Journal of Luminescence 134 (2013) 240–243

Contents lists available at SciVerse ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Ultraviolet electroluminescence from n-ZnO/p-NiO heterojunction light-emitting diode

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ARTICLE INFO

Article history:
Received 22 June 2012
Received in revised form
3 August 2012
Accepted 17 August 2012
Available online 28 August 2012

Keywords:
Thin films
Heterojucntions
Light-emitting diode
Electroluminescence

ABSTRACT

The n-ZnO/p-NiO heterojunction was prepared by depositing a p-type NiO film on a *c*-plane sapphire by rf magnetron sputtering and then growing a n-type ZnO film on the NiO film by plasma-assisted molecular beam epitaxy. The heterojunction shows a diode-like rectification characteristic with a turn-on voltage of ~3.6 V and emits UV light upon putting a forward bias. The intensity of the UV emission increases as injection current increases from 0.5 to 3.5 mA, but the wavelength of the UV emission decreases from 404 to 387 nm. It is demonstrated that the UV emission comes from near band-edge radiative recombination of electron and hole in the ZnO layer. The mechanism of the UV electroluminescence is discussed in the present work.

1. Introduction

Zinc oxide, with a wide direct band gap of 3.37 eV and an exciton binding energy of 60 meV, is one of the most promising candidates for preparation of short-wavelength light emitting diodes (LEDs) and lasing devices (LDs) as well as photodiode devices [1–3]. Upto now, although electroluminescence (EL) of ZnO p–n homojunction LEDs has been realized, it is still difficult for further commercial application because of the lack of reproducible and stable p-type ZnO thin films [1]. On the other hand, heterojunction-based LEDs are expected to exhibit improved current confinement comparing to homojunction LEDs, for this reason, considerable efforts have been denoted to fabricating ZnO-based heterojunction by employing n-type ZnO active region and other p-type semiconductors, such as GaN, Si, AlGaN, Cu_2O, $SrCu_2O_2$, SiC, ZnTe and NiO [1,4–15]. Moreover, EL is observed in some of these heterojunction devices. However, the EL spectrum consists of UV and visible emission bands in many cases, and the intensity of the visible emission is usually stronger than that of UV emission, [13,16], which is related to not only lattice mismatch and band alignment at the interface of the heterojunction but also electronic structure and electrical properties of the p-type semiconductors. Hence, it is important to select suitable p-type semiconductor for realizing single and strong UV EL in the heterojunction. It is known that NiO is a natural p-type semiconductor with direct wide band gap of 3.7 eV and can be fabricated by simple technique, the former usually make the heterojunction have high emission efficiency, and the latter leads to low cost. Recently, a single UV EL was observed in ZnO/NiO based heterojunction with a complex structure of n^+-GaN/n-ZnO/i-$Mg_{1-x}Zn_xO$/p-NiO [15], indicating that the NiO is good p-type semiconductor suitable to preparation of UV ZnO-based heterojunction. However, such complex structure including GaN is dependent on complex fabrication technique, leading to difficulty in fabrication and expensive cost. Thus, it is necessary to design and produce ZnO/NiO based heterostructure with a simple structure for research and application of UV ZnO/NiO based heterojunction LED. In the present work, fabrication and EL of an n-ZnO/p-NiO heterojunction with simple structure are investigated.

2. Experimental details

P-type NiO (p-NiO) thin film with a hole concentration of 2×10^{16} cm^{-3} and a Hall mobility of 6 $cm^2/V\,s$ was deposited on *c*-plane sapphire substrate by rf magnetron sputtering a Ni target with the mixture of Ar and O_2 gases. For depositing n-type ZnO (n-ZnO) layer with high crystal quality on the NiO film, an n-ZnO layer was deposited on the as-deposited p-type NiO film by plasma-assisted molecular beam epitaxy (P-MBE). The electron concentration and mobility of the n-type ZnO layer are determined to be 4×10^{17} cm^{-3} and 8 $cm^2/V\,s$, respectively. The Ni/Au alloy and indium metal were used as electrodes of the p-type NiO

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http://dx.doi.org/10.1016/j.jlumin.2012.08.039

and n-type ZnO layers, respectively. The Ni and Au layers were deposited on the NiO layer in sequence at room temperature by thermal evaporation in a vacuum system using evaporation sources for Ni and Au. The metal In was sintered on the ZnO layer at 150 °C for 5 min in a vacuum system with a pressure of $\sim 10^{-3}$ Pa. Electrical properties of the ZnO and NiO thin films as well as current-voltage (*I*–*V*) curves of the heterojunction were measured by Lakeshore 7707 Hall measurement system. The structures of the thin films were characterized by x-ray diffraction (XRD) with CuKα1 radiation (λ=0.15406 nm). In the standard θ–2θ scanning process, the x-ray tube voltage and current are 50 kV and 150 mA, respectively. The scan rate and scan step size are set to be 1 degree/min and 0.02 degree, respectively. The cross-sectional morphology was observed by using field-emission scanning electronic microscope (FESEM). Photoluminescence (PL) measurement was performed using a He–Cd laser with 325 nm line as excitation source. The EL spectra from the heterojunction were recorded by a Hitachi F4500 spectrometer and a continuous-current power source was used to excite the heterojunction diode. All the measurements were carried out at room temperature (RT).

3. Results and discussion

We first examined the structures of the fabricated ZnO/NiO heterojunction using XRD and SEM. Fig. 1(a) shows the XRD pattern of the n-ZnO/p-NiO heterojunction. The peak near diffraction angles of 41.7° is due to diffraction of (0 0 6) lattice plane of Al_2O_3 (0 0 6) and is used to calibrate the diffraction peak position of the ZnO and NiO thin films. The peaks at 34.47° and 36.94° is ascribed to the diffraction of the (0 0 2) plane of the hexagonal ZnO (PDF#800075) and the (1 1 1) plane of the cubic NiO (PDF#780643), respectively, indicating that the ZnO and NiO thin films have (0 0 2) and (1 1 1) preferential orientation, respectively. It is calculated that the lattice mismatch is about 4% between the (0 0 2) plane of the ZnO and the (1 1 1) plane of the NiO, implying that the heterojunction composed of the ZnO film with (0 0 2) preferential orientation and the NiO film with (1 1 1) preferential orientation should have good quality in p–n junction region, which benefits diffusion of electron (or hole) from n-ZnO (or p-NiO) layer to p-NiO (or n-ZnO) layer and improvement of recombination efficiency of electron and hole, and hence obtaining UV EL with strong emission intensity. Fig. 1(b) shows the field emission scanning electron microscopy (FESEM) image of the cross-section of the n-ZnO/p-NiO heterojunction, respectively. The thickness of the NiO and ZnO thin films is estimated to be 1.1 and 0.8 μm, respectively.

The RT *I*–*V* curve of the n-ZnO/p-NiO heterojunction is shown in Fig. 2. A diode-like rectification behavior was observed. The inset of Fig. 2 shows *I*–*V* characteristics of the Au/Ni alloy contacted on p-NiO layer and metal In contacted on n-ZnO layer, respectively, indicating that good ohmic contacts are formed for both electrodes. These results confirm that the rectification behavior arises from the n-ZnO/p-NiO heterojunction but not from Schottky contacts. The forward turn-on voltage is measured to be ~3.6 V, which is slightly larger than the band gap of the ZnO due to high contact resistance of the electrodes on the ZnO layer [17]. The high turn-on voltage was also reported in some literatures previously reported. [16,18,19].

Importantly, we observed the UV EL in the ZnO/NiO heterojunction. Fig. 3(a) shows the EL spectra of the n-ZnO/p-NiO heterojunction under injection currents of 0.5, 2.0, 3.0 and 3.5 mA, indicating that each EL spectrum consists of an UV emission band and a very weak visible emission band with wide wavelength range of 450–650 nm. As the injection current increases from 0.5 to 3.5 mA, the intensity ratio of the UV to visible emission band increases remarkably, but the wavelength of the UV peak decreases from 404 to 387 nm. It is noted that the photon energy of UV emission band (3.07–3.20 eV) is closed to band gap of ZnO (3.37 eV), but much smaller than band gap of NiO (3.7 eV), implying that the UV EL may come only from radiative recombination in the ZnO layer. To clarify the origin of the EL emission, on the one hand, RT PL spectrum is measured for the n-ZnO layer and the NiO layer. No PL is observed in the NiO layer, implying that no radiative transition can be realized in the NiO layer. However, a dominant UV emission centered at 376 nm is observed in the ZnO layer, as shown in Fig. 3(b). The PL band

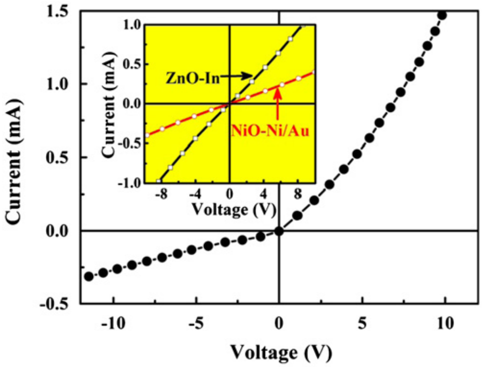

Fig. 2. RT *I*–*V* characteristics of n-ZnO/p-NiO heterojunction. The inset shows Ohmic contact characteristics of Au/Ni contacts to p-NiO and In contacts to n-ZnO.

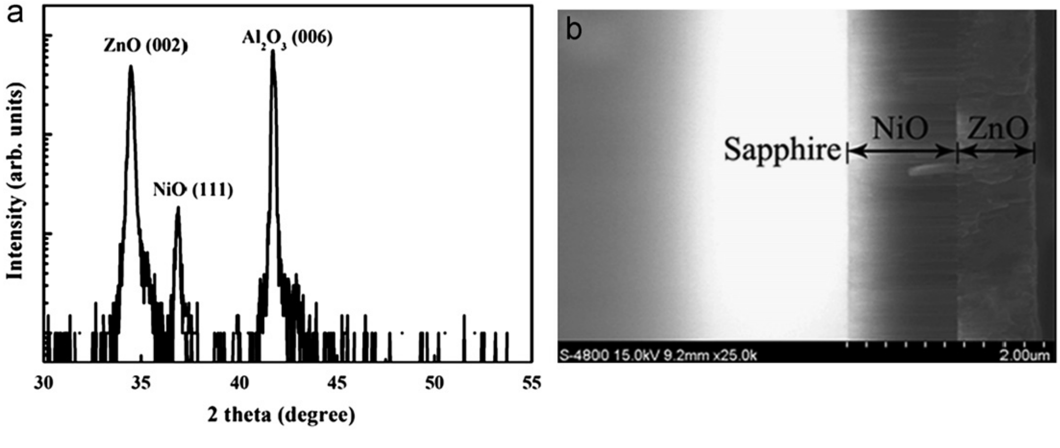

Fig. 1. (a) XRD pattern of n-ZnO/p-NiO heterojunction fabricated on c-sapphire substrate. (b) Cross-sectional SEM image of n-ZnO/p-NiO heterojunction LED.

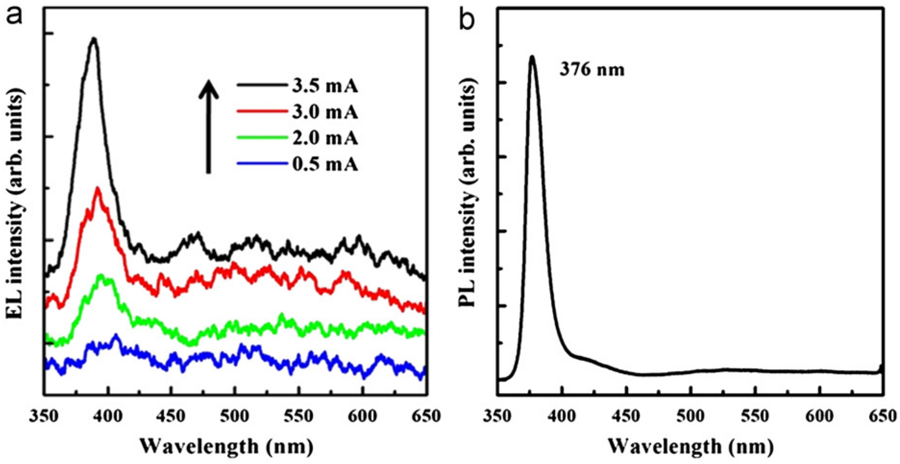

Fig. 3. (a) RT EL spectra from n-ZnO/p-NiO heterojunction under the forward currents of 0.5, 2.0, 3.0 and 3.5 mA. (b) RT PL spectrum from the n-ZnO layer.

located at 376 nm (3.297 eV) is usually attributed to the radiative recombination of the free exciton in ZnO. A comparison of the EL spectra with the PL spectrum of ZnO indicates that the emission in the EL spectra should originate from radiative recombination in the n-ZnO layer. Furthermore, the UV emission peak at 387–404 nm in the EL spectra is ascribed to near-band-edge (NBE) emission of the ZnO. The redshift in the UV emission wavelength of the EL relative to the PL is common phenomenon observed in many experiments and is due to the lower efficiency of the electrical pumping in comparison with efficiency of the optical excitation [20,21].

On the other hand, the conduction-band (CB) and valence-band (VB) offsets between the ZnO and NiO were measured by x-ray photoelectron spectroscopy (XPS) [22], which is 2.93 and 2.6 eV, respectively. Since the CB offset is larger than the VB offset and the mobility of the hole in the p-NiO is similar to that of the electron in the n-ZnO, the potential barrier is higher for electrons than for holes, and the holes can diffuse from the p-NiO layer into the ZnO layer easily as applying a forward bias, but the electrons diffuse from the n-ZnO layer into the p-NiO layer difficultly and accumulate on the ZnO side near the p–n junction, which leads to that radiative recombination occurs in the ZnO layer and has high efficiency and strong UV emission.

The blueshift of the UV peak with increasing injection current is also observed in GaN/ZnO heterojunction [23]. It is well known that electron structure of semiconductor is related to its crystal quality. As the crystal quality is poor, there are many defect states in the band gap. Some of defect states near band edges will form so-called tail states. Obviously, the photon energy of emission from radiative recombination of the electron and hole in the tail state is smaller than the band gap. The crystal quality is poor in the region near p–n junction due to lattice mismatch and hence there exists the tail state. As a forward bias is low (or injection current is small), the electrons and holes usually recombine near p–n junction region, emitting light with energy smaller than band gap. However, with increasing the forward bias, the more charge carriers (electron and hole) can penetrate into region far from the junction region, where the film has better crystal quality and the tail sate is little. The recombination comes from electron in CB and hole in VB, emitting photon with energy near band gap. Therefore, the emission wavelength shows blueshift and emission intensity increases with increasing injection current.

It is known from Fig. 1(a) that the n-ZnO/p-NiO heterojunction fabricated in the present work consists of ZnO film with (0 0 2) preferential orientation and NiO film with (1 1 1) preferential orientation, which make the heterojunction have small lattice mismatch. From a point of view of crystal structure, this heterojunction should have good p–n junction, benefiting to diffusion of holes from NiO layer to ZnO layer and hence improving recombination efficiency. On the other hand, since the CB offset of the ZnO and NiO is higher than VB offset, the hole in NiO can penetrate the junction easily into ZnO layer as a forward bias is applied, while electron in the ZnO layer diffuses difficultly into the NiO layer and accumulates on the ZnO side near the p–n junction, which can improve recombination probability of the electron and hole and hence UV EL emission intensity. Therefore, the n-ZnO/p-NiO heterojunction is suitable to preparation of UV LED. However, in the present work, the p-NiO only is of carrier concentration of 10^{16} cm^{-3}, which is too low to realize strong UV EL. Therefore, it is important to increase carrier concentration of p-NiO for obtaining strong UV n-ZnO/p-NiO heterojunction LED in the further work.

4. Conclusions

In summary, the n-ZnO/p-NiO heterojunction was fabricated on *c*-plane sapphire substrate. The heterojunction has small lattice mismatch (about 4%) at the interface and hence is favorable to improving recombination probability of electron and hole. The heterojunction showed a diode-like rectification characteristic with a turn-on voltage of $\sim$3.6 V, and realizes distinct UV EL emission with wavelength of 387 nm at the injection current of 3.5 mA. It is demonstrated that the EL comes from near band-edge radiative recombination of electron and hole in the ZnO layer, which proves that n-ZnO/p-NiO heterojunction can be used to realize UV LEDs.

Acknowledgments

This work was supported by the Key Project of National Natural Science Foundation of China under Grant no. 50532050, the "973" Program under Grant no. 2006CB604906, the National Natural Science Foundation of China under Grant nos. 11274135, 61205038, 10874178, 60776011, and 60806002, Natural Science Foundation of Jilin province under Grant no. 201115013, Swedish Research Council and National Found for Fostering Talents of Basic Science under Grant no. J1103202.

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