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Low-Temperature Aqueous Chemical Growth of Inorganic-Organic Hybrid Junction with ZnO Nanorods/Polyfluorene Structure

In this paper, we report the inorganic-organic hybrid junction synthesized on ITO glass substrate, which was consisted of an n-type ZnO nanorods (NRs) grown by low-temperature aqueous chemical growth method and a p-type Polyfluorene (PF) organic film fabricated by spin-coating. The results indicate that densely and uniformly distributed ZnO nanorods were successfully grown on the PF layer. The thickness of the PF layer plays a dominant role for the current-voltage (I-V) characteristic of the ZnO NRs/PF inorganic-organic hybrid junction device, and a p-n junction with obviously rectifying behavior was achieved with optimal PF layer thickness. The photoluminescence (PL) spectrum covering the broad visible range was obtained from the n-ZnO nanorods/p-polyfluorene (PF) structure, which was originated from the combination of the PF-related blue emission and the ZnO-related deep level emission.

Keywords: Nanorods, Polyfluorene, Hybrid junction, Photoluminescence
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1. Introduction

Recently, white-light emitting diode (LED) is triggering a revolution of general illumination. As a novel, convenient and low-cost approach to straightforward white-light electroluminescence, the inorganic-organic hybrid junction devices are being studied extensively around the world, which take advantage of the high carrier mobility of inorganic materials and the high luminescence efficiency of organic materials at very low cost [1-3]. Among the numerous inorganic semiconductors, ZnO is a very promising inorganic material suitable for a wide range of applications due to its wide and direct band gap and large exciton binding energy [4]. In particular, ZnO nanostructures have currently got more interests due to the large surface area to volume ratio, quantum size effect as well as the their self organized growth on almost any substrates regardless of the lattice mismatch between ZnO and the substrate [5]. So far, there have been several reports on the realization of electroluminescence from ZnO based inorganic-organic heterojunction nanostructures [6-8]. However, most emissions are from either ZnO only [2,8] or the organic layer only [3]. Bright white-light electroluminescence was recently achieved from ZnO nanorod (NR)/polyfluorene (PF) inorganic-organic heterojunction light-emitting diodes (LEDs), confirming the ZnO NR/PF inorganic-organic

heterojunction is very promising for developing high brightness straightforward white-light emitting diodes [9]. An important and key issue for the development and application of such inorganic-organic hybrid junction devices is to realize the controllable growth for desired functionality. Therefore, fundamental understanding of the effects of preparation parameters and carrier transport mechanism of such ZnO NR based inorganic-organic hybrid junction devices are desirable and essential.

In our very recent studies, controllable growth of well-aligned ZnO NRs with high optical quality was successfully achieved by low-temperature aqueous chemical growth method via adjusting the preparation parameters [5]. Low-temperature aqueous chemical growth method has been proven to be a high performance growth technique for ZnO NRs, due to its excellent advantages such as low cost, low temperature, non-toxic operation and environmental friendliness. There are different options of the choice for the p-type polymers to be combined with n-type ZnO NRs to form the inorganic-organic hybrid junction devices [10-12]. Among the possible candidates, PF are novel and promising blue light emitting materials with extremely high efficiency. In addition, the advantage of using PF polymer was the possibility of growing the ZnO NRs by low temperature approaches on

large substrates and hence the potential of developing large area white light emitting sources.

In this work, the inorganic-organic hybrid junction with n-ZnO nanorods/p-polyfluorene (PF) structure was grown with low-temperature aqueous chemical growth method. The results indicate that densely and uniformly distributed ZnO nanorods were successfully grown on the PF layer, and a p-n junction with reasonable rectifying behavior was formed at the interface between ZnO NR inorganic layer and PF organic layer. White-light photoluminescence was achieved by combining the PF-related blue emission with ZnO-related deep level emission.

2. Experiment

The ZnO NR/PF inorganic-organic hybrid junction device was designed and schematically illustrated in Fig. (1a), in which the ZnO NRs and the organic film served as the n- and p-type component, respectively. Polyfluorene (PF) was used as the organic layer and spin-coated on ITO glass substrate to serve as p-type layer, then, a very thin ZnO seeds layer (~30nm) was deposited on the as-grown PF layer to facilitate vertically aligned nanorods by radio frequency (RF) magnetron sputtering with Ar used as the working gas. The Ar flow rate, RF power, and chamber pressure were maintained at 15 SCCM, 180 W, and 3.5 Pa, respectively. Subsequently, ZnO NRs were grown on ZnO seeds layer from an aqueous solution composed of 0.025mol/L zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, reagent-grade) and hexamethylenetetramine (HMT) ($\text{C}_6\text{H}_{12}\text{N}_4$, analytic-grade) with a ration of 1:1 at a low temperature of 95°C for 5h in a sealed container. A detailed process for ZnO NRs growth by low-temperature aqueous chemical growth method has been described elsewhere [13]. After growth, the samples were cooled down to room temperature naturally, rinsed thoroughly in deionized water, and dried in air, and then embedded in an insulating PMMA layer that is spin coated from PMMA solution. The PMMA layer in the device is used to provide isolation for the individual ZnO NRs and prevent direct contact between the PF and the top electrode. The thickness of PMMA was accurately controlled to expose the tip of ZnO nanorod for metallization. To ensure good contacts of each layer, the sample is then annealed at 100°C for 30 min to remove the residual solvent. Finally, an aluminum layer is deposited by a conventional thermal evaporation through a shadow mask with bar shape hollow out to provide a contact for electron injection. The detailed device fabrication processes are schematically shown in Fig. (1b).

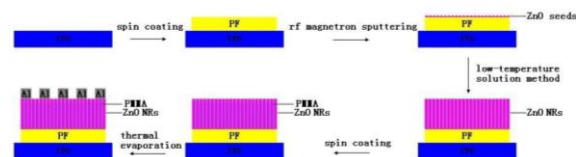


Fig. (1) (a) Schematic diagram of detailed ZnO NRs/PF inorganic-organic hybrid junction device fabrication processing procedure

Field emission scanning electron microscope (FE-SEM) was used to investigate the morphology of the as-grown structure on HITACHI S-4800. To investigate the electrical properties of the ZnO NRs/PF inorganic-organic hybrid junction device, the current-voltage (I-V) characteristic measurements were carried out using a Keithley 2611A semiconductor diode parameter analyzer. To investigate the optical properties, PL measurements were performed at room temperature by a Jobin Yvon HR320 spectrometer using a He-Cd laser (30mW) with an excitation wavelength of 325 nm.

3. Results and Discussion

3.1 Microstructure and morphology

Figure (2a) shows the SEM cross-section image of as-grown ZnO NRs grown on ITO substrate. It can be clearly observed from the figure that the ZnO well-defined nanorods array was successfully grown densely and vertically on the substrate, and the average diameter of the ZnO nanorods is 120nm. Figure (2b) shows the SEM image of as-grown ZnO NRs grown on PF thin films after PMMA embedding, inset is a magnified image.

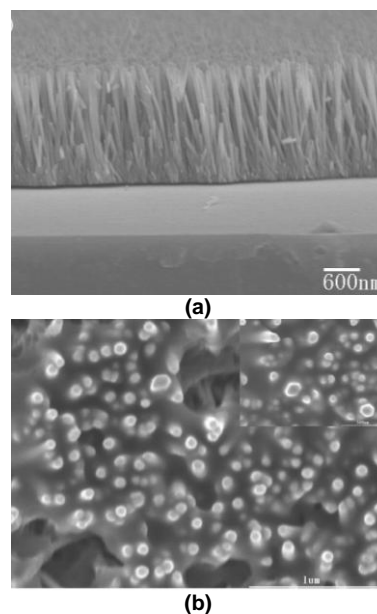


Fig. (2) (a) shows the SEM cross-section image of as-grown ZnO NRs grown on ITO substrate. (b) shows the SEM image of as-grown ZnO NRs grown on PF thin films after PMMA embedding, inset is a magnified image

The bright spots are the ZnO NRs and the dark area is the space between the NRs filled with PMMA. Therefore, it indicates that a thin PMMA coating on top of the ZnO NRs with a suitable thickness can be achieved, and the space between the ZnO NRs is solidly filled with PMMA to effectively prevent short-circuit between individual ZnO NRs. Moreover, it is clearly observed that some of the ZnO NRs tips are not covered with the PMMA insulating layer, allowing the possibility to contact them with electrodes. The relatively poor homogeneity can be understood considering the fact that not all the ZnO nanorods have the same height. This implies that it is necessary to optimize the growth process in order to obtain ZnO nanorods having the same height so more efficient LED can be achieved, since more ZnO nanorods will be contributing to the emission.

3.2 Optical properties

The photoluminescence (PL) was performed to investigate the optical emission and access the quality of our grown PF thin film and ZnO NRs. To distinguish the peaks origination in the fabricated structure, the PL characteristics of the ZnO NR/PF hybrid structures were measured at room temperature before and after the growth of the ZnO NRs. Figure (3) shows the PL spectra of ZnO NR/PF hybrid structures before (Fig. 3a) and after (Fig. 3b) the growth of ZnO nanorods.

In Fig. (3a), two intensity peaks and a broad band were observed centered at 422nm, 438nm, and 527nm, respectively, which corresponds to the PF polymer material as expected [9]. The blue emission of PF polymer is originating from excitonic emission and its vibronic progression from non-interacting single chains.

In Fig. (3b), similar characteristics with Fig. (3a) can be clearly identified. Comparing Fig. (3a) with Fig. (3b), it can be observed that the PF-related blue emission peaks have shifted from 422nm and 438nm in Fig. (3a) to 438nm and 465nm in Fig. (3b), after the growth of ZnO NRs on PF polymer layer. The red-shift of PF-related blue emission could be attributed to the instability and impurity of PF polymer material [14,15]. In addition, the vanish of ZnO-related near band edge UV emission (~380 nm) and superposition of the broad deep level emission (DLE) band of ZnO NRs implies that, in current ZnO NR/PF configuration, the PL intensity of PF is much stronger than that of ZnO NRs [16]. It is known that the peak position can be different in different samples due to the fact that the DLE is a superposition of different contributions from specific defect related bands [17,18]. However, the obvious difference between Fig. (3a) and Fig. (3b) provided convincing evidence that the grown ZnO NRs have contributed observable emission in the visible region of the ZnO NR/PF hybrid structure as expected. It is important to mention that the hybrid organic

inorganic white light structure discussed above, can utilize the different emission possibilities in organic LEDs, e.g., exciton emission, exciplex emission, and together with the DLE form the ZnO nanorods [19].

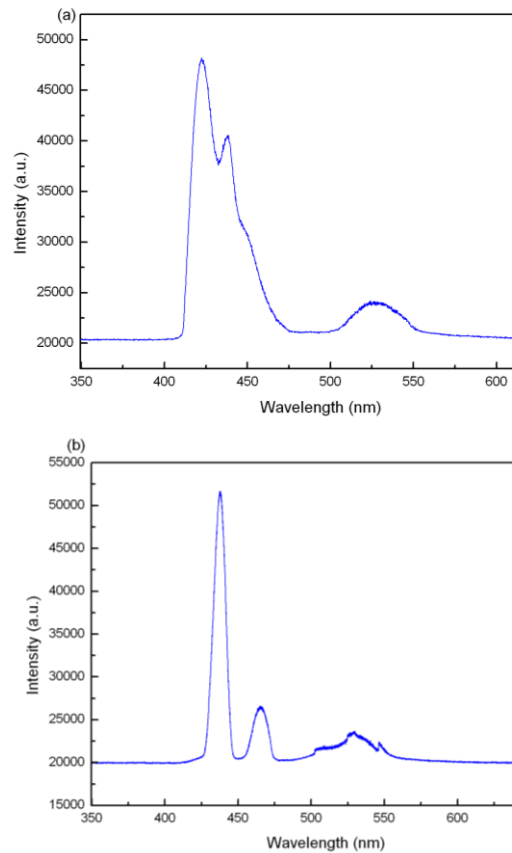


Fig. (3) The room temperature PL spectra of the ZnO NRs/PF hybrid structures before (a) and after (b) the growth of the ZnO nanorods

3.3 Electrical properties

As direct Hall Effect measurements to obtain reliable electrical properties of individual layer of the ZnO NRs/PF hybrid structure are difficult to accomplish, because the extremely high resistance for PF film and the necessary 2D configuration of the Hall contacts is hard to achieve for ZnO NRs. A simple and reliable method to investigate the electrical properties of the ZnO NRs/PF hybrid structure is to study the current transport mechanism via I-V characteristic. Fig.4 represents the typical I-V characteristic for ZnO NRs/PF heterojunction at room temperature (RT). Three kinds of device with different structures, ITO/PF/Al (device A), ITO/PF/ZnO NRs:PMMA/Al (device B), ITO/ZnO NRs:PMMA/Al (device C), were fabricated for comparison, and their cut-in voltages are about 5V, 6V, and 8V, respectively. For the PF single-layer device (device A), it has been found that the thickness of the PF layer play a dominant role for the I-V characteristic of the obtained device. If the PF thin film is too thin, the devices will breakdown. When the PF thin film is too thick, the rectification characteristic will degrade. The optimized PF thin

film thickness is found to be around 80nm.

Figure (4) shows the I-V curve for the PF single-layer device (device A) with optimized PF thin film thickness in terms of rectification characteristic. While for the ZnO NRs single-layer device (device C), a symmetrical I-V characteristic is obtained. That is to say, the potential barrier between ITO and ZnO NRs is similar to that between ZnO NRs and Al. It also indicates that the ZnO NRs directly contact the ITO substrate would lead to the large current leakage. This finding is similar to previous report by C.Y. Lee [9].

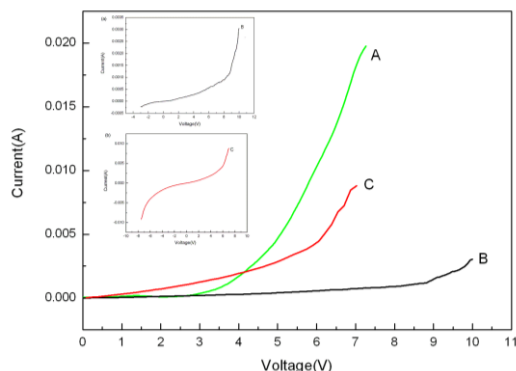


Fig. (4) The room temperature I-V curves of device A, B, and C. Insets (a) and (b) are room temperature I-V curves of device B and C, respectively

For the PF/ZnO NRs double-layer structure, a reasonable p-n junction characteristic is demonstrated. The value of the ideality factor was roughly estimated to be in the range 3~4. The higher value of the ideality factor indicates that the transport mechanism is no longer dominated by the thermoionic emission. Non ideal behavior is often attributed to defect states in the band gap of the semiconductor or at the interface providing other current transport mechanisms such as structural defects, surface contamination, barrier tunneling or generation recombination in the space charge region and to variations in interface composition. In our case, a much high density defect states are supposed to be present at the interface between ZnO NR inorganic layer and PF organic layer due to the large lattice mismatch and the extremely low growth temperature. Compare with the single layer devices of PF thin film and ZnO NRs, the PF/ZnO NRs double-layer has a smaller current. The reason could be related to the residual PMMA isolated layer on top of ZnO NRs, but further investigations are certainly needed.

4. Conclusions

In this paper, the n-ZnO NRs/p-PF inorganic-organic hybrid structure are suggested as a solution to avoid the well known ZnO p-type doping

difficulties and still utilize the potential of ZnO for optoelectronic appliance. The results indicated that densely and uniformly distributed ZnO nanorods were successfully grown on the PF layer, and a p-n junction with obviously rectifying behavior was formed at the interface between ZnO NR inorganic layer and PF organic layer. A photoluminescence (PL) spectra covering the broad visible range was achieved from the n-ZnO nanorods/p-polyfluorene (PF) structure, which was resulted from the combination of the blue PF-related emission and the ZnO-related deep level emission. The achievement of the n-ZnO NRs/p-PF inorganic-organic hybrid junction reported in this work should provide a convenient and low-cost route toward the realization of ZnO-based white-light EL devices with low-temperature processes in the future.

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