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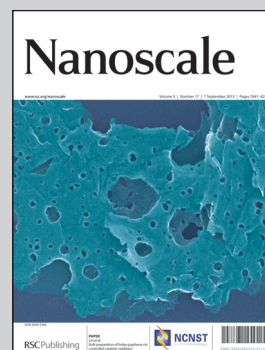
Intense emission from ZnO nanocolumn Schottky diodes

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Zinc oxide (ZnO) nanocolumns have been prepared by a metal–organic chemical vapor deposition technique, and structural and optical characterization reveal that the nanocolumns have high crystalline and luminescent qualities. Au/MgO/ZnO/In structured Schottky diodes have been fabricated from the nanocolumns. An intense emission can be detected from the diodes under the drive of bias voltage, and the output power can reach 3.7 μW. The intense emission comes from both the high crystalline and luminescent qualities of the ZnO nanocolumns, and the ideal Schottky contact formed in the Au/MgO/ZnO/In structures.

Introduction

Zinc oxide (ZnO) has recently been highlighted for its wide bandgap and large exciton binding energy. The wide bandgap makes it a suitable candidate for applications in ultraviolet (UV) optoelectronics, and the large exciton binding energy promises that efficient emissions and low-threshold lasers may be realized from ZnO-based materials.[1–7] Although much attention has been paid to the UV light-emitting devices and lasers of ZnO, the performance of such devices is still far below expectation. One of the reasons for the low performance may be due to the poor crystalline quality of the ZnO materials. Self-assembled nanostructures usually have a high crystalline quality, which is favourable for high performance optoelectronic devices.[7] ZnO has rich nanostructures, and various examples such as nanowires, nanobelts, nanorods, nanosheets and nanorings have been prepared, and a variety of devices including sensors, photodetectors,[6] lasers[8] and electricity generators[9] have been constructed from these nanostructures. Nevertheless, although there have been some reports on ZnO nanostructure based light-emitting devices,[10–17] the performance of such devices is

still very low, which means that the relatively high crystalline quality unique to ZnO nanostructures, has not been fulfilled.

In this communication, vertically aligned ZnO nanocolumns have been prepared, and the nanocolumns show a well-faceted side and top surface. Structural and optical studies reveal the relatively high crystalline and luminescent qualities of the nanocolumns. Au/MgO/ZnO/In structured Schottky diodes have been constructed from the nanocolumns. Intense emission has been observed from the diodes under the drive of bias voltage, and the output power can reach several microwatts, which is one of the best values ever reported for ZnO-based light-emitting devices.[18]

Experimental

The ZnO nanocolumns were grown using a metal–organic chemical vapor deposition (MOCVD) technique employing *a*-plane sapphire as a substrate. The precursors used were diethylzinc and oxygen, and high-purity (9 N) nitrogen was used as a carrier to lead the precursors into the growth chamber. Prior to the growth, the sapphire substrates were pretreated at 650 °C under 10^{-5} Pa for 30 minutes to remove any absorbed contaminants. The ZnO samples were prepared at 650 °C and the pressure in the growth chamber was kept at 3×10^{3} Pa. After 2 hours of growth, the samples were taken out from the MOCVD chamber, and loaded into a magnetron sputtering chamber for the deposition of a MgO layer. Finally, a gold contact and an indium contact were deposited onto the MgO and ZnO layer by vacuum evaporation, respectively, to form Au/MgO/ZnO/In structured Schottky diodes. The morphology of the ZnO nanocolumns was characterized in a Hitachi S4800 field-emission scanning electron microscope (SEM). A Bruker D8 X-ray diffractometer was used to evaluate the crystalline properties of the ZnO nanocolumns. Electroluminescence (EL) measurements of the Schottky diodes were carried out in a Hitachi F4500 spectrometer with a continuous-current power source. The output power of the Schottky diodes was measured in a Nova 2 display Rohs power-meter. Photoluminescence (PL)

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measurements of the ZnO nanocolumns were carried out employing the 325 nm line of a He–Cd laser as the excitation source.

Results and discussion

Fig. 1 shows the morphology and structural properties of the ZnO nanocolumns. One can see from the plan-view SEM image of the structure shown in Fig. 1a that spot-like nanostructures are formed. Fig. 1b shows the magnified SEM image of the nanostructures tilted by 30°; one can see from the image that the nanostructure shows a well-faceted hexagonal shape with very smooth side and top surfaces, the height of the nanocolumns is around 120 nm, and they are grown vertically onto the smooth ZnO surface. Fig. 1c shows the X-ray diffraction (XRD) powder diffraction of the ZnO nanocolumns; two peaks at 34.47° and 37.84° can be observed from the pattern. The former comes from the wurtzite ZnO (0002) facet, while the latter from the sapphire substrate. The inset of Fig. 1c shows the X-ray rocking curve of the nanocolumns, from which a Gaussian lineshape can be observed, with a full width at half maximum (FWHM) of around 0.5°. The phi-scan pattern of the nanocolumn sample is shown in Fig. 1d, and six well-defined peaks with the equivalent spacing of 60° are visible in the pattern, which indicates the six-fold symmetry of the nanocolumns. The SEM and the XRD results reveal the high crystalline quality of the ZnO nanocolumns, which lays a solid ground for light-emitting devices fabricated from these nanocolumns.

The optical properties of the nanocolumns are assessed by PL studies, as shown in Fig. 2. The room temperature PL spectrum shows a peak at around 3.28 eV, which corresponds to the near-band-edge emission of ZnO. The 12 K PL spectrum of the nanocolumns displays five peaks at around 3.374 eV, 3.363 eV, 3.318 eV, 3.246 eV and 3.175 eV. The peak at
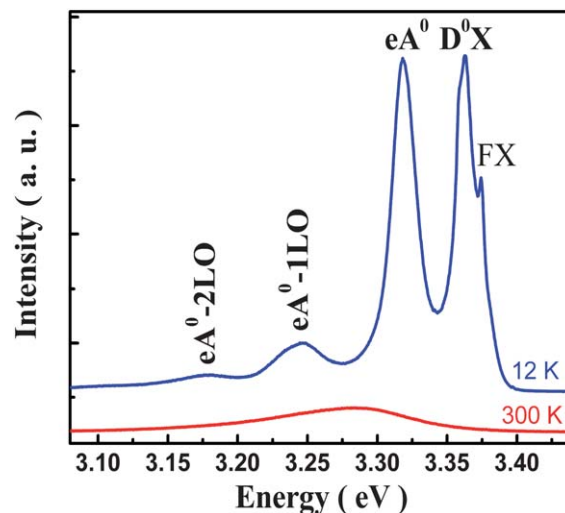

Fig. 2 PL spectra of the ZnO nanocolumn sample at 12 K and 300 K, respectively.

3.374 eV can be attributed to the free exciton (FX) emission of ZnO.[19,20] According to their positions, the peaks at 3.363 eV and 3.318 eV can be attributed to the emission from the neutral donor-bound exciton (D^0X), and the transition between the free electrons in the conduction band and the acceptor levels (eA^0) of ZnO, respectively.[19,20] As for the peaks at 3.246 eV and 3.175 eV, since their energy difference with eA^0 is almost identical to the phonon energy of ZnO (72 meV), they can be attributed to the first and second phonon replicas of eA^0.[19,20] The appearance of a free exciton emission at 12 K reveals the relatively high luminescent quality of the ZnO nanocolumns, which is favourable for realizing intense emission from the nanocolumns.

To fabricate light-emitting devices from the ZnO nanocolumns, Au/MgO/ZnO/In structured Schottky diodes have been constructed. The inset of Fig. 3a shows the schematic illustration of the Au/MgO/ZnO/In structure; note that the thickness of the MgO layer is about 150 nm. The schematic bandgap diagram of the structure is shown in Fig. 3b. Considering that the electron affinities of ZnO and MgO are 4.35 eV and 0.80 eV, respectively,[21,22] and the work function of Au is 5.10 eV,[23] the conduction band offset (CBO) at the ZnO–MgO interface can be determined to be 3.55 eV, and the offset at the Au–MgO interface to be 4.30 eV. To realize efficient emission from a Schottky diode, an ideal Schottky contact is essential. To assess the carrier transportation in the Schottky diode, the current–voltage (I–V) curve of the diode has been measured, as indicated by the scattered open circles in Fig. 3a. One can see from the curve that the current increases slowly with the bias voltage initially, and then abruptly when the forward bias voltage is larger than 5 V. It is accepted that the current in a Schottky diode is mainly caused by majority carriers, that is electrons in our case. There are two major channels for electron transportation in a Schottky diode; one is tunnelling current, which is caused by carriers that can tunnel through the Schottky barrier, and the other is the thermionic current, which is caused by thermally activated
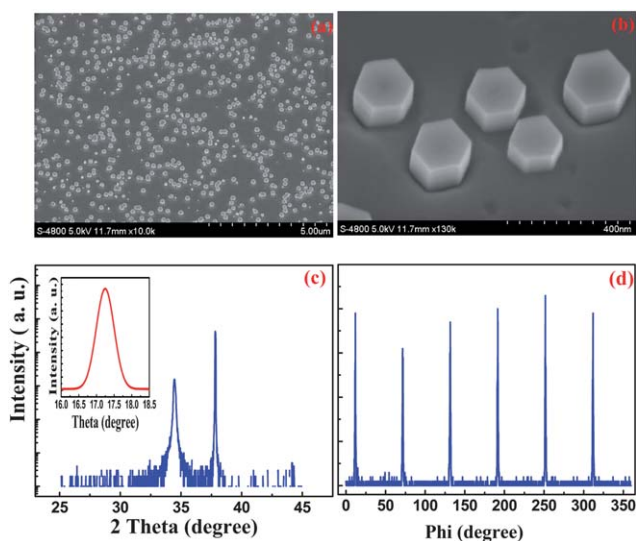

Fig. 1 The plan-view SEM image (a) and the 30° tilted image (b) of the ZnO nanocolumns; the XRD powder pattern (c), X-ray phi-scan spectrum of the nanocolumns (d), and the inset of (c) shows the X-ray rocking curve of the nanocolumns.
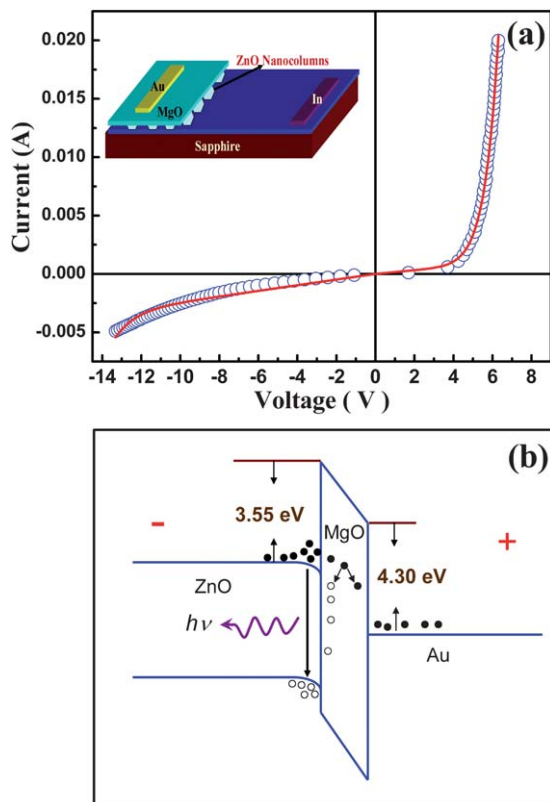
Fig. 3 (a) *I–V* characteristics of the Au/MgO/ZnO/In Schottky structure, in which the scattered open circles are experimental data, while the solid line is a fitting to the experimental data using eqn (1). (b) Schematic bandgap diagram of the structure under forward bias.

electrons that can pass across the Schottky barrier. Then, the dependence of the current on the bias applied in a Schottky diode can be expressed by the following formula:[24]

$$I = k_1 V \exp\left(\frac{q}{k_B T} a\sqrt{V} - \psi_B\right) + k_2 V^2 \exp(-k_3/V) \qquad (1)$$

In which q, k_B, T are the elementary charge, Boltzmann constant, and absolute temperature, respectively, and k_1, k_2 and k_3 are variable parameters. $a = (q/4\varepsilon_i d)^{1/2}$, where ε_i is the dielectric constant and d is the thickness of MgO; ψ_B is the potential barrier of the Schottky contact. In eqn (1), the first part on the right side of the formula is the contribution of thermionic current, while the second part is the contribution of the tunnelling current.

One can see from Fig. 3a that a good fit for the experimental data can be found using eqn (1). At the positive bias region, the best fitting yields $k_1 = 8.7 \times 10^{-3}$, $k_2 = 4.1 \times 10^{-2}$, $k_3 = 2.8 \times 10^{-1}$, and the Schottky barrier of $\psi_B = 3.51$ eV, which is very close to the CBO at the ZnO–MgO interface (3.55 eV). At the negative bias region, the best fitting yields $k_1 = 1.0 \times 10^2$, $k_2 = 2.8 \times 10^{-4}$, $k_3 = 28.2$, and the Schottky barrier of $\psi_B = 4.33$ eV, which is close to the valence band offset (VBO) at the Au–MgO interface (4.30 eV), as indicated in Fig. 3b. It is known that under a positive bias voltage, the electrons in the ZnO have to pass through the MgO barrier, and the height of the Schottky

barrier roughly equals the CBO at the ZnO–MgO interface, that is 3.55 eV. While at negative bias region, the electrons in the Au have to pass through the MgO barrier, and the barrier height approximately equals the VBO at the Au–MgO interface, that is 4.30 eV. The good accordance between the barrier heights derived from the fitting and the values obtained from the bandgap diagram at both positive and negative bias regions reveals that an ideal Schottky contact has been formed in the Au/MgO/ZnO/In structure.

The carrier transportation process in the Schottky diode can be understood as follows: under the effect of the thermal fluctuation energy, some electrons may gain enough energy that they are able to pass across the MgO barrier layer, which constitutes the thermionic emission current in eqn (1). Meanwhile, some other electrons can enter the MgO layer under the drive of the bias voltage, which constitutes the tunnelling current in eqn (1). Considering that almost all the bias will be applied onto the MgO layer due to its dielectric nature, the electric field in the MgO layer can be over 10^5 V cm^{-1} when the bias voltage is larger than 5 V. Then, the electrons that enter into the MgO layer will be greatly accelerated by such a large electric field. The electrons will gain a lot of energy, and they will impact the lattice of the MgO layer to release their energy. Electrons in the valence band of the MgO will then be excited to the conduction band, thus free holes are left. In this way, additional electrons and holes are generated through this impact ionization process.[25] Under the drive of the bias voltage, the generated holes will be injected into the ZnO layer, and they will recombine radiatively with the electrons in this layer, thus emission may be observed from this Schottky diode.

To test the above idea, a forward bias is applied onto the Schottky diode, and a typical emission photograph of the Schottky diode is shown in Fig. 4b. One can see from the picture that an intense blue emission can be observed from the active layer of the diode. The emission spectra of the diode are shown in Fig. 4a. An obvious emission at around 382 nm has been detected from the Schottky diode, which is the typical near-band-edge emission of ZnO as its position is very close to the room temperature PL of the ZnO nanocolumns shown in Fig. 2 (about 378 nm). The dependence of the output power of the Schottky diode on the injection current is shown in the inset of Fig. 4a. The output power increases monotonically with the injection current in the investigated current range, and it can reach 3.7 μW when the injection current is 15.0 mA. We note that there are only two reports demonstrating the output power of ZnO-based LEDs to date.[18,26] Nakahara *et al.* reported ZnO LEDs with an output power of around 70 μW when the injection current is 30 mA,[18] and Kato *et al.* demonstrated a ZnO LED with the output power of around 30 μW when the injection current reaches 20 mA.[26] One can see from the above facts that the output power reported here is one of the best values ever reported for ZnO-based light-emitting diodes. It is anticipated that both the high crystalline and luminescent qualities of the ZnO nanocolumns and the ideal Schottky contact formed in the Au/MgO/ZnO/In structure contributes to the intense emission of the Schottky diode.
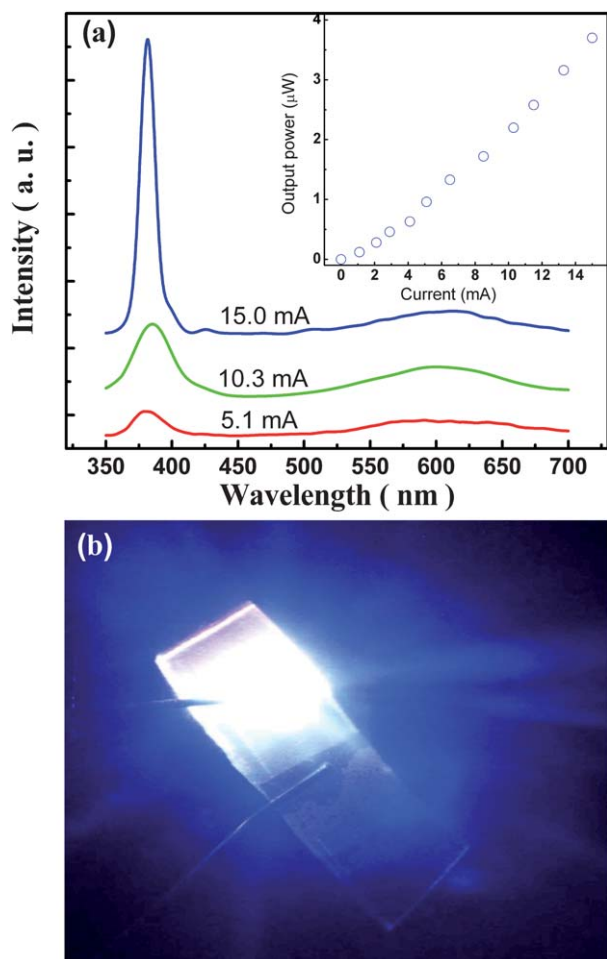
Fig. 4 (a) EL spectra of the Au/MgO/ZnO/In Schottky diode under different injection currents, and the inset shows the dependence of the output power of the diode on the injection current. (b) Emission photograph of the diode at an injection current of 15 mA.

Conclusion

In summary, ZnO nanocolumns with high crystalline and luminescent qualities have been prepared, and Au/MgO/ZnO/In structured Schottky diodes have been constructed from the nanocolumns. An intense emission at around 382 nm has been observed for the diode, whose output power can reach 3.7 μW when the injection current is 15 mA, which is one of the best values ever reported for ZnO-based light-emitting diodes. The above results promise that high-performance light-emitting devices may be prospected from ZnO.

Acknowledgements

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