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2014

Iwan, S., Zhao, J., Tan, S., Bambang, S., Hikam, M., Fan, H., et al. (2015). Ion-dependent electroluminescence from trivalent rare-earth doped n-ZnO/p-Si heterostructured light-emitting diodes. Materials Science in Semiconductor Processing, 30, 263-266.

https://hdl.handle.net/10356/81333

https://doi.org/10.1016/j.mssp.2014.09.048

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Ion-Dependent Electroluminescence from Trivalent Rare-Earth Doped n-ZnO/p-Si Heterosctructured Light-Emitting Diodes (LEDs)

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Abstrak

We have demonstrated rare earths (REs) doped ZnO-based heterojunction light-emitting diodes (LEDs) on *p*-Si substrates by ultrasonic spray pyrolisis (USP). Room-temperature electroluminescence were clearly observed from reverse-biased *n*-ZnO:REs/*p*-Si diodes, which red and blue color emissions were realized from Eu and Tm ions, respectively. The narrow line-width emissions are attributed to the transitions within the shielded 4f levels of the trivalent REs ions that resulting from direct electron impact excitation during reverse bias.

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1 Introduction

Rare earths (REs), also known as lanthanides, are commonly used as dopants for optoelectronics applications, such as fiber amplifiers, lasers, phosphors, and luminophors [1,2]. By selecting the right RE ions, intense and narrow line-width emission could be expected from the transition between the shielded 4f energy level. The long luminescence lifetime, narrow emission line-width, and wide range of emission wavelength of RE-doped materials are of greatest importance for the development of optoelectronic devices especially light-emitting diodes (LEDs). The green emission were realized by doping Er [3] and Tb ions [4]. Meanwhile, the red and blue emission could be realized by doping Eu, Pr, Sm and Tm, Ce ions respectively [5]. In order to demonstrate REs luminescence, variety of hosts material has been used such as Si [6], GaN [7], SnO_2[8], ZnO [3,9], CaF_2 lanthanide OBr-based powder phosphors and Al_2O_3 [10,11]. Others reported that co-dopant (such as F^-, Li^+ ions, etc) and use of wide band-gap semiconductors are could be used to enhance luminescence by electrically excite RE ions [9,12]. Due to wide direct band gap (3.4 eV) and large exciton binding energy (60 meV) at room temperature [13], ZnO is a potential candidate as host material for RE doping. The large energy gap of ZnO would offer large spectral area for rare earth emissions and give polychromatic display [14].

The REs doped ZnO have been fabricated by several methods such as ion implantation [15, 16], pulsed laser deposition (PLD) [17], ultrasonic spray pyrolisis (USP) [3]. Among them, USP possesses the advantages of low cost, simple, low equipment cost, high deposition rate, and low growth temperature [3].

In this work, the n-ZnO:REs/*p*-Si heterostructured LEDs were fabricated and investigated. The ZnO:REs films were deposited on *p*-Si by ultrasonic spray pyrolysis (USP) without any co-dopants. We found that electroluminescence (EL) was originated from the transition between 4f levels of REs ions due to direct electron impact excitation of REs ZnO films [18, 19]. Moreover, the effects of REs doping, current transport and photoluminescence (PL) properties were discussed.

2 Experimental details

Undoped ZnO and ZnO:REs thin films were deposited on *p*-type Si substrates by USP [3,20]. Zinc acetate dehydrate [$Zn(CH_3COO)_2.2H_2O$] and thulium (III) acetate hydrate [$Tm(C_2H_3O_2)_3.xH_2O$], europium (III) acetate hydrate [$Eu(C_2H_3O_2)_3.xH_2O$] were chosen as host and dopant precursors, respectively. The zinc acetate (0.02 mol/ml) were mixed with the thulium (III) acetate hydrate (8 wt%) and europium (III) acetate hydrate (8 wt%), then diluted in de-ionized (DI) water. The aerosol of the precursor for each solution were then generated by a commercial ultrasonic nebulizer (frequency of 1.65 MHz), and injected onto a Si substrates heated at 450°C for 10 minutes. The *n*-ZnO:REs/*p*-Si heterostructure LEDs were fabricated using Au as Ohmic contacts. Au electrodes were deposited on *n*-ZnO:REs and the backside of *p*-Si wafers by direct-current magnetron sputtering. The Au electrodes were patterned into circular pads with a diameter of 1 mm using a shadow mask. By Hall measurement, the carrier concentration in the REs doped ZnO layer (~10^{16} cm^{-3}) is much lower than that of the *p*-Si substrate (~10^{19} cm^{-3}).

3 Results and discussion

The crystal structure of undoped and REs doped ZnO thin films were characterized by X-ray diffraction (XRD) measurement with CuK α radiation (Siemens D5005 X-ray Diffractometer). Fig. 1 shows the x-ray diffraction (XRD) spectra of undoped ZnO, Tm doped ZnO, and Eu Doped ZnO. The XRD spectrum of undoped ZnO thin film posses polycrsytalline wurtzite structure with the planes (100), (002), (101), (102), and (103). As shown in the figure, XRD spectrum of Eu doped ZnO shows the intesities decrease significantly with the existences of crystal planes at (002) and (101). Furthermore, no diffraction peaks from other phases such as Eu_2O_3. It is predicted to be due to Eu^{3+} ions substitute at Zn^{2+} sites. Meanwhile, by introducing Tm^{3+} ions into ZnO thin films, the XRD pattern has two kind of phases such as ZnO and Tm_2O_3 with various crsytal planes.

The photoluminescence (PL) spectra at room temperature were detected by using Renishaw micro-PL system with 325 nm He-Cd laser as the excitation source. Fig. 2 shows the room-temperature PL spectra of the undoped ZnO and ZnO:REs which consists of excitonic-related UV emission (~375 nm) and defect-related green band (GB) emission (~530 nm). There is no emission related to the intra-atomic transition of REs were observed in the PL spectrum for all the ZnO:REs films. It is suggesting no energy transfer occurs between the semiconductor and the REs. Nevertheless, it can be predicted that the intra-atomic level transition saturates at a much lower excitation power compared to the band to band transition of ZnO [3]. As results, the REs-related emission is much lower than the ZnO emission at high power laser excitation [3]. In order to evaluate the concentration of intrinsic defects, the intensity ratio of UV and GB is expressed by UV/GB [21]. As can be seen from fig. 1, the UV/GB intensity ratio of the undoped ZnO,

ZnO:Tm, and ZnO:Eu are 0.59, 0.93, and 4, respectively. It is clear that the UV/GB intensity ratio of the undoped ZnO and ZnO:REs increases with the REs incorporation. The increasing of UV/GB intensity ratio predicts that the f orbit of Eu atoms interact with s and p orbital of ZnO stronger than Tm [3].

Fig. 3 shows the typical current-voltage (I-V) characteristics of ZnO:REs/Si heterostructure diodes at room temperature. The I-V curve of a *n*-ZnO:REs/*p*-Si heterostructure LEDs shows diode-like rectification characteristics with low breakdown voltage at reversed bias. During the operation in reverse bias mode, electroluminescence was observed from the ZnO:REs/Si heterostructure diodes. Contrary to PL spectra, the emissions corresponding to transitions within the 4f levels of the trivalent RE ions were clearly observed at room temperature under reverse bias (as can be seen in Fig. 3). During the reverse bias mode of operation, electron-hole pairs are created by band to band tunneling in the depletion layer due to the high electric field [3]. Then, accelerated electrons inject into conduction band which has sufficient kinetic energy to excite or ionize REs ions or ZnO itself. Moreover, hot electron accelerated in conduction band can excite the RE ions by direct exchange of energy between the hot carriers and the 4f electrons or even to ionize the semiconductor in order to induce electron-hole pair recombination at internal defect levels of ZnO [22]. The direct exchange of energy between the hot carries and the 4f electrons of REs ions responsible for the luminescence of the excitation in the core level [5, 19-21]. Fig. 5 shows the relevance energy level of REs (Eu^{3+}, Tm^{3+}) ions which containing transitions from the excited state to the ground state level [2].

Fig. 4 shows the room temperature EL of *n*-ZnO:REs (Eu and Tm)/*p*-Si heterostructured LEDs, together with the emission photos. The room temperature of *n*-ZnO:Eu/*p*-Si heterostrucured has a broad band EL ranging from 500 to 850 nm during the reverse bias operation with a current injection of 0.2 A. The light output could be observed by naked eyes at room temperature with an orange-greenish color when reverse biased was applied. Therefore, the EL spectra of *n*-ZnO:Eu/*p*-Si heterostructure demonstrated high energy electrons are able to excite by impact both the emissive center of Eu^{3+} and ZnO itself. Moreover, the EL spectra which originating from the intra atomic emissions of 4f-4f transition of Eu^{3+} peaking at 540, 570, 620, and 670 nm were observed yet unclear. The peaks at 540, 570, 620, and 670 nm correspond to the transitions from $^5D_1$ to $^7F_1$, $^5D_0$ to $^7F_1$, $^5D_0$ to $^7F_2$, and $^5D_0$ to $^7F_3$, respectively [9]. The one that most intense peak due to excitation of Eu^{3+} ions in the core level observed at 670 nm. On the other hand, broad band emission which attributed to internal defect level of ZnO was clearly observed [23, 24].

Furthermore, the room temperature EL of *n*-ZnO:Tm/*p*-Si heterostructured LED was observed also at reverse biased applied with high current injection 50 mA. The light output from *n*-ZnO:Tm/*p*-Si heterostructure LED shows blue color which can be seen by naked eyes when reverse biased at room temperature. Nevertheless, the EL spectrum of *n*-ZnO:Tm/*p*-Si shows two peaks in the blue region at 477 nm and near infra red (NIR) at 800 nm. The peak at 480 nm corresponds to the transition from the $^1G_4$ level to the $^3H_6$ ground state of Tm. The NIR line at 800 nm can be associated with either the transition between the $^3H_4$ and $^3H_6$ levels or between the $^1G_4$ and $^3H_5$ levels [9, 25, 26]. Moreover, the most intense peak of EL spectra of *n*-ZnO:REs/*p*-Si heterostructure indicating the

number of hot electron to excite the RE ions in the certain excited state level higher than others level [26]. Meanwhile, the *n*-ZnO:Tm/*p*-Si shows no emission originating from ZnO itself. The absence of an emission could be attributed either to high EL yield of Eu^{3+} and Tm^{3+} compared to ZnO, to a high concentration of Eu^{3+} and Tm^{3+} in the depletion layer, or the injection current was not high enough to excite ZnO itself [27].

4 Conclusion

In summary, we have fabricated the rare earths (REs) doped ZnO based heterojunction light emitting diodes (*n*-ZnO:REs/*p*-Si) without any co-dopants. The EL spectra from *n*-ZnO:REs (Eu^{3+},Tm^{3+})/*p*-Si shows multicolor emission under reverse biased operation. It is demonstrated that the emission corresponding to transitions within the 4f levels of the trivalent RE ions and ZnO itself due to hot electron accelerated in the conduction band by direct impact excitations process.

Acknowledgment

Financial support from Science and Engineering Research Council of Agency for Science, Technology and Research of Singapore (Nos. 0921010057 and 0921510088) are gratefully acknowledged.

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Figure captions

Fig. 1. The XRD spectra of undoped ZnO, Tm doped ZnO, and Eu doped ZnO thin films

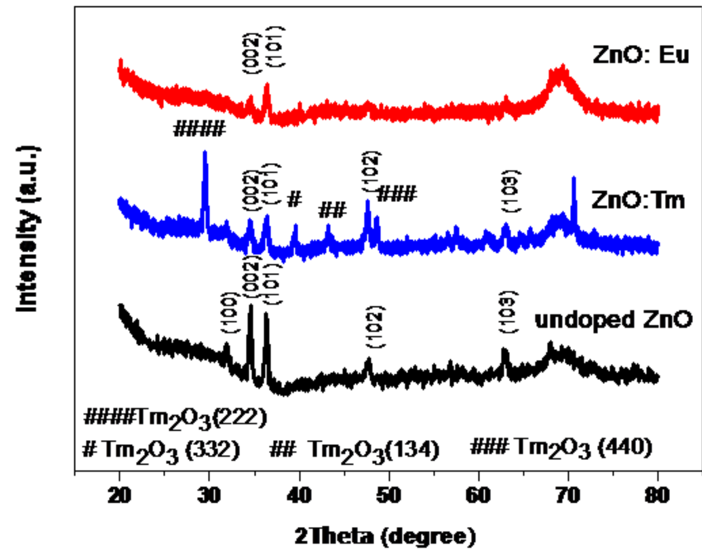
Fig. 2. Room temperature PL spectra of undoped ZnO and ZnO:RE thin films

Fig. 3. The I-V characteristic of n-ZnO:REs/p-Si heterostructure LEDs

Fig. 4. Room temperature photos and EL spectra of n-ZnO:REs/p-Si heterostructure LEDs under reverse biased operation

Fig. 5. The observed transition of energy level of REs ions (Eu^{3+} and Tm^{3+}) from excite state level to ground state level under reverse biased operation [2]

Figure 1 by S. Iwan et. al



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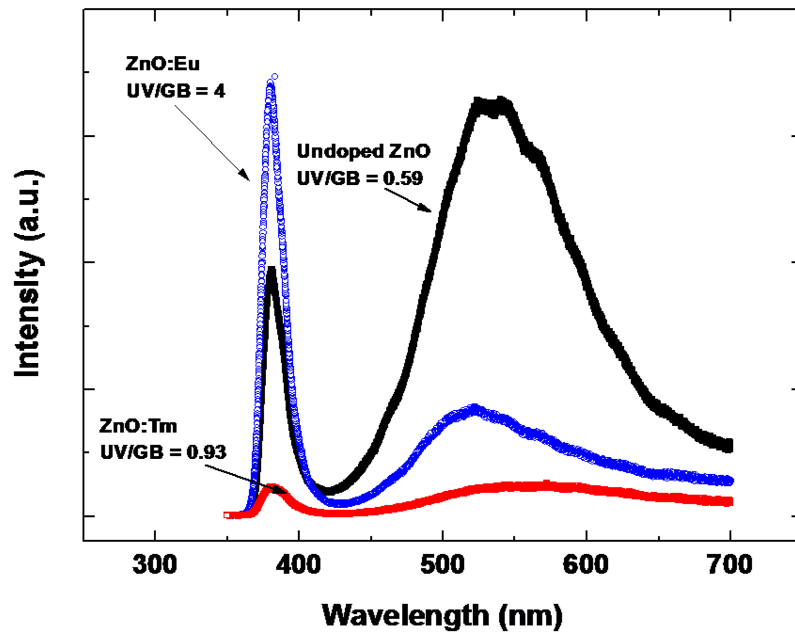

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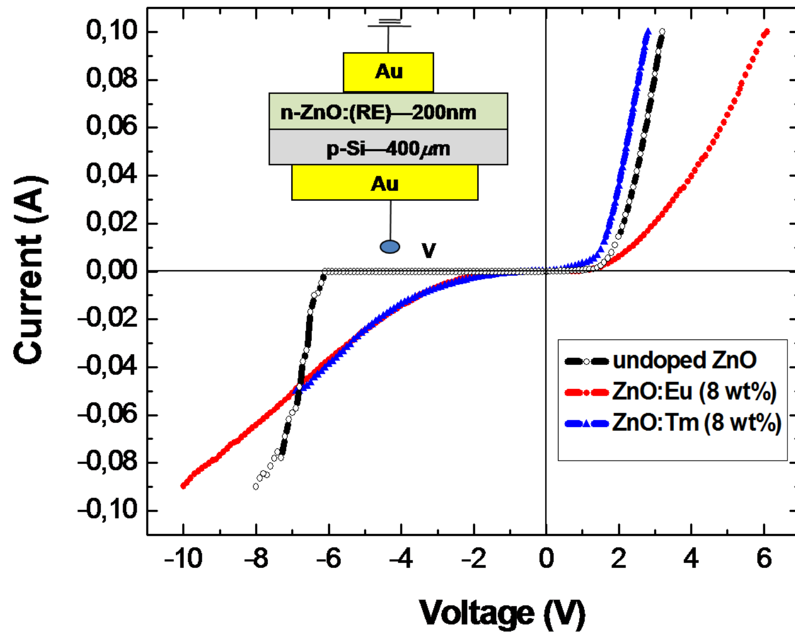

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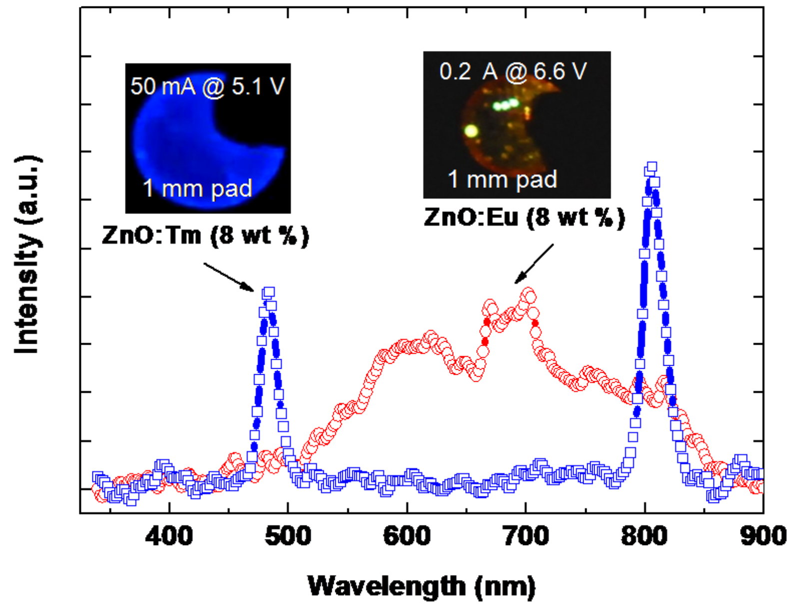

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