated on the top of ZnO nanorods and p-type SiC substrate by sputtering, separately.

The morphology and structure properties of samples were investigated by a field-emission scanning electron microscopy (FESEM, Hitachis-4800), an energy-dispersive X-ray spectroscopy (EDS, GENE SIS 2000 XMS 60S, EDAX, Inc.) attached to the SEM, a D/max-RA X-ray spectrometer (Rigaku). Photoluminescence (PL) measurements were performed using a He–Cd laser line of 325 nm as the excitation source. The absorption spectrum of the ZnMgO films was measured in a Shimadzu UV-3101PC scanning spectrophotometer. Electroluminescence (EL) measurements were performed by a fluorescence meter (F4500 Hitachi). The current–voltage (*I–V*) curve was measured by a semiconductor parameter analyzer with a sensitivity of 0.1 pA.

3. Results and discussion

The morphologies of the as-grown ZnMgO films and ZnO nanorods were characterized by using FESEM. Fig. 1a shows the SEM image of as-grown ZnMgO films, the films are composed of regular grains with average diameter in the range of 100–150 nm, and present smooth dense surface. Fig. 1c shows the corresponding EDS spectrum, which indicates that there are zinc, oxygen and magnesium in the films, the Mg content in the ZnMgO films determined by X-ray photoelectron spectroscopy is about 15%. C, Si and Al originate from SiC substrate and aluminum tray. Fig. 1b shows ZnO nanorods with well-defined facets on the ZnMgO films/SiC substrate. The ZnO nanorods have a typical diameter of about 50 nm and a length of 2 micrometers (shown in Fig. S1). In order to investigate the structure and orientation of ZnMgO films and ZnO nanorods, the XRD measurement was performed as shown in Fig. 1d. Fig. 1d shows the XRD pattern of ZnMgO films and ZnO nanorods. For each sample, the diffraction peaks in the pattern belong to the (1 0 0), (0 0 2), (1 0 1), (1 0 2) and (1 1 0) directions of the ZnO wurtzite structure, no other diffraction peaks from any other material can be detected. Compared with undoped ZnO films, the (0 0 2) diffraction peak position of ZnMgO films shifts to the large-angle side clearly (as shown in the inset of Fig. 1d), which due to the Mg ions substitute the Zn sites [13]. From the XRD and EDS results, Mg ions diffused into the ZnO crystal lattice and formed ZnMgO films. In addition, to our knowledge [15–17], in the growth process of ZnO nanorods, ZnO films were usually used as the seed films to control the orientation of the growth of nanorods. The (0 0 2) diffraction peak is dominant in the spectra of ZnMgO films, which means the as-grown samples have a preferred orientation along the *c*-axis and can be suitable for the growth of ZnO nanorods. In addition, the stronger intensities of ZnO nanorods indicate that the crystalline quality and orientation of ZnO nanorods are better than ZnMgO films.

To confirm the band gap energy, the optical properties of ZnMgO films and ZnO nanorods were investigated. Fig. 2a shows the absorption spectrum of the ZnMgO films, an obvious absorption edge at about 3.5 eV can be obtained, which means ZnMgO has a strong absorption in the UV region and transparent in the visible region. And these films can also be used as the barrier layers in ZnO based device [8,12,18]. Fig. 2b shows room temperature PL spectra of ZnMgO films and ZnO nanorods. For ZnMgO films, an ultraviolet (UV) emission located at 355 nm which is due to band gap of as-grown films and a weak visible emission related to the defect are observed. For ZnO nanorods, the UV emission has a red-shift from 355 nm to 387 nm which is due to the band gap excitonic emission and no visible emission can be detected means as-grown nanorods had a better crystalline quality accord with XRD result.

The room temperature EL spectra of the ZnO nanorods heterojunction show in Fig. 3 with different voltages (12–33 V). The schematic structure and *I–V* curve of the ZnO nanorods heterojunction are also shown in insets of Fig. 3. The typical diode rectifying behavior could be observed and the EL from this heterojunction can be obtained when forward-bias was applied. A emission band could be observed centered at 450 nm under the injection voltage of 12 V. The origination of the emission was contributed to the SiC [9]. When the injection voltage increased to 27 V, a UV emission could be observed besides the band emission around 450 nm. When the injection voltage was 33 V, a emission centered at 388 nm could be detected. Based on the previous reports [9,18–20], EL emission is usually generated by carrier recombination at the near interface between the two semiconductors [18]. Then, from the PL result, the near-band-edge emission peak of ZnO is 387 nm, and we may deduce the origination of the emission peak located at 388 nm is contributed to ZnO.

In addition, the energy band diagram of this heterojunction was used to confirm the origination of the emission and the function of introduced ZnMgO films as shown in Fig. 4. As above mentioned, SiC emission was usually dominant in EL of ZnO/SiC heterojunction, due to the electrons injection from ZnO into SiC was easier than holes injection from SiC into ZnO [8,12,21]. However, in our heterojunction, the introduced ZnMgO layer changed the band gap structure. The electron affinity of ZnO, ZnMgO, SiC are 4.35 eV, 4.0 eV and 3.8 eV and the band gap of ZnO, ZnMgO, SiC are 3.37 eV, 3.5 eV and 3.3 eV, respectively.

In the interface of ZnO/SiC, the energy barrier ΔE_{C1} for electrons is:

$$\Delta E_{C1} = \chi_{ZnO} - \chi_{SiC} = 4.3 - 3.8 = 0.5 \text{ eV} \quad (1)$$

and the energy barrier ΔE_{V1} for holes is:

$$\Delta E_{V1} = Eg_{ZnO} + \Delta E_{C2} - Eg_{SiC} = 3.37 + 0.5 - 3.3 = 0.57 \text{ eV} \quad (2)$$

In the interface of ZnO/ZnMgO, the energy barrier ΔE_{C2} for electrons is:

$$\Delta E_{C2} = \chi_{ZnO} - \chi_{MgZnO} = 4.3 - 4 = 0.3 \text{ eV} \quad (3)$$

and the energy barrier ΔE_{V2} for holes is:

$$\Delta E_{V2} = Eg_{ZnO} + \Delta E_{C2} - Eg_{MgZnO} = 3.37 + 0.3 - 3.5 = 0.17 \text{ eV} \quad (4)$$

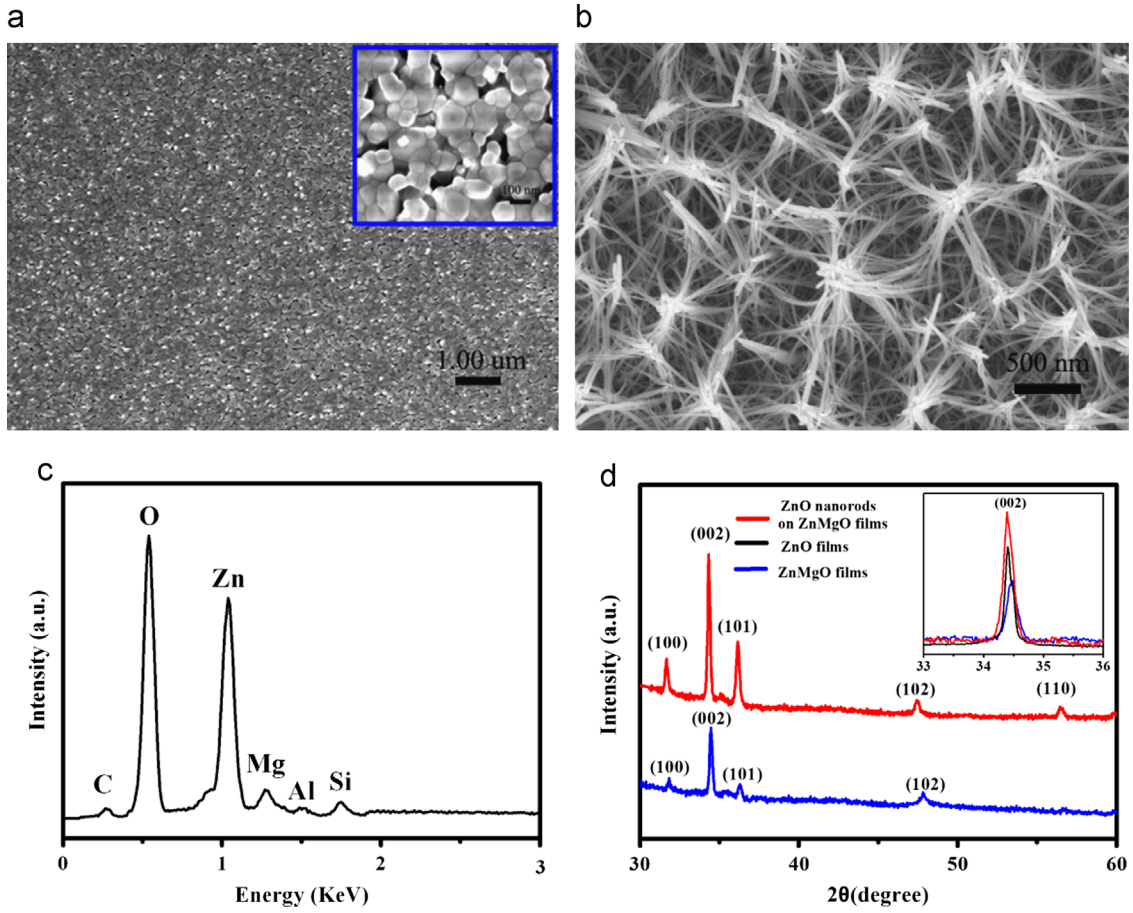

Fig. 1. SEM images of ZnMgO films (a), ZnO nanorods on ZnMgO films (b), EDX spectrum of ZnMgO films (c), XRD patterns of ZnMgO films and ZnO nanorods (d).

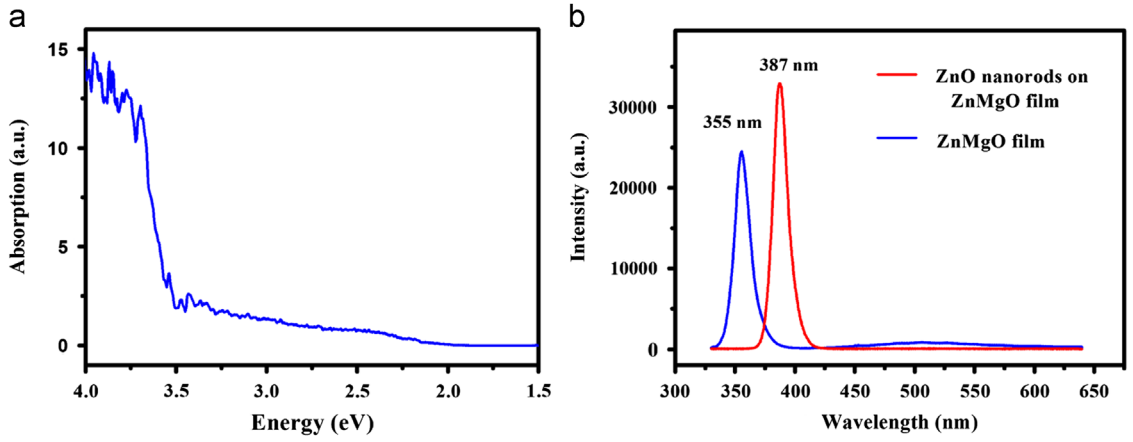

Fig. 2. Absorption spectra of ZnMgO films (a) and PL spectra of ZnMgO films and ZnO nanorods (b).

In the interface of ZnMgO/SiC, the energy barrier ΔE_{C3} for electrons is:

$$\Delta E_{C3} = \chi_{MgZnO} - \chi_{SiC} = 4 - 3.8 = 0.2 \text{ eV} \quad (5)$$

and the energy barrier ΔE_{V3} for holes is:

$$\Delta E_{V3} = Eg_{MgZnO} + \Delta E_{C1} - Eg_{SiC} = 3.5 + 0.2 - 3.3 = 0.4 \text{ eV} \quad (6)$$

Therefore, the electrons injection from ZnO into ZnMgO was easier than injection into SiC, but the holes injection from SiC into ZnMgO was also easier than injection into ZnO. Thus, a part electrons from ZnO and holes from SiC could be limited on both sides of ZnMgO and radiate through tunneling and the EL from ZnO nanorods could be obtained. To further prove ZnMgO barrier layer function. ZnO nanorods were remove, a ZnMgO/SiC heterojunction can be obtained. However, during this situation, the electrons of ZnMgO could also inject into SiC because of the smaller energy barrier for electrons in ZnMgO (ΔE_{C3}). As the result, it also exhibited the SiC emission in ZnMgO/ SiC heterojunction as shown in Fig. 5.

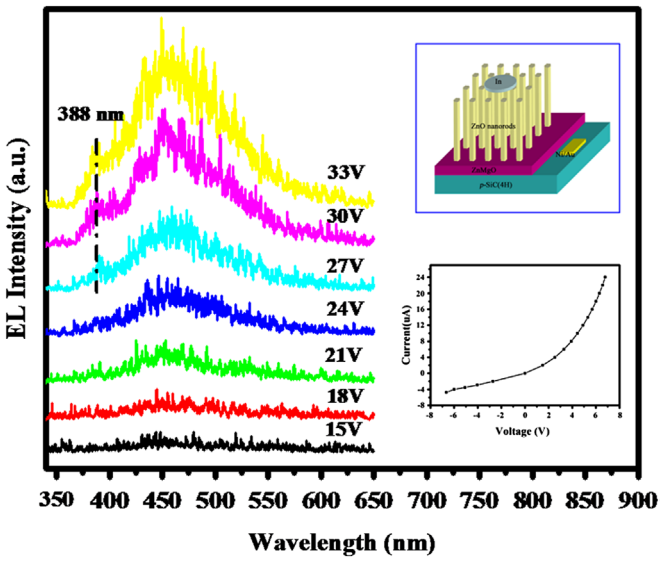

Fig. 3. EL spectrum of the ZnO nanorods heterojunction. The inset is schematic of the ZnO nanorods heterojunction and *I–V* curves of heterojunction.

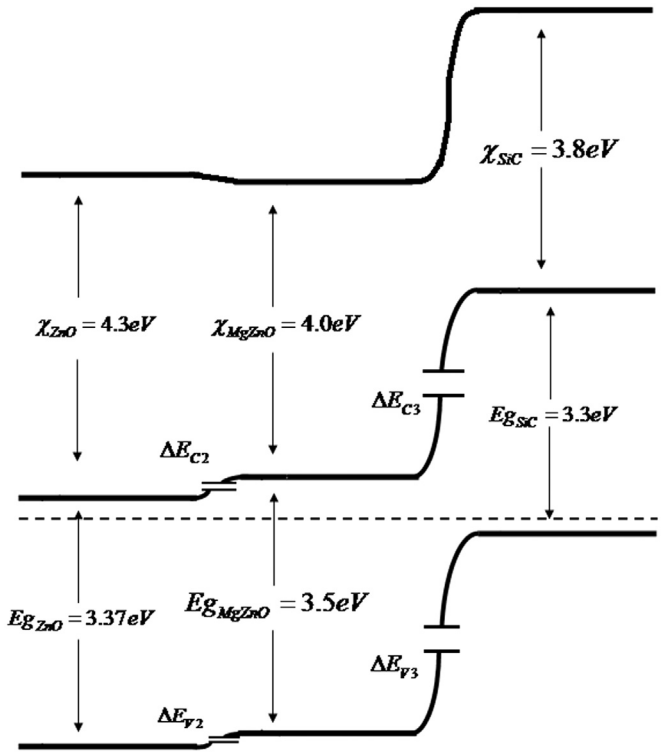

Fig. 4. The energy band schematic diagram of ZnO nanorods/ZnMgO films/p-SiC heterojunction.

4. Conclusions

In conclusion, the ZnO nanorods/ZnMgO films/ p-SiC heterojunction LED were prepared by sol–gel and hydrothermal method. The XRD results shown that as-grown ZnMgO films could keep ZnO wurtzite structure and used for the ZnO nanorods growth. The absorption spectrum indicated the ZnMgO films band gap energy was about 3.5 eV. In heterojunction, ZnMgO films could act as the barrier layers, conduction-band offset (ΔE_C) and valence band offset (ΔE_v) could be reduce, therefore, under a forward bias some electrons from ZnO can be injected in ZnMgO films, then holes from SiC can be injected in ZnMgO films. Thus, the electrons and holes, on the two sides of as-grown ZnMgO films would be radiated through tunneling. And we obtained blue EL emission in ZnO nanorods/p-SiC structure. The electroluminescence from ZnO nanorods could be observed under 27 V in EL spectrum of heterojunction LED. The present results demonstrate that ZnMgO films can be applied for band-gap engineering of ZnO NWs heterojunction LED and obtain ZnO blue electroluminescence, which is important for ZnO NWs light-emitting nanodevices.

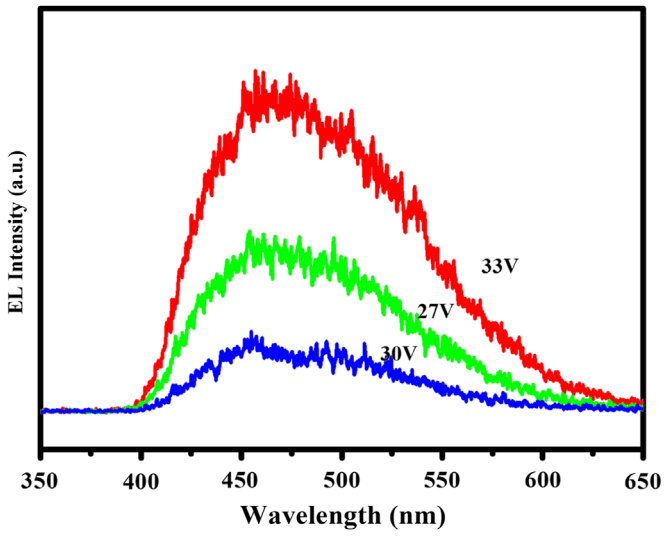

Fig. 5. EL spectrum of the ZnMgO/SiC heterojunction.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.physe.2013.12.010.

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