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ZnO-organic hybrid white light emitting diodes grown on flexible plastic using low temperature aqueous chemical method

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We demonstrate white light luminescence from ZnO-organic hybrid light emitting diodes grown at 90 °C on flexible plastic substrate by aqueous chemical growth. The configuration used for the ZnO-organic hybrid white light emitting diodes (WLEDs) consists of a layer of poly (9, 9-dioctylfluorene) (PFO) on poly (3, 4-ethylenedioxythiophene) poly (styrenesulfonate) coated plastic with top ZnO nanorods. Structural, electrical, and optical properties of these WLEDs were measured and analyzed. Room temperature electroluminescence spectrum reveals a broad emission band covering the range from 420 to 750 nm. In order to distinguish the white light components and contribution of the PFO layer we used a Gaussian function to simulate the experimental data. Color coordinates measurement of the WLED reveals that the emitted light has a white impression. The color rendering index and correlated color temperature of the WLED were calculated to be 68 and 5800 K, respectively. [doi:10.1063/1.3475473]

I. INTRODUCTION

Zinc oxide (ZnO) is one of the prime materials for photonic applications with potential advantages over the III-nitride system due to many reasons, among them is the existence of many deep radiative levels.[1] These deep levels emit different colors covering the whole visible spectrum.[1] Such property makes ZnO, based white light emitting diodes (WLEDs) potentially useful in efficient solid state lighting where intrinsic white light can be achieved by using an appropriate external p-type electrode.[2] In addition ZnO has attracted a renewed global interest due to the fact that it also possesses a rich family of nanostructures which can be grown on any substrate without the need of lattice matching.[1] ZnO nanorods (NRs) may offer additional advantages for light emission due to the increased junction area, enhanced polarization dependence of reflectivity, and improved carrier confinement in one-dimensional nanostructures.[2,3] At the same time, both ends of ZnO NRs are extremely smooth, making them perfect mirror planes and vertical NRs are like natural waveguide cavities for making the emitted light to travel to the top of the device, also minimizing partial leakage and thus enhancing the light extraction efficiency from the surface.[4] The growth of ZnO NRs can be achieved using different high as well as low temperature (<100 °C) growth approaches.[5] The most usual high temperature techniques used are metalorganic chemical vapor deposition and vapor liquid solid.[1] The low temperature and low cost techniques are restricted to aqueous chemical growth process. In addition to the above mentioned properties ZnO possesses a large number of radiative intrinsic and extrinsic deep level defects.[6–8] Specifically ZnO, beside the ultraviolet (UV) emission due to the bandgap, emits blue, green, yellow, and red colors; which covers the whole visible region.[6–8] Therefore, the optical properties of ZnO have been extensively studied. ZnO typically exhibits one sharp UV peak and possibly one or two deep level broad band emissions due to deep defect states in the bandgap.[7,8] The dominant emitted colors depend on the growth method and its parameters and this implies that the emitted color lines can be controlled.[6] Hence ZnO has great potential to the development of intrinsic WLEDs. In recent years ZnO-organic hybrid LEDs becomes one of the most exciting research areas. The hybrid materials promise good properties that may not easily be available from conventional materials such as combining the high flexibility of polymers with the structural, chemical, and high functional stability of inorganic materials may lead to flexible electronic and photonic devices.[9] Yin and Alivisatos[10] reported the extended interface areas available in nanohybrid thin films exhibit highly efficient charge transfer processes and strong optical effects that are not observed in homogeneous materials. It has been reported that inorganic materials and organic materials could form a device to realize emissions from both kinds of materials.[11] There have been only few reports about ZnO nanohybrid LEDs on flexible substrate.[9,12,13] However, to our best knowledge, no results have been reported for the white light luminescence from ZnO-organic hybrid LEDs grown at 90 °C on flexible plastic substrates.

The poly (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) is today probably the most successful intrinsically conducting polymer and if finds applications in different fields such as electrically conducting electrodes in organic LEDs, photovoltaic devices, and field effect transistors because of the optical transparency and the well spin-coated properties.[14] The main advantages of the PEDOT:PSS-based electrodes are their mechanical flexibility, high transparency, and low price.[15,16] Due to the high processing temperature the direct growth of ZnO NRs on plastic substrates remains unexplored.[17] The low temperature growth of ZnO NRs on plastic substrates would open up for

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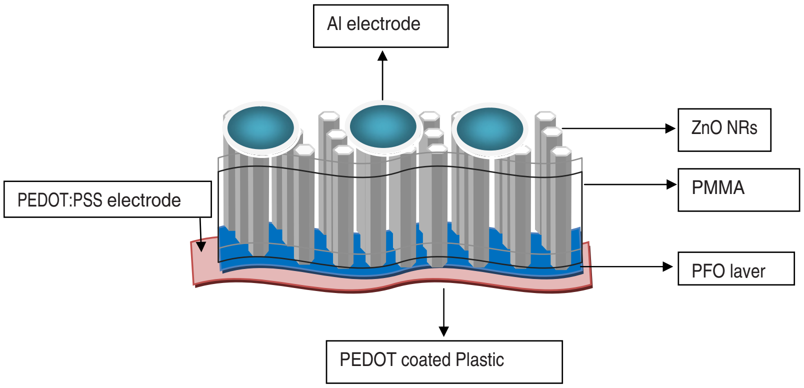

FIG. 1. (Color online) Schematic illustration of ZnO NRs/PFO hybrid device on PEDOT:PSS coated flexible plastic.

many photonic and electronic applications. The combination of ZnO NRs with low temperature growth process and low cost transparent flexible substrates may pave the way for the apprehension of large-area electronic devices such as flat panel screens and flexible electronics that can be folded up.[18] Here we demonstrate that vertically aligned ZnO NRs can be grown onto transparent flexible plastic substrates to produce WLEDs. These results suggest that ZnO NRs based WLEDs could serve as building blocks for the next generation of flexible display panels. ZnO NRs based WLEDs gives lighting designers the ability to put flexible white light panels in places previously impossible or prohibitively expensive.

Recently some organic-inorganic different LED configurations employing poly (9, 9-dioctylfluorene) (PFO) and ZnO thin film were reported on different substrates.[19–22] The ZnO thin film was mainly employed as electron injector and no interest on the emission from the ZnO thin film was intended and the quality of the film was not of high emitting grade. Nevertheless, these configurations were on ZnO thin films and the polymers face the challenge of been produced on large area with low cost. Here we present an approach which can provide the same performance with the possibility of achieving large-area lighting sources with low cost since it is based on discrete large number of pn junctions connected by one contact. In this paper we report white light luminescence from ZnO-organic hybrid WLEDs grown on PEDOT:PSS coated flexible plastic substrate by low temperature aqueous chemical technique. The PEDOT:PSS coating layer is used as an electrode for the ZnO-organic hybrid WLEDs and structural, electrical, and optical properties of WLEDs were measured and analyzed using different techniques, including scanning electron microscope (SEM), current-voltage (I-V), room temperature (RT) photoluminescence (PL), electroluminescence (EL), and color coordinates measurements. The EL spectrum reveals a broad emission band covering the whole visible range. In order to distinguish the white light EL spectrum components and the contribution of the PFO polymer layer we used a Gaussian function to simulate the experimental data. Finally the color quality was investigated for this ZnO-organic hybrid WLEDs.

II. EXPERIMENTAL DETAILS

To fabricate ZnO-organic hybrid WLEDs on PEDOT:PSS coated flexible plastic substrate, the substrate was washed in ultrasonic cleaner in isopropyl alcohol, acetone, and deionized water sequentially. We cover a small portion of the PEDOT:PSS which later work as electrode and the PFO was spun-coated on the substrate and backed at 100 °C for 5 min. The PFO was mixed at a 1:1 molar ratio in toluene solvent. This gave a PFO film with 20 nm thickness. To improve the ZnO NRs growth quality, distribution, and density a seed layer is spun-coated and baked for 5 min at 100 °C.[23] To grow ZnO NRs we use a low temperature chemical growth technique. In this method 0.01 M zinc nitrate hexahydrate $[Zn(NO_3)_2 \cdot 6H_2O]$ were mixed with 0.01 M hexamethyl tetramine $(C_6H_{12}N_4)$. The sample was placed in the solution and was heated at 90 °C. After growth, the samples were used to process LEDs. Prior to the ohmic contacts on the ZnO NRs, an insulating polymethyl methacrylate (PMMA) layer was deposited between the NRs. Recently it was shown that the use of PMMA as an insulating layer between NRs will lead to enhance the emission intensity due to the modification of surface states.[24] To ensure that no PMMA was on the top of the NRs, oxygen plasma cleaning was performed prior to the contact metal deposition. Then Al circular contacts of 1 mm in diameter and thickness of 500 Å were evaporated onto a group of NRs. Nevertheless, as the ZnO NRs are partially covering the total area, using the SEM we estimated the LED active area to be around 0.7 mm^2. A schematic diagram of the device is shown in Fig. 1. The device structure was characterized by SEM, and photoluminescence at RT. The RT-EL measurement of the ZnO-organic hybrid WLEDs was carried out using a photo multiplier detector under dc-bias condition. The light was collected from the topside of the device.

III. RESULTS AND DISCUSSION

The ZnO NRs grown were found to be aligned vertically and distributed uniformly as shown in the SEM image in Fig. 2. The I-V characteristics of the hybrid WLED is shows in Fig. 3. The turn on voltage of the hybrid diode is 2.5 V as shown in Fig. 3. The thermionic emission model was used to examine the hybrid diode behavior. The semilog plot of the I-V characteristics is shown in the inset of Fig. 3. The value of the ideality factor of the hybrid WLED is determined from the slop of the straight line region of the forward bias ln(I)-V characteristics. The ideality factor was found to be in the range 3–4 for all the diodes investigated which is comparable to the recently reported value of ideality factor for polymer heterojunctions.[25] The higher value of the ideality

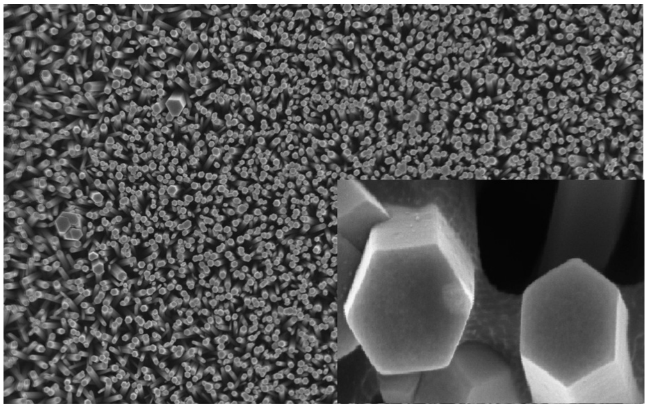

FIG. 2. SEM image of the as grown ZnO NRs on PFO polymer and the inset shows the SEM image after spin coating and followed by soft backing.

factor indicates that the behavior of the hybrid diode deviates from the ideal thermionic behavior. This may be due to the presence of surface states in ZnO. These surface states provide additional energy states which are responsible for the existence of multiple current pathways.[25] In our case a lot of defects have been verified by defect related PL emissions due to ZnO NRs, which provide additional energy states and hence multiple current pathways.

To be able to separate the emission sources we grew ZnO NRs on the same plastic substrate without the use of an underlying polymer films. Figure 4(a) shows the RT-PL spectrum of the ZnO NRs. As clearly seen, a sharp UV peak is observed indicating that high crystal quality ZnO NRs have been achieved. In addition two broad deep level emissions (DLEs) centered at the green and red wavelengths are also appearing. The RT-PL spectrum of the ZnO-organic hybrid structure consisted of UV emission centered at around 380 nm, PFO violet and blue emissions at 435 nm and 464 nm, respectively, and two DLE bands from ZnO NRs. These are the green at 513 nm and the red at 666 nm as shown in Fig. 4. It is extensively reported that the DLE is a superposition of many different deep levels emitting at the same time.[26] Different samples have different defect configuration due to the different growth methods and growth conditions so due

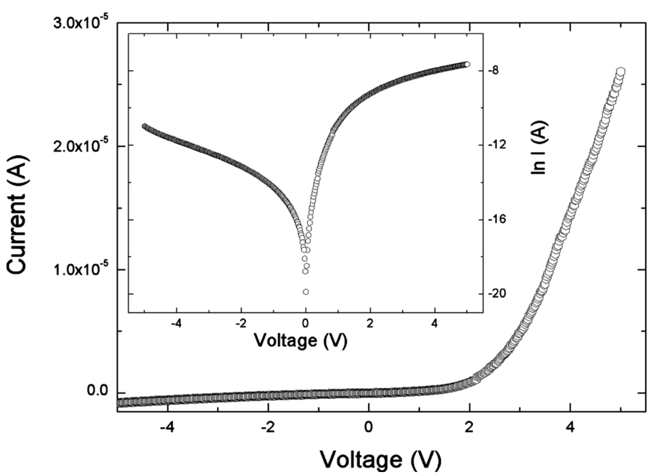

FIG. 3. Typical RT I-V characteristics of the ZnO NRs/PFO hybrid WLED and the inset show the semilog plot of I-V characteristics.

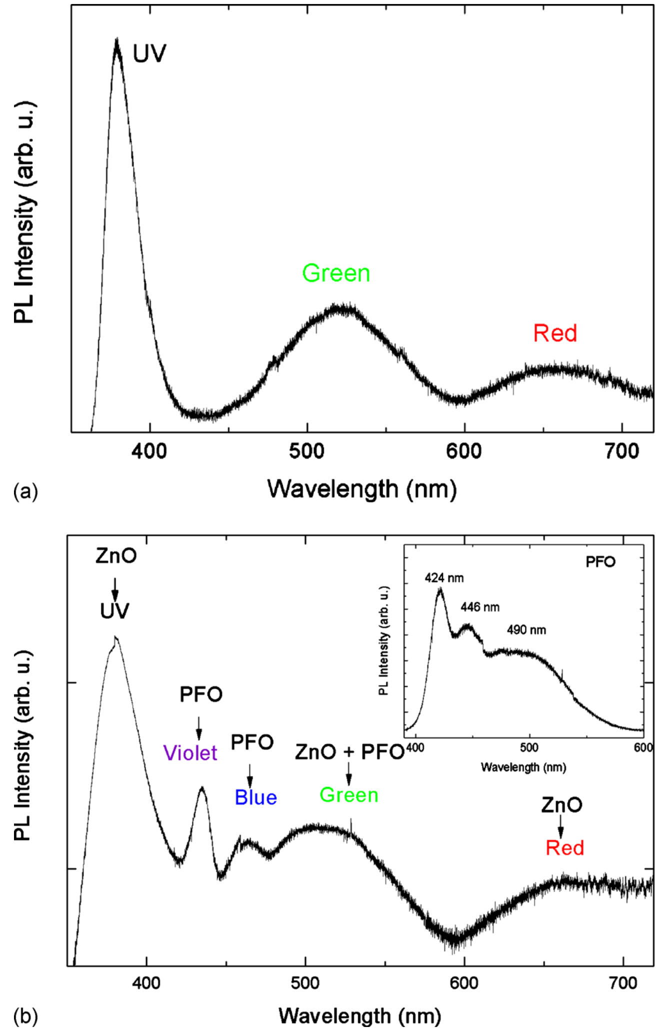

FIG. 4. (Color online) (a) RT-PL spectrum of the ZnO NRs grown by the same parameters on plastic substrate with no PFO film. (b) RT-PL spectrum of the ZnO NRs/PFO hybrid structure and the inset shows the RT-PL spectrum of the PFO on PEDOT:PSS plastic.

to this fact the origin of the DLE has been controversial for decades. The peak position of the deep band emission is defined according to the relative density of these radiative defects. The probable intrinsic deep level defects in ZnO are oxygen vacancy (V_O), zinc vacancy (V_{Zn}), oxygen interstitial (O_i), zinc interstitial (Zn_i), oxygen antisite (O_{Zn}), and zinc antisite (Zn_O). These deep level defects often control directly or indirectly the luminescence efficiency in semiconductors.[27]

The RT-PL spectra of the PFO (without ZnO NRs) reveals two violet emissions at 424 nm and 446 nm, and one broad blue emission centered at 490 nm as shown in the inset of Fig. 4(b). However it was difficult for the PFO to obtain pure and stable blue emission due to the presence of undesirable green emission from the EL devices which might originate from an oxidation of 9-monoalkylated fluorenes during device processing.[28] Two justifications have been given for this green emission; one was the keto defect and the other was excimer.[28,29] Lu *et al.*[28] reported that green light will be emitted at high voltage as a result of the forma-

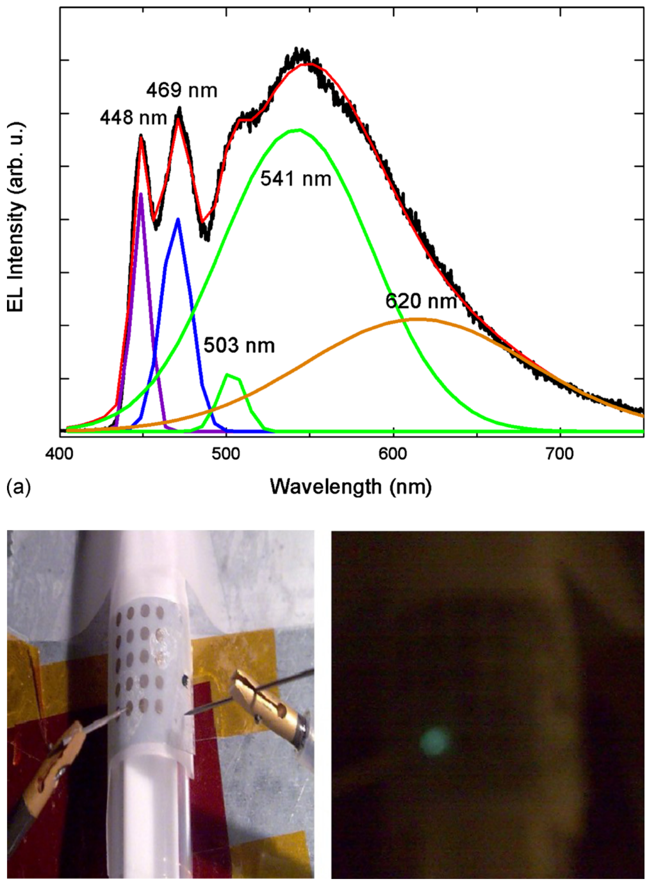

FIG. 5. (Color online) (a) RT-EL spectrum and Gaussian fitting of the PFO/ZnO hybrid WLED. (b) A photograph of white light emission from flexible device folded at a large angle during operation.

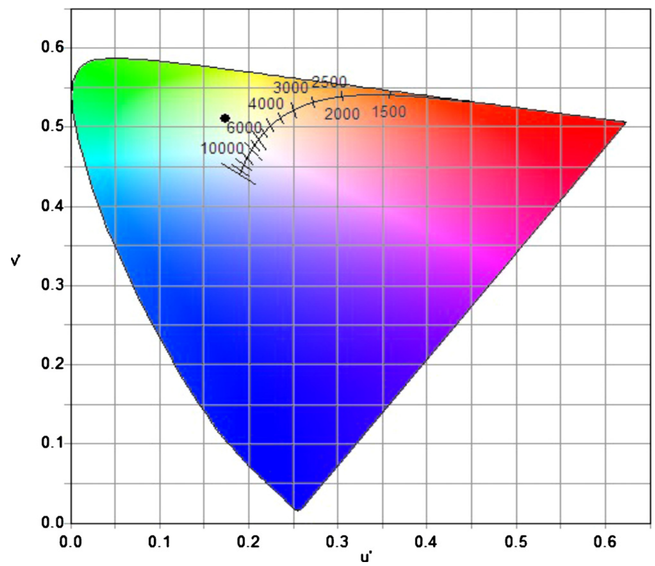

FIG. 6. (Color online) Typical color coordinates characteristics of the ZnO–PFO hybrid WLEDs.

tion of excimer, and this green light emission will give rise to higher brightness and efficiency. Recently PFO peaks at 424, 446, and 520 nm were reported.

Figure 5(a) shows the EL spectrum of the hybrid WLED which reveals a broad emission band from 420 to 750 nm. In order to distinguish the white light EL spectra components and the contribution of the PFO emission we used a Gaussian function to simulate the experimental data. The simulated EL spectrum shows five different emissions at 448 nm, 469 nm, 503 nm, 541 nm, and 620 nm which are associated with violet, blue, green, and red, respectively. The emissions at 448 and 469 nm are due to exciton emission of PFO. The minute contribution in green emission at 503 nm from PFO is due to the formation of excimer as stated above. It is reported that the EL emission spectrum of PFO changes during the device operation and differs from its corresponding PL spectra.[28] In our PL spectra of PFO the three peaks appear at 424, 446, and 490 nm while in the EL spectra these peaks emerge at 448, 469, and 503 nm which is consistence with the previous reports. The emissions at 541 nm (green) and 620 nm (orange-red) are associated with intrinsic deep level defects in ZnO. The green band is the most investigated and most debated band in ZnO. The variation in the green emission peak position is attributed to different relative contributions, e.g., V_O, V_{Zn}, Zn_i, O_i, and extrinsic Cu caused by fluctuations in the growth conditions for different growth methods.[30] The green emission has been explained to be originating from more than one deep level defect; V_O and V_{Zn} with different optical characteristics were found to contribute to the broad green luminescence band.[8,30] The orange-red emission was proposed to be due to transition from Zn_i to O_i.[6] However no consensus has been reached regarding the origin of the different observed colors, partly due to the different defect configuration in different samples.[6] The white light EL might be attributed to the excitonic emissions resulting from the recombination of the electrons and the holes at ZnO NRs/PFO interface. The lifetime of the electrons existing in the ZnO/PFO interface is much larger than that in the ZnO NRs.[31] The electrons existing at the interface between the conduction band edge of the ZnO NRs and the lowest unoccupied molecular orbital level of the PFO layer slowly drop to the lower states due to their longer life time. Therefore the emission with various wavelengths is emitted due to continuous recombinations between the electrons and the holes during electron transitions from the upper states to the lower states.[31] We have many states in the ZnO band gap due to native defects in ZnO. The energy states of various native defects had been calculated or experimentally measured in the band gap of ZnO. The commonly observed green emission is frequently attributed to transition from conduction band to V_O and the orange-red emission is proposed to be due to transitions from Zn_i to O_i. The EL emissions at 448 nm (violet) and 469 nm (blue) are due to the exciton emission in the PFO.[28] These PFO related violet and blue emissions combined with ZnO defect related emissions results in the white light emission. The combination of ZnO NRs with low temperature growth process and the low cost transparent flexible substrates makes the organic-inorganic hybrid junction LEDs attractive for the development of large-area electronic devices such as flat panel screens and flexible electronics that can be folded up. Figure 5(b) shows a photograph of the white light emission from flexible device.

Finally the color quality was investigated for the ZnO-organic hybrid WLEDs. Figure 6 shows the color coordinates measurement of the present ZnO-organic hybrid WLEDs. Figure 6 reveals that the emitted light has a white impression. The color rendering index (CRI) and correlated color temperature (CCT) of the WLEDs were calculated to be 68 and 5800 K, respectively.

IV. CONCLUSION

In conclusion, white light luminescence from ZnO-organic hybrid LEDs grown at 90 °C on flexible plastic substrate has been demonstrated. The configuration used for the ZnO-organic hybrid WLEDs consists of a layer of PFO PEDOT:PSS coated plastic with top ZnO NRs. The PEDOT:PSS coating layer is used as electrode for ZnO-organic hybrid WLEDs. The EL spectrum reveals a broad emission band covering the whole visible region and hence provides white light. The emitted white light was found to be the superposition of a violet line at 448 nm, blue line at 469 nm from the PFO combined with green emissions at 503 and 541 nm, and a red emission at 620 nm due to deep level defect emissions in ZnO NRs. The CRI and CCT of WLEDs were calculated to be 68 and 5800 K, respectively. The possibility of the combination of ZnO NRs grown at low temperature (<100 °C) and transparent flexible plastic as a substrate makes the organic-inorganic hybrid junction of potential for the development of flexible large-area white lighting sources that can be folded. By optimizing the concentration of the PFO white light emission with higher CRI can be achieved.

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