Materials Science in Semiconductor Processing 81 (2018) 44–47

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp

Low cost inorganic white light emitting diode based on submicron ZnO rod arrays and electrodeposited Cu_2O thin film

Mahmoud Abdelfatah, Walid Ismail, Abdelhamid El-Shaer*

Physics Department, Faculty of Science, KafrelSheikh University, KafrelSheikh 33516, Egypt

ARTICLE INFO

Keywords:
ZnO rod arrays
Hydrothermal method
Electrodeposition
Cu_2O/ZnO heterojunction
White Light emitting diode

ABSTRACT

We present here the fabrication and characterization of low cost inorganic white light emitting diode (LED) based on submicron ZnO rod arrays and Cu_2O thin film. Firstly, n-ZnO rod arrays were grown on FTO substrate by hydrothermal method at 150 °C. Then, p-Cu_2O thin film was electrodeposited on top of ZnO arrays from alkaline cupric lactate solution at 60 °C. X-ray diffraction and scanning electron microscopy were employed to investigate the structural and the morphology of the prepared samples as well as the diode device. The results indicate the formation of hexagonal structure of ZnO arrays and cubic structure of polycrystalline Cu_2O thin film. The performance of LED device was investigated employing I-V and electroluminescence measurements. The heterojunction device showed good rectification behavior and a broad emission covering visible spectrum for all applied voltage which indicates the white electroluminescence of the heterostructure device. Therefore, the inorganic ZnO arrays/Cu_2O thin film is a promising heterojuniction for low cost and large-scale production of white LED.

1. Introduction

Zinc Oxide (ZnO) is n-type direct semiconductor with bandgap energy of 3.37 eV and a large exciton-binding energy of about 60 meV [1,2]. ZnO is earth abundant material which is inexpensive [3], non-toxic and chemically stable [4]. Therefore, ZnO is one of the most attractive candidates for the fabrication of light-emitting diodes (LEDs) [5]. Due to a lack of the growth of p-type ZnO semiconductor, a lot of efforts were employed to fabricate LEDs based on ZnO heterojunction with other p-type materials either organic or inorganic [6]. The heterostructure of ZnO with non-doped Gallium nitride (GaN), doped GaN, and Si were the mostly studied inorganic LEDs [6–8]. Although the high-performance of these heterostructures in LEDs, but the fabrication of such devices still an expensive process since they required ultra-high vacuum and high temperature techniques. Overcoming this problem could be achieved using Cu_2O which is a p-type direct band gap semiconductor with band gab about 2 eV and have a high absorption coefficient [9]. Cu_2O thin films could be easily grown by electrodeposition technique [10,11]. So, simple methods such as hydrothermal and electrodeposition, which based on aqueous solution are most effective to produce large-scale LED devices. Therefore, we report here the fabrication of inorganic submicron ZnO arrays/Cu_2O thin film heterostructure LED. Low cost and low temperature hydrothermal and electrodeposition techniques were employed to grow submicron n-ZnO rod arrays on FTO substrate and p-Cu_2O thin film, respectively. X-ray diffraction, and scanning electron microscopy were employed to investigate the structural and the morphology of rods and thin films as well as the diode device. The performance of inorganic ZnO arrays/Cu_2O thin film LED were investigated employing I-V and electroluminescence measurements.

2. Experimental methods

Submicron ZnO rod arrays were directly grown on 2 cm × 2 cm FTO substrate employing low cost hydrothermal method as reported previously [12]. Typically, 20 mL solution of 0.25 M Zinc nitrate hexahydrate and 20 mL solution of 7 M potassium hydroxide were added to each other and stirred to form homogenous mixture. This mixture was transferred into a steel-lined Teflon autoclave which was placed at 150 °C for 16 h where the following reaction takes place:

$$2\ Zn(NO_3)_2 + 2NaOH \rightarrow Zn(OH)_2 + 2NaNO_3 + 6H_2O \quad (1)$$

$$Zn(OH)_2 \rightarrow ZnO\downarrow + H_2O \quad (2)$$

After cooling down and to remove any chemical residues, the formed submicron ZnO rod arrays on FTO substrate was washed several times with deionized water and isopropanol, respectively. To fabricate LED device, p-Cu_2O thin film was electrodeposited on the top of ZnO

* Corresponding author.
E-mail addresses: Mahmoud.abdelfatah@sci.kfs.edu.eg (M. Abdelfatah), elshaer@sci.kfs.edu.eg, elshaera@yahoo.com (A. El-Shaer).

https://doi.org/10.1016/j.mssp.2018.03.004
Received 10 December 2017; Received in revised form 31 January 2018; Accepted 1 March 2018

rod arrays as has been previously reported [10,11,13]. The deposition solution was composed of 3 M lactic acid and 0.4 M copper sulfate anhydrous, while 4 M sodium hydroxide was added to adjust pH solution at 12.5. A constant potential of − 0.4 V was applied vs. the Ag/AgCl electrode using Bio-LogicSb-50 potentiostat and the solution temperature was fixed at 60 °C during the deposition process. In this process, the Cu_2O thin film was formed by the following reduction reactions [14]:

$$Cu^{2+} + e^- \rightarrow Cu^+ \quad (1')$$

$$2Cu^+ + 2OH^- \rightarrow Cu_2O\downarrow + H_2O \quad (2')$$

After the deposition was finished, the heterojunction device was rinsed with deionized water and isopropanol for several times to further characterization. X-ray diffraction (XRD, Shimadzu 6000) was employed to investigate the crystal structure of our samples, while the samples morphology was investigated using scanning electron microscope [JSM-651OLV]. A Solar simulator (Model CT50AAA) connected with Keithley was used for the current–voltage characterization. The spectral emission of LED device was measured by a fiber coupled Ocean Optics HR4000 spectrometer.

3. Results and discussion

Fig. 1 presents XRD patterns of ZnO rods, Cu_2O thin film, and Cu_2O/ZnO heterojunction, respectively. It is clear that submicron ZnO rod arrays were formed in hexagonal wurtzite crystal phase where ZnO directions planes of (100), (002), (101), (102), (110), (103), and (112) observed which were reported in other literatures [15,16]. Here, the high intensity of (002), (101), and (103) indicate the formation of ZnO rod arrays along the perpendicular direction of FTO substrate. The diffraction peak at 2θ value of 36.6 for the Cu_2O thin film, is corresponding to the (111) plane, which indicates the formation of polycrystalline Cu_2O with cubic structure, which agree well with other work [14]. For ZnO arrays/Cu_2O thin film heterojunction, the corresponding peaks of submicron ZnO rods and Cu_2O thin film were appeared, where the second-high intensity peak (top figure) is wide peak, which consist of (101) ZnO and (111) Cu_2O peaks. Moreover, another diffraction peak at 2θ value of 42.8 was observed which may be attributed to the (111) plane of pure copper nanoparticles [17].

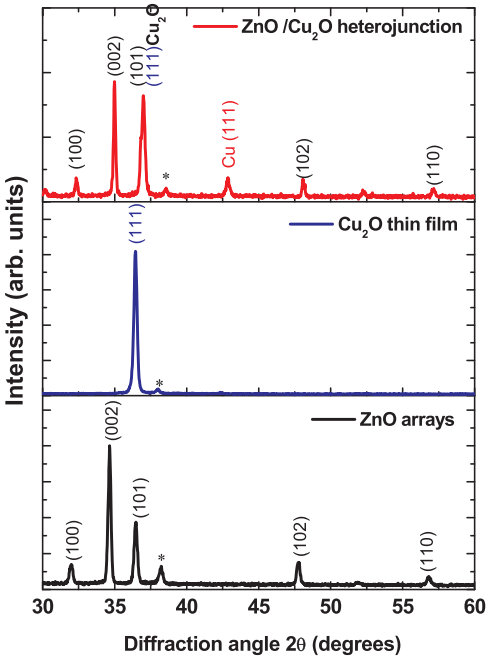

Fig. 1. X-ray diffraction patterns of ZnO rod arrays, Cu_2O thin film, and Cu_2O/ZnO heterojunction (* refers to FTO substrate).

Fig. 2.a, b, and c show top view SEM images of ZnO rods, Cu_2O thin film, and Cu_2O/ZnO heterojunction, respectively. The grown ZnO rod arrays were formed in hexagonal wurtzite structure with different alignment along the FTO substrate, while the directly deposited Cu_2O thin film on FTO was formed in pyramidal and cubic shapes which confirmed the XRD results.

The morphology of Cu_2O thin film in Cu_2O/ZnO heterojunction was different than the one prepared directly on FTO. This could be attributed to the less conductivity of ZnO arrays comparable to the FTO substrate and consequently the literal growth will be faster than the vertical growth. Some copper nanoparticles with white color were appeared on the top of heterojunction because of less conductivity of substrate. This means that to have the same thickness of Cu_2O thin film, the deposition time should be increased and therefore the portion of O^{2-} in Cu_2O reduces and portion of Cu is increased [18,19]. This result will be useful in the fabrication of LED device as electrode. Fig. 2.d illustrates the cross-sectional SEM images of the Cu_2O/ZnO heterojunction where ZnO arrays and Cu_2O thin film have the thickness of about 4 μm and 1 μm, respectively.

Fig. 3. a presents the current–voltage (I–V) characteristics curve of the inorganic ZnO arrays / Cu_2O thin film heterostructure LED device which measured under dark conditions and the schematic diagram of the device was shown insight graph. Under forward bias, the device exhibited a nonlinear increase in the current and therefore exhibited the p–n junction characteristics with a rectifying behavior. Fig. 3. b shows the measured electroluminescence spectra of ZnO arrays / Cu_2O thin film LED with different applied bias ranging from 8 V to 18 V. A broad emission covering the entire visible spectrum from around 450 nm to around 850 nm is observed for all applied voltage and this indicate the white electroluminescence of the device. The emission spectrum of ZnO/Cu_2O heterojunction exhibits relatively weak blue emission which may be attributed to the transition from zinc interstitial to zinc vacancy [6]. There are also two peaks were appeared in the spectra, the first one is a broad with centered value at around 660 nm which may be attributed to increasing of the carrier injection through the interface between n-ZnO arrays and p- Cu_2O thin film heterojunction and therefore increasing of the recombination rate with defect states [5,6]. The second peak at about 765 nm could be attributed to the injection of the holes from Cu_2O thin film towards ZnO rod arrays. The high surface to bulk ratio of ZnO arrays produce more bulk defects and surface states which increase the wide band of visible spectrum [6]. There is significant change in the shape of the EL spectrum as the applied voltage increasing where the peaks of the curve become clearer. Emission intensity enhanced with increasing of the applied voltage could be attributed to increase of radiative recombination centers in ZnO submicron rod arrays [6].

4. Conclusion

Inorganic heterojunction submicron ZnO rod arrays /Cu_2O thin film white light emitting diode device was fabricated employing low cost hydrothermal and electrodeposition methods. The results indicate that submicron ZnO rod arrays were formed in hexagonal wurtzite structure, while the polycrystalline Cu_2O thin film with cubic structure was deposited. The heterojunction device showed the diode behavior and the measured EL spectra from it were ranged from around 450 nm to around 850 nm. Emission intensity enhanced with increasing of the applied voltage which could be attributed to increase of radiative recombination centers in ZnO submicron rod arrays. Therefore, inorganic ZnO rod arrays/Cu_2O thin film heterojunction is a promising device on fabrication of low cost and high-performance LED with white electroluminescence.