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Abstract. Ultraviolet (UV) light-emitting diode using salmon deoxyribonucleic acid (sDNA)-cetyltrimethylammonium complex as an electron blocking layer and zinc oxide (ZnO) nanorods as emissive material was fabricated. UV emission, which was blue shifted up to 335 nm with respect to the band edge emission of 390 nm, was observed. This blue shift was caused due to accumulation of electrons in the conduction band of ZnO because of a high potential barrier existing at the sDNA/ZnO interface. © *2011 Society of Photo-Optical Instrumentation Engineers (SPIE)*. [DOI: 10.1117/1.3618630]

Keywords: ultraviolet light-emitting diodes; zinc oxide; electroluminescence; Burstein-Moss effect.

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1 Introduction

Though gallium nitride (GaN)-based ultraviolet (UV) light-emitting diodes (LEDs) are now commercially available, they are expensive and their fabrication pollutes the environment because GaN is grown at temperatures above 500°C.[1] Zinc oxide (ZnO) is another promising semiconductor, which can be used for fabricating ultraviolet LEDs. Its bandgap is 3.37 eV at room temperature and the excitonic binding energy is high, ~60 meV.[2] Free excitonic recombination, which is more efficient than the free electron-hole recombination can, therefore, easily produce UV electroluminescent emission. However, the main disadvantage of using ZnO for the fabrication of UV LED is that even by using nanostructures, the band edge UV emission remains unchanged at 3.37 eV and deeper UV emission is not possible. This is because the exciton Bohr radius of ZnO is low, ~1.4 nm (Ref. 3), and, therefore, quantum confinement effect, which is normally available in all nanostructures to increase the bandgap, is not possible in the case of ZnO. Even by using the most sophisticated techniques such as metal organic chemical vapor deposition, radio frequency sputtering, molecular beam epitaxy, etc., it has not been possible to fabricate ZnO nanorods of diameter <10 nm that is much higher than its excitonic Bohr's radius. Some workers, such as Chen et al.,[4] have observed a blue shift in the UV emission of ZnO nanorods, which was attributed by them to the surface states of the nanorods. No blue shift in the band edge exciton emission was observed by these authors. A blue shift of 90 meV in UV emission was observed by Yang et al.[5] when the diameter of the ZnO nanowires used by

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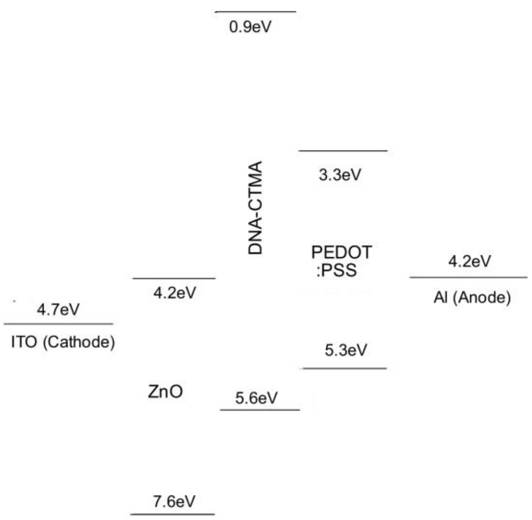

Fig. 1 Energy level diagram of heterostructure LED.

them was changed from 700 to 50 nm. Since the diameter of these nanowires is too high as compared to Bohr radius, quantum confinement effect cannot be considered to be the cause of the observed blue shift. These authors attributed the observed blue shift to the Burstein-Moss band-filling effect[6,7] under the excitation provided by the high-energy electron beam obtained from cathodoluminescence spectra.

In the present work, using a salmon deoxyribonucleic acid cetyltrimethylammonium complex (sDNA-CTMA) layer in between the ZnO nanorods and the aluminum (Al) anode in the LED structure: Indium Tin Oxide (ITO)/ZnO nanorods/sDNA-CTMA/poly[3,4ethylenedioxythiophene]poly[4-styrenesulfonate] (PEDOT:PSS)/Al, we blocked the electrons injected from the ITO cathode in the conduction band of the ZnO nanorods. The energy level diagram of the LED structure is shown in Fig. 1. The various energy levels were taken from literature.[8,9] It can be seen from Fig. 1 that the injected electrons cannot overcome the high potential barrier existing at the ZnO/sDNA-CTMA interface due to extremely low lowest unoccupied molecular orbital (LUMO) level (∼0.9 eV) of sDNA. The level of electron states in ZnO filled by the accumulated electrons depends on the bias current between the cathode and anode. The higher the bias current, the higher the injection of electrons will be, and hence, the higher the energy level of the electron states occupied by these accumulated electrons will be. Therefore, the blue shift observed by the band edge UV emission can easily be controlled by varying the bias current. Using the Burstein-Moss effect in this manner, we succeed in obtaining UV emission in the energy range ∼335 to 352 nm from our LED structure.

The novel feature of this LED is that we have succeeded in obtaining a range (335 to 352 nm) of UV emission rather than obtaining emission at a single UV wavelength.[10] Further, we have used the DNA-CTMA layer as an electron-blocking layer instead of a low molecular weight material, which has to be vacuum evaporated and cannot be spin coated.[10] The DNA-CTMA layer used in the work is totally nonemissive and does not interfere with the emission of ZnO.

1.1 Burstein-Moss Effect

It was reported by Burstein[6] and Moss[7] that while the optical absorption in intrinsic indium antimonide (InSb) is at 7.0 microns, the absorption limit of an impurity doped *n* type InSb can reach up to 3.2 microns when the doped carrier concentration exceeds 1×10^{18}/c.c. This anomalous absorption effect was explained by Burstein-Moss by assuming that the free electrons

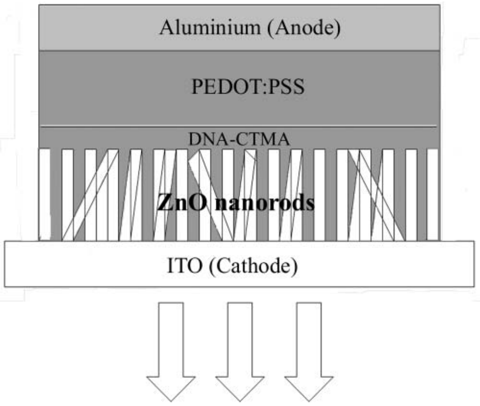

Fig. 2 Schematic diagram of heterostructure LED.

donated by impurity atoms fill the conduction band up to a certain energy level $E_{m.}$ The optical transitions then occur between the energy level (m_e/m_h) E_m below the top of the valence band and E_m resulting in an increase in optical transition energy, which is higher than the intrinsic band gap of the material. For semiconductors having spherical band structure, the Burstein-Moss shifts ΔE_m to a higher energy under conditions of high free carrier concentration and is given by[5]

$$\Delta E_m = \left(1+\frac{m_e^*}{m_h^*}\right)\left[(3/\pi)^{2/3}\left(h^2 n_c^{2/3}/8m_e^*\right) - 4KT\right] \tag{1}$$

where n_c is the concentration of electrons in the conduction band, m^*_e and m^*_h are the effective masses of electron and hole, respectively, T is the absolute temperature, k is Boltzmann constant, and h is the Planck constant.

The emission from ZnO can, thus, be shifted to lower wavelengths in the UV region if the injected electrons from the cathode can be made to accumulate in the conduction band of ZnO due to a very high potential barrier existing at the ZnO-sDNA interface. The concentration of accumulated electrons will obviously increase with increase in the bias current and, therefore, the effective bandgap of the material will be a function of the bias current leading to a blue shift in the band edge luminescence. With the increased accumulation of electrons with increase in bias current, the conduction band states of ZnO start filling up. This is known as Burstein-Moss effect resulting in the blue shift of the EL emission with respect to the band edge emission.

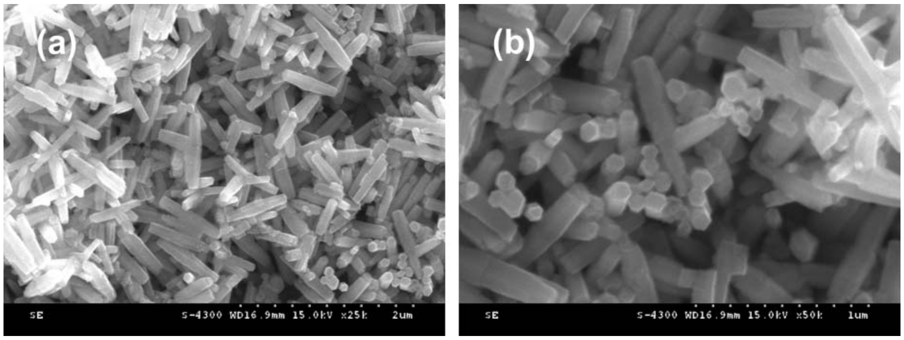

Fig. 3 (a) FESEM images of the as grown nanorods and (b) top view of (a).

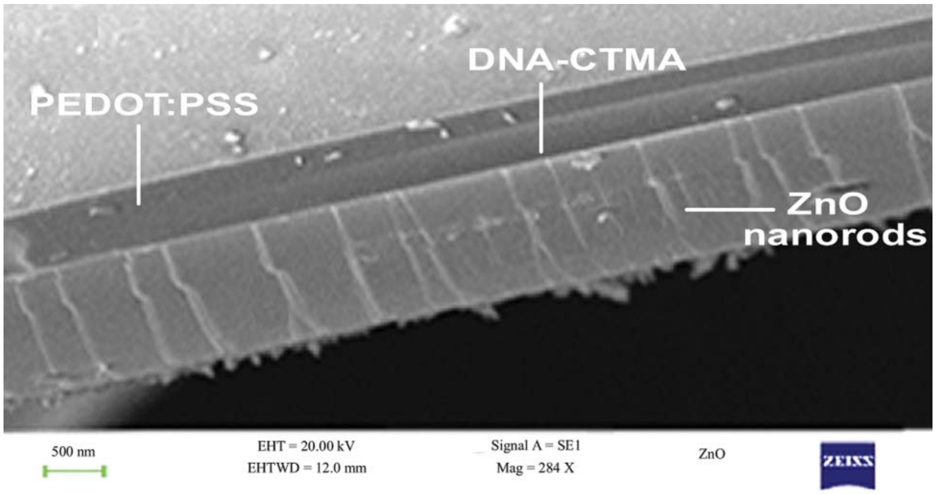

Fig. 4 Cross sectional SEM images of the LED structure (ZnO nanorods with DNA and PEDOT: PSS layer).

2 Experimental Details

LEDs with structure: ITO/ZnO nanorods/s-DNA-CTMA /PEDOT: PSS/Al were fabricated using the following procedure. PEDOT: PSS (2.8 wt% in water), salmon DNA, and CTMA were purchased from Sigma Aldrich. A patterned ITO coated glass substrate (sheet resistance ~15 Ω/square) was taken and cleaned using acetone by ultrasonication. ZnO nanorods were grown over the ITO substrate using an electrochemical deposition technique.[9] For this, an aqueous solution for electrolysis was prepared by dissolving 9 mM zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot 6H_2O]$ and a precursor, equimolar hexamethylenetetramine ($C_6H_{12}N_4$) (procured from Merck) in 200 ml deionized water (conductivity ~0.16 μS). ITO coated glass and a platinum plate of the same dimensions were used as cathode and anode, respectively. The anode and cathode were immersed in this aqueous solution and the set up was placed on a hot plate at a uniform temperature of 90° C. A constant current density of 0.25 mA/cm^2 was applied between anode and cathode using a Keithley source meter (SMU 2400). After about 15 min of electro deposition, ZnO nanorods were obtained on ITO substrates. The sDNA-CTMA complex was prepared using the technique suggested by Wang et al.[11] This complex was dissolved in butanol and spin coated over the ZnO nanorods (emissive). The spin rate of DNA-CTMA solution was kept at 4000 rpm for 10 s. The thickness of the DNA layer is ~20 nm. The thickness of the film was measured with the help of a Talystep and the film thickness was found to be uniform within ±10%. The average molecular distance in DNA chains is about ~20 nm. If the thickness of the film is higher than this, the DNA chains will not lie in the plane of the film but will have a

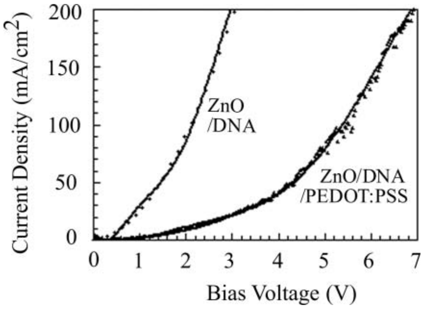

Fig. 5 Current density-voltage characteristics of the heterostructure LED.

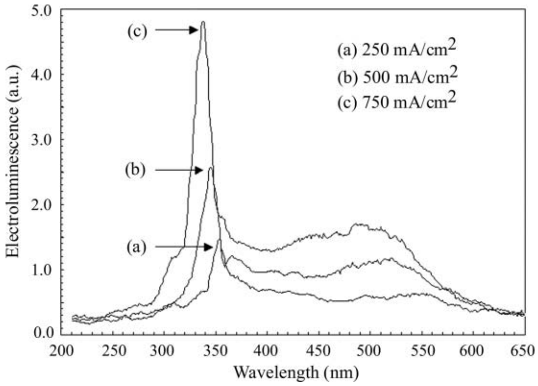

Fig. 6 Electroluminescence spectra of the heterostructure LED.

random orientation.[8] The EBL, in that case, will not be effective and Burstein-Moss effect will not occur and there will be no EL emission. A layer of PEDOT: PSS with thickness ∼80 nm was spin coated over the DNA layer at 3500 rpm for 30 s. PEDOT: PSS serves as a hole-transporting layer and also prevents short circuit between Al anode and the DNA layer. The composite sample was annealed for 2 h at 50°C in a vacuum oven. The Al anode of thickness ∼100 nm was then vacuum coated on the PEDOT: PSS layer. The schematic diagram of heterostructure LED is shown in Fig. 2.

The area of the device was ∼2 mm × 2 mm. The structural morphology of the nanorods was observed using a field emission scanning electron microscope (Hitachi S4300 SE/N). The current density-bias voltage (J–V) characteristics of the LED were studied using a Keithley sourcemeter. The EL emission was measured using a spectrofluorophotometer (Shimadzu RF-5301 PC) with the device being driven using a Keithley sourcemeter.

3 Results and Discussion

The SEM images of ZnO nanorods grown using the electrochemical deposition technique are shown in Fig. 3(a). The ZnO nanorods exhibit standard hexagonal cross sections [Fig. 3(b)] and are uniformly distributed. However, it is found that the orientation of the nanorods is not completely vertical. The average length and diameter is observed to be 730 and 145 nm, respectively.

The cross sectional SEM image of the ZnO nanorods coated with DNA and PEDOT: PSS is also shown in Fig. 4. It is found that the DNA besides forming EBL also fills the space between the nanorods. The SEM image for Fig. 4 is observed using Zeiss EVO MA15. The current density-voltage characteristics of the heterostructure LEDs with and without a PEDOT: PSS layer is shown in Fig. 5. It is found that the threshold voltage of the device increases when the PEDOT: PSS layer is added in the structure. The turn on voltage of the device with and without a PEDOT: PSS layer is found to be ∼1.5 and 5 V, respectively.

The electroluminescence spectra of the device for different current densities are shown in Fig. 6.

The EL spectra exhibits two distinct regions: 1. A strong UV emission, which is blue shifted from the usual near band edge emission of 390 nm (Ref. 12) and 2. A weak visible broadband emission (400 to 600 nm), which is attributed to defect-related transitions.[13,14] It is found that as the bias current increases, the UV EL peak shifts toward lower wavelengths up to 335 nm at a current density of 750 mA/cm^2. It can be seen that as the positive bias increases, more and more electrons get accumulated at the ZnO-sDNA interface resulting in shifting of the Fermi level into the conduction band of ZnO. As the current density is increased beyond 750 mA/cm^2, the device is found to deteriorate. The blue shift in EL emission from ZnO is attributed to the Burstein-Moss effect under high carrier concentration.

4 Conclusion

A ZnO nanorods/sDNA-CTMA ultraviolet LED has been fabricated emitting in the range 352 to 335 nm, which is blue shifted from the usual band edge emission at 390 nm. The purpose of using a DNA-CTMA layer is to block electrons at the ZnO/sDNA interface due to its extremely low LUMO level of ~0.9 eV. The high potential barrier encountered by electrons at the interface leads to accumulation of electrons resulting in filling of conduction band of ZnO. Hence, the EL emission is shifted to lower wavelengths.

Acknowledgments

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