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A Review on Fabrication of Polymer/ZnO Nanowires Hetero-junction Based Light Emitting Diode by Wet Chemistry Method

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Abstract

In our daily life the traditional incandescent lighting sources consume a big amount of electricity. Light emitting diodes (LEDs) have potential to replace these high electricity consumable traditional light sources. Basically LED is a p-n junction diode. A LED consists of p-type and n-type semiconductors to create a p-n junction.

There are several fabrication methods used for LEDs fabrication, like Metalorganic chemical vapour deposition (MOCVD), Molecular beam epitaxy (MBE), Sputtering, Pulse laser deposition (PLD), Spray pyrolysis, Chemical vapor deposition (CVD) and Wet chemistry. Among all methods the wet chemistry is a low cost, low temperature method.As compared to other method lesssophisticated apparatus are required in this method.

Znonaowire sreveal n-type conductivity while the polymers discussed in this article are p-type in nature. The combination of both n-Zno/p-polymers form p-n hetrojunction which is useful in different optoelectronic applications.

In this review article we summarized only the wet chemistry method with spin coating method for zno nanowires and polymer based thin film light emitting diode fabrication by low temperature.

Index Terms: *ZnO, nanowires, Polymer, p-n hetrojunction; sol-gel, spin coating.*

1. Introduction:

Zinc Oxide (ZnO) Nanowires is a chemically stable and environmentally friendly inorganic material which behaves as a n-type semiconductor. ZnO, is a II-IV wide band semiconductor with exciton binding energy (60 meV), has excellent physical and structural properties makes it promising material for optoelectronic devices[1,2]. ZnO NWs can be grown on any substrate without the need of lattice matching [3].

P-type doping is difficult with ZnO [4]. This factor motivates the researchers to grow n-type ZnO NWs on other p-type substrate i.e. GaN[5], NiO[6], Si[7] and Polymers[8] etc. for Light emitting Diodes .

P-type conducting polymers have many advantages including easy fabrication, flexibility, and tunable carrier densities. Synthesis of polymer with n-type conductivity is difficult and it has poor stability in air and poor solubility [8-10].In most organic material the mobility of electron is much lower than that of holes, which causes imbalanced carrier injection inorganic electroluminescence devices [11].On the contrary, ZnO have higher electron mobility.

Hence ZnO/organichetrostructure provides an approach forthe balance of the hole and electron current densitiesto construct high performance electroluminescence devices [11].

Various groups reported a good p–n heterojunctionbetween n- type ZnO nanorods and the p-type polymer for LED [12-14]. The ZnO/Polymer light emitting diode can be made by different method, and hydrothermal method. But here we discuss only hydrothermally grown ZnO/Polymer light emitting diode fabrication. Wet chemistry method has several advantages like low temperature process, inexpensive manufacturing, large area uniformity [15]. Since it is a low temperature method, thin films can be prepared on plastic type flexible substrate also.

2. Device Fabrication Process steps:

ZnO has self-organized growth, excellent luminescent properties with n type conductivity. The hetrostructuresof ZnO/Polymer light emitting diode was fabricated by different groups and they found also the electroluminescence from this combinations [12-14]. In order to fabricate the device, first the PEDOT:PSS polymers were spin coated on glass or plastic, then p-type polymers (MEHPPV,PFO etc) layers spin coated followed by the ZnO seed layer. A low temperature hydrothermal method is used to form ZnO nanowires on seed layer. The substrate was submerged upside down in solution for 2h. The beaker contains solution keep inside the conventional oven at temperature less than 100ºC. Different groups grow the nanowires in different temperature ranging from 50-95ºC.

After nanowires growth, insulating layer is spin coated on nanowires thin film to prevent the direct contact between p-polymers thin film and nanowires metal contact. Before depositing final layer an oxygen plasma etching process is perform. This process exposethe upper tip of nanowires and allow them for metallization. All polymer/ZnOnanowires based hetrojunction light emitting diode discussed in this review were fabricated by using the same steps. The layer deposition method of each layer is summarized in Table 1.

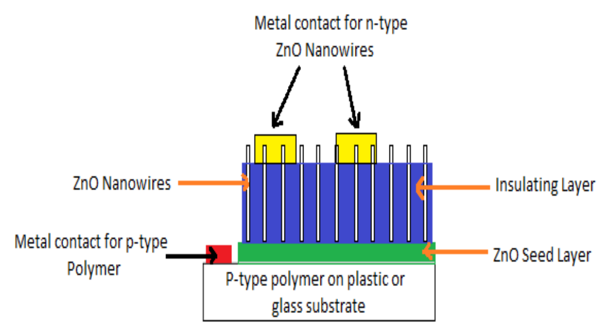

Figure1. Schematic diagram of the Polymer/ZnO nanowires based Light Emitting Diode

The Scematic diagram of LED is shown in figure 1 and the process steps in short are shown in flow chart.

The flow chart in figure 2 shows the procedure for preparing polymer/ZnO nanowire based herojunction light emitting diode via wet chemistry method-

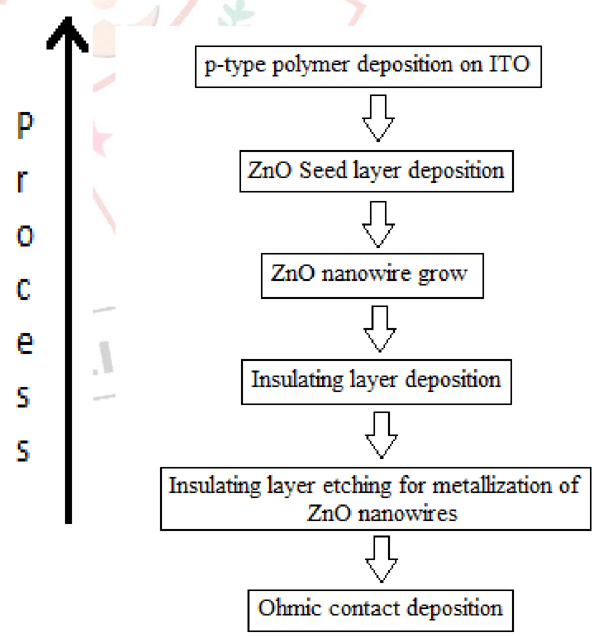

Figure 2. Flow chart

The deposition method of each layer is given in table 1.

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Layer Name	Layer Deposition Method
Ohmic Contact/Metallization	Thermal Evaporation Method
Insulating Layer	Spin coating
ZnO Nanowires	Wet Chemisty Method
ZnO Seed layers	Sol-Gel with Spin Coating or Dip Coating
p-type polymer	Spin coating

Table 1. Layer deposition method of each layer

3. Role of each Layer in LEDs :

3.1 p-type Polymers-There are different p-type polymers are reported i.e. Poly (3,ethylenedioxythiophene) poly(styrenesulfonate)PEDOT:PSS, Poly(N-vinylcarbazole) (PVK), (4,4-N,N-dicarbazolebiphenyl) (CBP), (4,4'-bis[N-(1-napthyl)-N-phenyl-amino]biphenyl) (NPD), poly(9,9-dioctylfluorine) (PFO),Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] **(**MEHPPV), Polyaniline (PANi) etc which film can act as a hole injecting layer.

The advantage of using polymers is their solubility in different solvents. Polymer solution can be easily prepared by using an appropriate solvent . The spin coating can be used for film synthesis of desired thickness.

Another advantage of polymer/ZnO hetrojunction is tuning the wavelength of light by using different polymers, like MEHPPV is orange red emissive polymer while PFO is blue emissive polymer[16]. Polyaniline (PANi) was selected as the hole conducting layer because of its facile synthetic process, good environmental stability, easy conductivity control, and cheap production in large quantities[17]. PVK is often used as a hole injection and transport layer in LEDs[18].

All the polymers can be dissolved easily in Toluene, chloroform and chlorobenzene. The solutions of polymers can be easily spin coated or dip coated on the substrate or any other layer.

3.2 Seed Layer:

Prior togrow ZnO nanowires on p-type Polymers, the seed layer deposition is recommended. The ZnO Seed layer provides nucleation to ZnO nanowires in hydrothermal method [19]. To deposit seed layer mostly sol-gel with spin coating method is used [12]. The length , diameter and density of the nanorodsstrongly depends on quality of seed layer [20]. The size of grains and seed layer quality is a key factor that influences the nucleation of ZnO NWs arrays. As the grain size increases, the density of ZnO nanowires also increased [21]. Seed Layer also effects the verticalalignment of ZnO nanowires [21]. Greene et al. reported that the ZnO seed orientation determined the nanowires orientation and the alignment of the rods is normal to the substrate by using a seed layer prepared from zinc acetate solution [22].

The Annealing temperature of seed layer also effects the nanowires orientation. It was noticed that when the amorphous seed layer annealed at temperature of 130º C, the ZnO nanowires arrays grown on this thin film are vertically aligned to the substrate [21].

3.3 ZnO nanowires:

A general property of nanowires based LED is that each nanowire can act as a waveguide, minimizing side scattering of light, thus enhancing light emission and extraction efficiency[4]. ZnO nanowires are the best nanostructure among the other oxide nanostructure as they can easily synthesize via wet chemistry method. Straindue to lattice mismatch can easily release for nanorods when compared to thin film[4].The ZnO nanowires is n-type due to intrinsic defects such as zinc interstitial and oxygen vacancies which are source of donors in ZnO.Intentional n-type doping can be done by using group III elements such as Al, Ga, and In, which can easily substitute Zn ions. These elements highly increase the conductivity [23].

Vertically aligned, ZnO nanowires act as a natural waveguides which helps to emitted light to travel top of the devices. It also enhances the light extraction efficiency by minimizing partial leakage [3]. The degree of alignment and the achieved aspect ratio was dependent of the seed layer used and fabrication condition [24-26].

3.4 Insulating Layer:

Insulating layer is use to fill the free spacesbetween the ZnO nanowires and prevent direct contact between p-polymer and top electrode [27]. The insulting layer also helps to reduce the surface leakage current, resulting LED performance improved [27]. Different groups used poly (methylmethacrylate) (PMMA)[13],Polysterene [28] Photoresist [4], Spin on glass (SOG) (an polysiloxane based dielectric material) [14] as insulating material. To fill the insulating layer between zno nanowires the spin coating method is used.

3.5 Metal Electrodes

Ohmic contact is also a key factor for improving device performce. The ohmic contact should be thermally stable and has low resistance. Silver [4,28] , PEDOT:PSS polymer layer [29,30], Indium Tin Oxide (ITO) [13,14,31] were used as an low cost electrode for p-type electrode while many reserchers used Ag/Au [28] , Al[14,30], Au/Ti [4] as an electrode for n-type ZnO nanowires.

4. Material Characterization –During the fabrication process or after the completion process,the different characterization techniques are used which are as follows-

4.1 X-ray Diffraction (XRD) - XRD is a non – destructive characterization technique. It is widely used to determine crystal structure, degree of crystalline perfection, lattice parameters, orientation of single crystal, particle size , thin film analysis etc. This characterization tool is used for determination of crystallanity of ZnO nanowire grown on polymer coated substrate.

4.2 Scanning Electron Microscope (SEM)-

SEM is very useful technique to study the morphology structure of grown ZnO nanowires on Polymer.The nature of materials prepared and nanowires length and diameter etc. can be found from such studies.

4.3 UV Visible Specroscopy orAbsorption Spectra:

The absorption spectra will be recorded and the band gap of the material will be determined by plotting a graph between $(\alpha h\upsilon)^2$ and $(h\upsilon)$, (where α is the absorption coefficient and $h\upsilon$ is the photon energy) i.e. Tauc's plot. The absorption spectra will be recorded by using UV-Visible absorption spectrophotometer.

4.4 Electroluminescence (EL) -

The electroluminescence (EL) is a process in which optical devices were characterized with electrical input and optical output. During this characterization, an electrical signal (current or voltage) were applied to properly bias the pn junction who emits the light. The acquired emitted spectrum is the result of electron-hole radiativerecombinations process in the device.The electroluminescence measurement is very crucial and has considered being a figure ofmerit for the light emitting diodes (LEDs).

4.5Photoluminescence Spectroscopy (PL) –

Photoluminescence (PL) is a non-destructive technique used for determination of extrinsic and intrinsic properties of the materials (semiconductors). In this technique the semiconductor under investigation is excited using laser irradiation and then the PL spectrum of the spontaneous emission from radiativerecombinationin the material band gap was acquired.

This technique has been used to determine the band gap and impurity levels, we can also use it to investigate the intrinsic and the extrinsic properties and recombination process in the SemiconductorZnO nanowire.

4.6 Current-voltage characteristics

The current versus voltage (I vs V) measurements were performed for the fabricated LEDs by using semiconductor parameter analyzer (SPA). TheI-V curves provide different information about the information about the LEDs such as its turn-on voltage, breakdown voltage forward and reverse currents, ideality factor, and parallel and series resistance of the fabricated LEDs.

5. Polymer/Nanowire Based hetrostructure for light emitting diode structure reported by different groups-The various groups fabricated ZnO nanowires hetrostructures with different polymers. C Y Lee et al. fabricated poly(9,9-dioctylfluorine) (PFO)/ ZnO hetrostructure organic/inorganic white light LED.A Zainelabdin et al fabricated ZnO Nanowires/PFO/TFB on flexible PEDOT:PSS substrate. Chun-Yu Lee et al reported ZnO Nanowires/P3HT hetrostructure. They modified ZnO seed layer by adding some glycerol in seed layer solution. PFO/ ZnO nanowires and MEH: PPV / ZnO nanowires and p-Blended polymer(PFO and MEH:PPV)/ZnO nanowires different white Light Emitting Diodes fabricated by M Willander et al. reported ZnO nanowires/PFO hybrid white light emitting diode. M Willander et al. blended poly(9, 9-dioctylfluorine) (PFO) with (4, 4'-bis [N-(1-napthyl)-N-phenyl-amino] biphenyl) (NPD) and spin coat a layer of blended polymers. The ZnO nanowires grown on this layer in order to fabricate blended p-polymer/ZnO nanowires LED hetrostructure . The same group blended poly(N-vinylcarbazole) (PVK) with poly(9,9 – dioctylfluorene – co – N(4-butylphenyl)diphenylamine) (TFB) and the ZnO nanowires grown on the film of this blended polymer.

6. Conclusion:

In this review we discussed on simple fabrication of hetrojunction LED based on Polymer/ZnO nanowires by low temperature wet chemistry method. The LEDs made by the process reported here is not only high in efficiency and easy to fabricate but they are low in cost as well.

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