Hydrogen effects on the electroluminescence of n-ZnO nanorod/p-GaN film heterojunction light-emitting diodes

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Through a facile low-temperature solution process, vertically n-type ZnO nanorod arrays were grown on a GaN film to form a n-ZnO nanorod/p-GaN film heterojunction. A study of the electroluminescence (EL) characteristics of the heterojunction in air and in air with 2000 ppm hydrogen revealed the sensitivity of such a device to the surrounding atmosphere. The additional hydrogen shallow donors increased the effective electron concentration in ZnO nanorods and the EL recombination zone changed from the ZnO nanorods to the GaN film, which can be identified visually from the color change.

1. Introduction

Zinc oxide (ZnO), especially ZnO nanostructures, are a valuable raw material in the field of the short wavelength optoelectronics.[1–6] This is not only because ZnO has some superior properties, with a wide band-gap (3.37 eV) and a large exciton-binding energy (60 meV), but also due to the fact that ZnO nanostructures can be fabricated by some simple growth methods *via* chemical and physical vapor-phase approaches.[7,8] The inherent large specific surface area makes ZnO nanostructures highly susceptible to the surrounding conditions. The sensitivity to the processing conditions and the environment can also affect the properties of ZnO nanostructure based optoelectronic devices. The effects of moisture, water, hydrogen and phosphoric acid solution on p-i-n ZnO light emission diode (LED) characteristics have been investigated and significant degradation of electrical and optical properties were observed in all cases.[9]

Hydrogen is a shallow donor in ZnO forming a variety of impurity-defect complexes to enhance the n type conductivity of ZnO.[10–13] Hydrogen can be easily incorporated into ZnO during epilayer growth and device fabrication. It was also reported that an applied external electrical current or field could induce hydrogen migration in ZnO.[14,15] In this work, we have investigated the effect of hydrogen on the electroluminescence (EL) properties of n-ZnO nanorod/p-GaN film heterojunction LEDs. With the absorption of hydrogen, the EL recombination zone of the LEDs shifted from the ZnO nanorods to the GaN film, which induced the EL emission color to change from cyan to violet. This result implied the device could be used as a fluorescent hydrogen sensor.

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2. Experimental

A commercial p-GaN/Al_2O_3 wafer was used as the substrate with a hole concentration of 1.4×10^{16} cm^{-3} and a mobility of 6 cm^2 V^{-1} s^{-1} as determined by a four-point Hall measurement. A low-temperature solution growth method was performed to fabricate a vertical ZnO nanorod array on top of p-GaN. Zinc acetate [$Zn(Ac)_2 \cdot 2H_2O$] (0.01 M) and hexamethylenetetramine (0.01 M) were dissolved in water (Milli Q, 18.2 MΩ cm). Then the above 30 ml mixed solution were transferred to a Teflon-lined stainless autoclave of 50 ml capacity. The autoclave was heated in an electric oven at 90 °C for 20 h. After reaction, the sample was washed with deionized water and dried in air at 60 °C for several hours. Photoluminescence (PL) was performed by using a He–Cd laser line of 325 nm as the excitation source and a micro-Raman spectrometer in a backscattering geometry configuration to detect the emission spectra.

To construct the LEDs, Ni (50 nm)/Au (200 nm) was vacuum-evaporated on the p-GaN film serving as an electrode. For the electrode of ZnO nanowires, in order to keep a free interspace between the nanowires and the insulation between the GaN film and the electrode, an In slice with diameter of 1 mm was pressed on the top of nanowires.

3. Results and discussion

Because of the low lattice mismatch (about 1.9%) between ZnO and GaN wurtzite structures, vertical ZnO nanorod arrays were found to be epitaxially grown on the p-GaN thin film by the hydrothermal method with nominal diameters of 100–500 nm and lengths of 3 μm (Fig. 1(a)). The density of nanowires is around 10 μm^{-2}. The device structure of the heterojunction LED is shown in the schematic diagram of Fig. 1(b). The device shows typical diode rectifying behavior which demonstrates p–n junction formation (as shown in Fig. 1(c)). The turn-on voltage is 3.6 V.

Fig. 2 shows the room-temperature PL spectra of the p-GaN thin film and the n-ZnO nanorod array, respectively. The emission from the p-GaN thin film is red-shifted from the

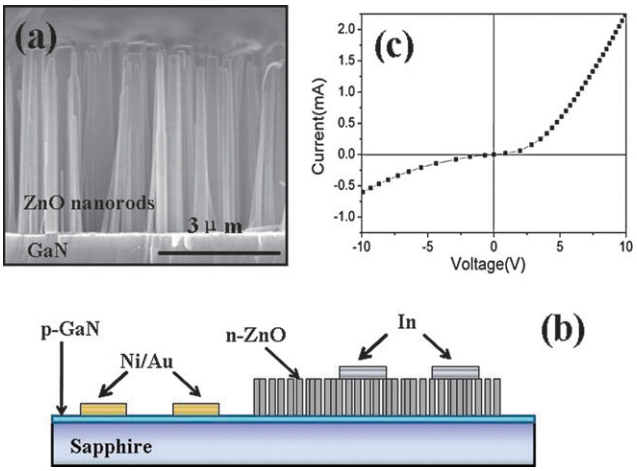

Fig. 1 (a) FESEM images of ZnO nanorod arrays grown epitaxially from a GaN thin film; (b) Schematic diagram of a n-ZnO nanorod/p-GaN heterojunction LED; (c) *I–V* curve of the heterojunction LED.

bandgap to around 430 nm, which is commonly observed in Mg-doped GaN due to dominant band to acceptor transitions.[16] The PL spectrum of the ZnO nanorods is composed of two main parts. The UV emission band (375 nm) is attributed to the near-band-edge excitonic emission. The visible emission band at around 505 nm is usually believed to originate from singly ionized oxygen vacancies.[17]

Hydrogen post-treatment on the LED was carried out under atmospheric pressure with a hydrogen flow rate of 2000 ppm at room temperature for 30 min. The EL spectra before and after hydrogen absorption are shown in Fig. 3 under the same injection current of 10 mA. It is clearly observed that the EL spectra changed significantly after the hydrogen treatment. For the as-grown devices, there are two emission bands (blue and green) with almost the same intensity in the spectra. However, after the treatment a new EL emission band located in the ultraviolet region could be observed to dominate the spectrum. The emission intensity of the green band also decreased rapidly, and the EL emission color turned from cyan to violet.

The EL emission band variation implies difference of the emission centers. To better understand the origin of EL

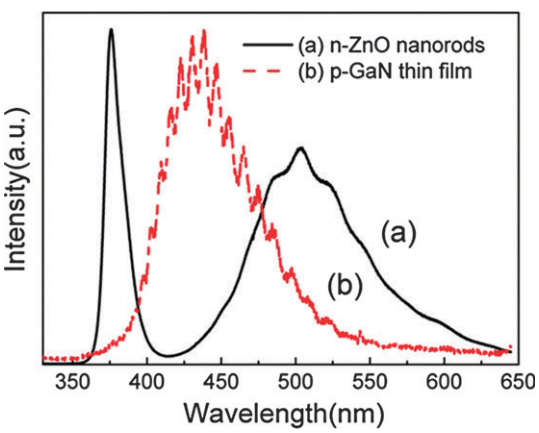

Fig. 2 Room-temperature PL spectra of (a) n-ZnO nanorods and (b) p-GaN thin film.

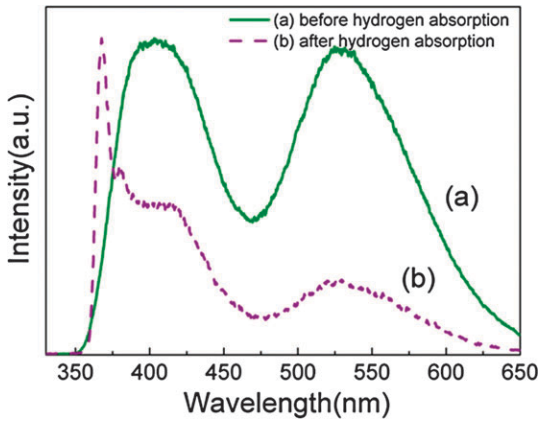

Fig. 3 Room-temperature EL spectra for a n-ZnO nanorod/p-GaN heterojunction LED before (a) and after (b) hydrogen absorption at 10 mA.

emission peaks and the effect of hydrogen absorption on such a device, EL spectra with different currents (between 3 and 16 mA) were measured at room temperature. For the LED without hydrogen absorption, EL emission could be observed visually with an injected current above 3 mA as shown in Fig. 4. The EL emission band is considered a combination of the various transitions observed in the PL spectra, which could be fitted by three peaks (shown in the inset of the Fig. 4), centered at I_1 = 385 nm, I_2 = 415 nm and I_3 = 530 nm. The peak positions I_1 and I_3 are attributed to the near-band-edge and deep level emission from ZnO nanorods, respectively, while I_2 is considered to originate from the acceptor to band transitions in the p-GaN thin film. Compared with the PL results, the red-shift of the EL peaks is well known, according to the self-absorption of the semiconductor. At low currents, only I_2 and I_3 could be detected. The intensities of the I_1 and I_2 peaks, as well as I_1/I_2 peak ratio, are increased with increasing the applied current, which indicates the recombination zone moves from the interface to the ZnO nanorods.

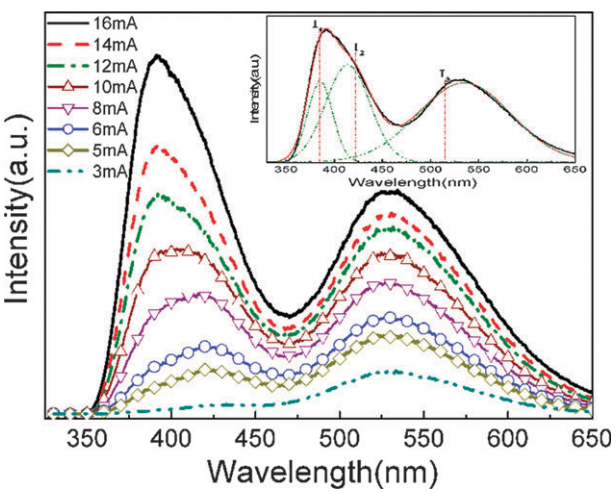

Fig. 4 Room-temperature EL spectra for an as-grown n-ZnO nanorod/p-GaN heterojunction LED for different currents. The inset shows an EL emission peak (at 16 mA) fitted with three Gaussian peaks at I_1 = 385 nm, I_2 = 415 nm and I_3 = 530 nm.

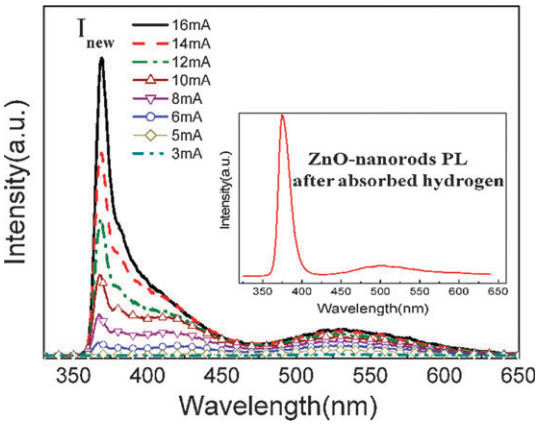

Fig. 5 Room-temperature EL spectra for a hydrogen-treated n-ZnO nanorod/p-GaN heterojunction LED for different currents. The inset shows the PL spectrum of ZnO nanorods after hydrogen absorption.

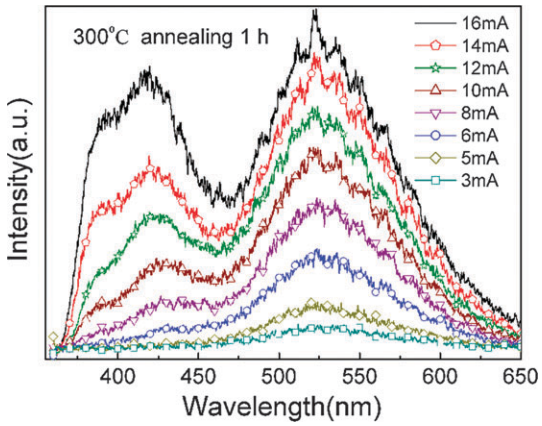

Fig. 6 Room-temperature EL spectra for the hydrogen-treated n-ZnO nanorod/p-GaN heterojunction LED after annealing at 300 °C for 1 h.

When hydrogen was introduced, a new EL emission peak located at 365 nm appears and dominates the EL spectra with increasing the injected current (Fig. 5), which is considered being originated completely from the GaN bandgap. At the low energy side of this peak, I_1, I_2, I_3 emissions could also be observed, but the intensities are quite weak at high applied current. The understanding of the behavior of the absorbed hydrogen in ZnO nanorods is the key to analyze the origin of the new emission peak.

The absorbed hydrogen, which is found to exhibit a very rapid diffusion in ZnO,[18] could be located in various ZnO lattice sites with a variety of different forms including H^+, H^-, neutral atomic hydrogen H^0 and H_2. Based on first-principles density functional calculations, only H^+ is the stable charge state for all Fermi-level positions, hence hydrogen exclusively acts as a donor in ZnO.[14] This behavior is very different from the roles of hydrogen in other semiconductors, in which hydrogen often acts as a compensating center and always counteracts the prevailing conductivity.[12,13] It forms a strong bond with oxygen, providing a powerful driving force for its incorporation in the ZnO. Walle's group studied complex formation between hydrogen and deep level defects (oxygen vacancies).[12] A complex consisting of an oxygen vacancy and a hydrogen atom also behaves as a shallow donor. The calculated binding energy, expressed with respect to H^+ and V_O^0, is 0.8 eV. Oxygen vacancies are low-energy defects[19] and may form in large concentrations. In n-type ZnO, these vacancies would be neutral and electrically inactive, but the addition of hydrogen turns them into shallow donors. Because the hydrogen atom is located close to the center of the vacancy, we can regard hydrogen impurity as a substitutional located on an oxygen lattice site. This hypothesis is in agreement with the PL result. The inset of Fig. 5 shows the PL spectrum of ZnO nanorods. After the hydrogen absorption, the visible emission band around 505 nm, which is related to the deep level defects, was almost quenched. In addition, our experiment confirmed that the hydrogen treatment process did not affect the electrical properties of the p-GaN thin film.[20] By sharp contract, hydrogen is not an effective dopant in GaN and there the main effect is the formation of the interfacial dipole layer without any significant bulk effects.[20] The much different recovery behavior of the ZnO, compared to its GaN counterpart, suggests that at least some part of the change in the diode upon hydrogen gas exposure. The EL emission occurring predominantly in the GaN thin film is also supported by an energy band diagram built using the Anderson model,[21] which shows a similar energy barrier for holes compared to that for electrons at the heterojunction interface between the ZnO nanorods and the p-GaN film (valence band offset ΔE_V = 0.13 eV; conduction band offset ΔE_C = 0.15 eV). The additional hydrogen shallow donors increase the effective electron concentration in ZnO nanorods, which induces the electron current from ZnO nanorods to the GaN thin film dominantly in this heterojunction diode. Therefore, we could conclude that the origin of the 365 nm EL emission is from the recombination of extra electrons in GaN that were injected across the junction.

Although hydrogen atoms can easily diffuse into ZnO, they also can be driven out by thermal annealing at 300–900 °C, as verified by experiments using secondary ion mass spectroscopy.[22–25] Fig. 6 shows the EL spectra of the above hydrogen absorbed sample, measured after annealing at 300 °C for 1 h. Although the annealing process degraded the LED in terms of the EL light intensity, the original peak position–current relation before hydrogen absorption was reproduced, which strongly verifies the effect of the hydrogen.

4. Conclusions

In conclusion, we have demonstrated the effect of hydrogen on the electroluminescence property of n-ZnO nanorod/p-GaN film heterojunction LEDs. This device showed high selectivity of hydrogen by changing the EL emission color from cyan to violet, which could be observed directly by the naked eye. The mechanism is considered as due to the additional hydrogen shallow donors increasing the effective electron concentration in ZnO nanorods, which induced the EL recombination zone change from the ZnO nanorods to the p-GaN thin film.

Acknowledgements

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