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Materials Today: Proceedings 15 (2019) 394–399

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ICMAM-2018

Synthesis and characterization of PEDOT:PSS/ZnO nanowires heterojunction on ITO coated plastic substrate for light-emitting diodes

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Abstract

In this paper we report on heterojunction between the hole transporting polymerpoly (3, 4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) and zinc oxide (ZnO) nanowires grown on an indium tin oxide (ITO) coated polyethylene terephthalate (PET) plastic substrate. For the fabrication of heterojunction simple and low cost solution methods are used. The deposited films and heterojunction are characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), photoluminescence (PL) and electroluminescence (EL) measurements. Electroluminescent and photoluminescent spectra of the hybrid heterojunction show one ultraviolet (UV) near-band-edge emission peak. The current-voltage characteristic confirms the junction formation between the polymer and ZnO nanowires and shows good rectifying p-n junction diode type behaviour of the fabricated structure. The charge transfer process in heterojunctionis explained by band energy diagram.

Keywords: ZnO nanowires, PEDOT: PSS, p-n- heterojunction, flexible electroluminescent diode.

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1.0 Introduction

ZnO nanowires are chemically stable and environmentally friendly inorganic materials, which behave as n-type semiconductor. ZnO, is an II-IV wide band gap semiconductor with excellent physical and structural properties, making it promising material for optoelectronic devices [1, 2]. ZnO nanowires can be grown on any substrate without the need of lattice matching [3]. Despite these advantages, it is very *difficult* to obtain stable *p-type ZnO*, therefore realization of *p*–n homojunction of *ZnO* is extremely *challenging* [4]. This factor motivates the researchers to grow n-type ZnO nanowires on different p-type substrate i.e. GaN [5], NiO [6], Si [7], polymers [8], etc., for light-emitting diodes (LEDs), solar cell and other device applications.

P-type conducting polymers have many advantages, including easy fabrication, flexibility, and tuneable carrier densities. Synthesis of polymer with n-type conductivity is difficult and it has poor stability in air and poor solubility [8-9].In most of the organic materials the mobility of holes is much higher than that of electrons, while the opposite is true in inorganic semiconductors [10].ZnO have higher electron mobility[1].Hence ZnO/organic heterostructure provides an approach for the balance of the hole and electron current densities with improve the performance of electroluminescence devices [11]. The ZnO/polymer heterojunction can be made by different methods, Pulse laser deposition [12], gas phase deposition [13], chemical vapour deposition [14], thermal deposition [14] and hydrothermal method [15-18]. Solution method has several advantages like low temperature process, inexpensive manufacturing, large area uniformity [19]. Since it is a low temperature method, thin films can be also prepared on plastic type flexible substrate.

There are reports about LEDs made of PEDOT: PSS/ZnO nanowiresheterojunctions [12-14].
Some groups prepared PEDOT: PSS/ZnO nanowiresheterojunctions LEDs using hydrothermal method [20-22].However, most of them shows emission in UV as well as visible region.

In this paper, heterojunction between PEDOT: PSS and ZnO nanowires on flexible plastic substrate are realized via low cost and low temperature hydrothermal method, without the need of sophisticated equipments. The PEDOT: PSS/ZnO nanowires based heterojunction reported in this paper show emission in UV region only. The structural and optical behavior of the heterojunction is studied. In these studies, the UV emission of ZnO is very dominant and the defect emissions are very weak. The prepared structure might help improve the performance of ZnO nanowire UV LEDs in the future

2. Experimental procedure

The ITO coated PET plastic substrate was cleaned by immersion in ethanol and methanol and then it was washed by deionised water. Finally, the substrate was dried in oven. The PEDOT: PSS solution (conductive grade, 1.3 % (by wt) dispersion in H_2O) purchased from Sigma Aldrich was filtered and then spin coated on the substrate at 3000rpm for 30 After drying at 110^oC to remove the solvent, the resulting PEDOT: PSS film thickness was 60 nm.The seed layer solution was prepared by dissolving0.01 M Zinc acetate dehydrate [Zn $(CH_3COO)_2 2H_2O$] and 0.03M sodium hydroxide [NaOH] in methanol [CH_3OH] and stirred at 60 °C for 2h. Several layers were deposited on PEDOT: PSS coated plastic substrate by spin coating method at the rate of 2500 rpm for 30 s. After each spin coating process, all the films were drying at 110 °C for10 min. in the oven. ZnO nanowires were grown using aqueous chemical growth (ACG) method. The solution was prepared by 25mM hexamethylenetetramine (HMT) [$(CH_2)_6N_4$] and 25mM zinc nitrate hexahydrate [*Zn* $(NO_3)_2.6H_2O$].The seed layer, coating the substrate was immersed in this mixture for nanowires growth. The solution was kept in an oven for 5h at 90 °C. Thermally evaporated aluminium film was used as a top contact (cathode) and ITO acts as a bottom contact (anode) for this heterojunction.

The deposited films and heterojunction were studied by different characterization methods. SEM was used to investigate the morphology and size of the ZnO nanowires. The crystalline and microstructure of the ZnO nanowires was confirmed by XRD. The optical properties were studied using PL and EL spectra measurements. The SEM morphology analysis was performed using the *Carl Zeiss* Ultra 55 field emission *scanning electron microscope. XRD* was done using Rigaku smart lab *high-resolution X-ray diffract meter* employing Cu Kα radiation at λ = 1.5406 Å. The photoluminescence (PL) measurement was performed at room temperature using Renishaw Image Microscope-2000 *model.*325 nm He-Cd laser source was used as an excitation source for PL characterization. An Ocean Optics HR2000 spectrometer was used for EL spectra recording. The current-voltage characteristic was measured by using a Keithley6485picoampere meter.

3. Results and discussion

The SEM images in figure 1 (a, b) show highly dense ZnO nanowires grown on PEDOT: PSS/ITO coated plastic substrate. Their diameter is in the range of 60-200 nm and the length - of about 3-5 µm.

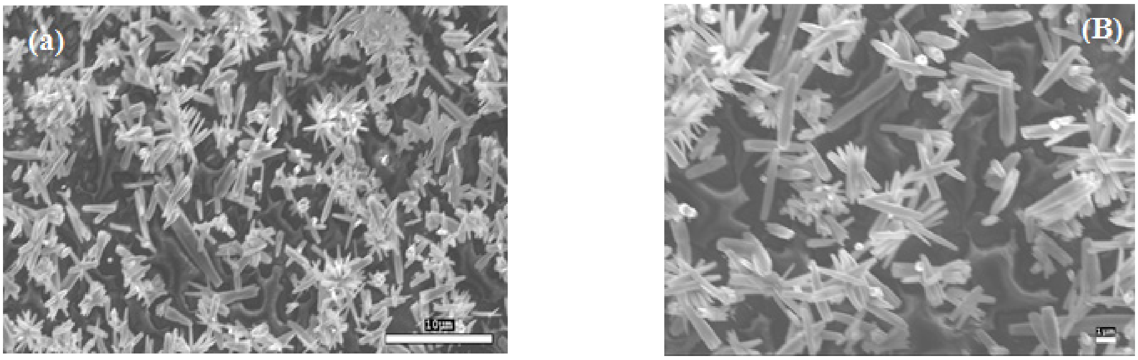

Figure 1(a, b) SEM image of nanowires grown on PEDOT: PSS coated ITO/PET substrate

The XRD measurements were carried out to investigate ZnO nanowires crystalline when grown on PEDOT: PSS/ITO coated PET. In figure 2 peaks at 2ϴ=31.84°, 34.44°,36.29°,46.84°,56.62°,62.90°and 67.95° can be observed, which correspond to ZnO (100),(002), (101),(102), (110),(103) and (112), respectively. All peaks of the pattern confirm that the ZnO nanowires are with hexagonal wurtzite structure having lattice parameter a=3.25 Å and c = 5.181 Å, which are very close to the standard values. The strong peak at 26.03°, corresponding to (020) plane in pattern, indicates the presence of PEDOT: PSS polymer.

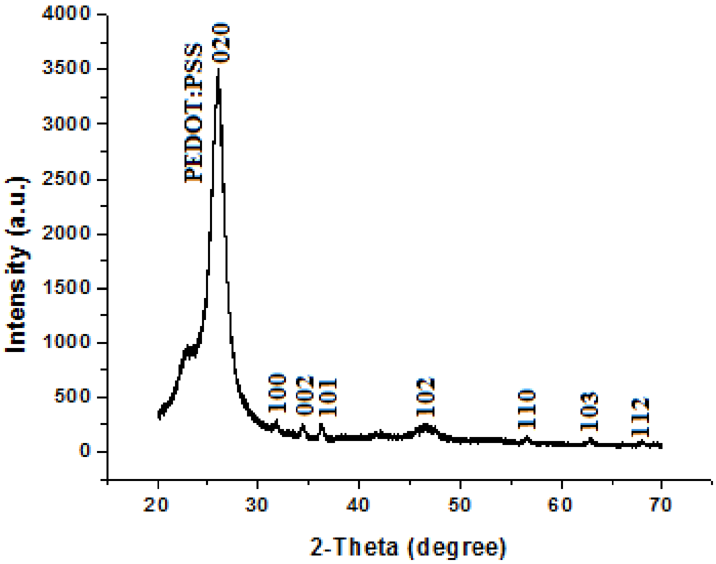

Figure 2 XRD pattern of ZnO nanowires grown on PEDOT: PSS / ITO coated PET substrate

Figure 3 shows PL spectrum measured at room temperature for an excitation wavelength of 325nm. It shows the emission from PEDOT: PSS polymer before and after ZnO growth. Two different peaks appeared in this spectrum, both in the UV region - one at 386 nm and the other at 367 nm. The peak, corresponding to 386nm is due to the band-to-band emission from ZnO nanowires [23, 24], while the 367nm peak shows emission from the PEDOT: PSS polymer. The PL spectrum of the PEDOT: PSS/ZnO nanowires heterostructure was not only red shifted, but increased in intensity, as well. These changes occur in the polymer's photoluminescence are probably due to the presence of ZnO. The defects on ZnO nanowires surface may be passivated by a p-type polymer, resulting in a decrease of the non-radiative recombination and increase in the light output [25].

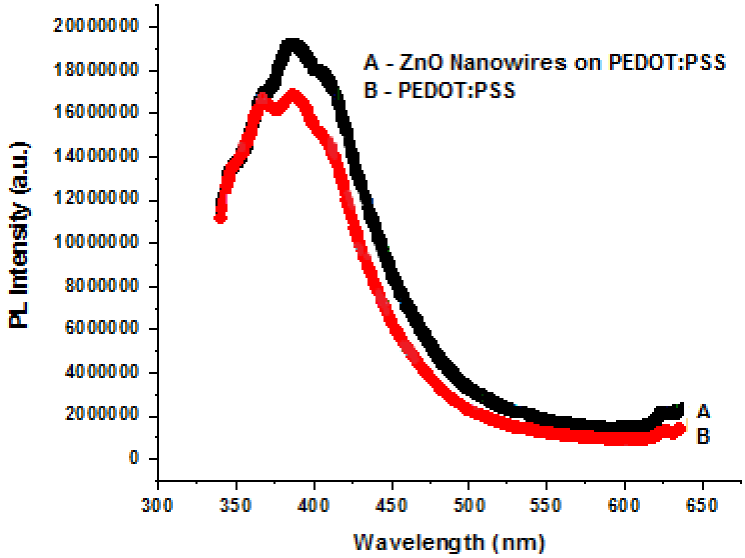

Figure 3 PL spectum of PEDOT:PSS polymer and PEDOT:PSS/ZnO nanowires heterostructure at room temperature

Figure 4 shows EL spectrum of PEDOT:PSS/ZnO nanowires hybrid heterojunction under forward bias, recorded at room temperature. It shows a single peak in UV region, located at 387 nm, originating from the near band edge emission [26].The heterojunction PEDOT: PSS/ZnO nanowires show single PL peak at 386nm, which is closely linked with the EL emission peak.

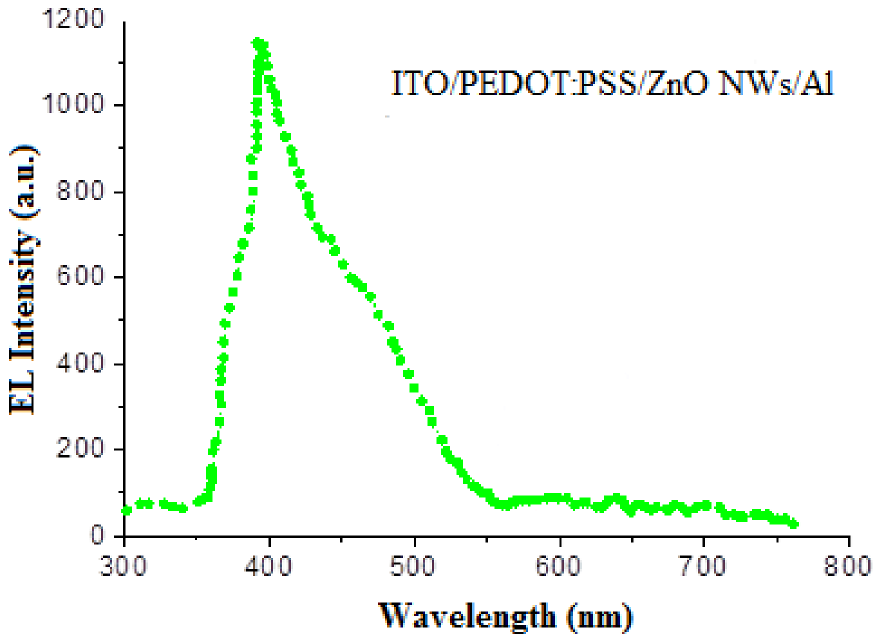

Figure 4 EL spectrum of PEDOT: PSS/ZnO nanowires heterojunction

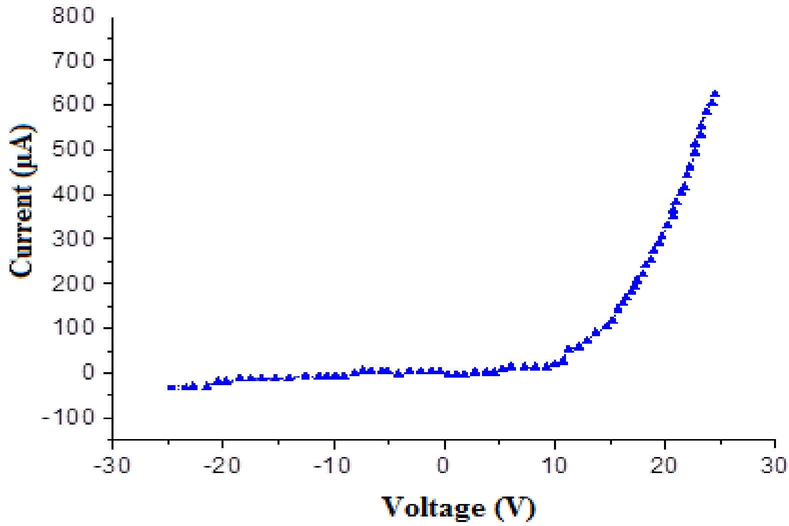

Figure 5 Current – voltage characteristic of PEDOT: PSS/ZnO nanowires heterojunction

In order to test the rectifying properties of the ITO/PEDOT:PSS/ZnO nanowires/Al heterostructure at room temperature current-voltage characteristic was measured (fig. 5).When connected in forward and reverse direction to the power supply, the structure exhibits typical curves for rectifying diode-like behaviour. This indicates the formation of a successful working hybrid organic/inorganic p-n heterojunction between the n-ZnO nanowires and the p-type PEDOT:PSS, useful for LED application.

Figure 6 shows band energy diagram assumed for the studied organic/inorganic heterojunction, which illustrates that there is a barrier between PEDOT:PSS and ZnO nanowires is, so to overcome it the holes and electrons need energy, corresponding to certain threshold voltage in forward bias. As can be seen from the electrical measurements this voltage is approximately 14 V. Possible reason for this relatively high value could be the irregular surface of the ZnO nanowires, which gets into contact with the next layer in a dot type manner.

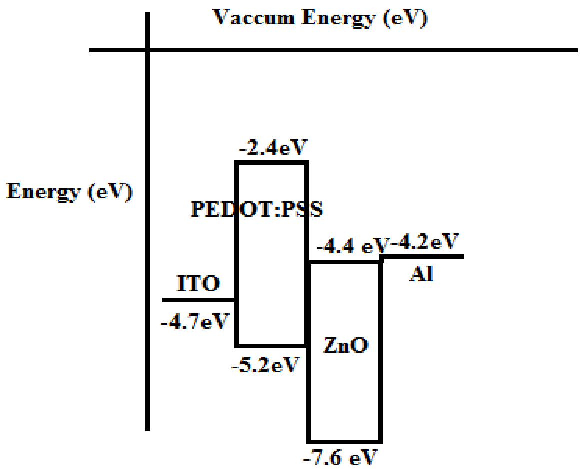

Figure 6 Band energy diagram of the proposed LED structure with PEDOT: PSS/ZnO nanowires heterojunction

The valance band energy and conduction band energy of ZnO nanowires are 7.6eV and 4.4eV, respectively [27, 28]. The highest occupied molecular orbital (HOMO) energy of the p-type PEDOT: PSS polymer is 5.2 eV [29] .The electron injection barriers between PEDOT: PSS the lowest unoccupied molecular orbital (LUMO) and conduction band of ZnO is 2.0 eV and barrier between ZnO conduction band and Al electrode is 0.2 eV. The hole injection barrier between the PEDOT: PSS HOMO and ZnO valance band is 2.4e V and the barrier between ITO and PEDOT: PSS HOMO is 1.5 eV. Due to these barriers, the electrons and holes accumulate at the interface of PEDOT: PSS/ZnO nanowires, forming space charge, which filed affects (hinder) the charge injection process. At voltages lower than the threshold value the current flow was negligible, as the barrier for electron and hole injection is high. After the voltage increase, the electrons from ZnO overcome the barrier and start to recombine with the holes of the PEDOT: PSS polymer, so the forward current increased rapidly and reached approximately 700 µA, as is confirmed by the current-voltage characteristic.

4. Conclusions

In conclusion, a multi-layered PEDOT: PSS/ZnO nanowires heterojunction has been fabricated on ITO coated plastic sheet of PET, using simple low temperature process without additional surface modifications. The device is flexible and the structural, optical and electrical characterization of the sample showed promising result for LED application. SEM images showed regular ZnO nanowires formation and the EL spectrum proofed radiative recombination in the UV region. The rectifying characteristic is evidence for a p-n junction formation. These results demonstrate that the ZnO/PEDOT: PSS hetero structure fabricated and discussed in this paper holds a strong potential for flexible UVLED and other optoelectronic applications.

Acknowledgement

Authors acknowledge the IIT Kanpur for characterization support and the grant DH 07/13 Bulgarian National Science Fund (BNSF).

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