Available online at www.sciencedirect.com

ScienceDirect

Photonics and Nanostructures – Fundamentals and Applications 12 (2014) 466–472

PHOTONICS AND NANOSTRUCTURES Fundamentals and Applications

www.elsevier.com/locate/photonics

Hybrid p-type copper sulphide coated zinc oxide nanowire heterojunction device

Ian Y.Y. Bu *

Department of Microelectronics Engineering, National Kaohsiung Marine University, Nanzih District, Kaohsiung City 81157, Taiwan, ROC

Received 25 January 2014; received in revised form 7 June 2014; accepted 13 June 2014
Available online 4 July 2014

Abstract

A novel heterojunction was formed between zinc oxide nanowires and copper sulphide. The proposed device was fabricated by a fully solution-based process that consists of hydrothermal growth method and chemical bath deposition. The optoelectronic properties of the proposed heterojunction were evaluated by scanning electron microscopy, energy dispersive spectroscopy, X-ray diffraction, UV–vis spectroscopy, photoluminescence measurements and current voltage characteristics.

Keywords: ZnO; Nanowires; Heterojunction; Copper sulphide

1. Introduction

One-dimensional (1D) nanomaterials have recently attracted intensive research attention [1,2] due to their potential enhancement in optoelectronic properties. Among the available nanomaterials, ZnO has been extensively studied due its large number of adaptable geometries [3,4]. Previous studies have successfully demonstrated the synthesis of ZnO nanorods [5], nanowires [6,7], nanoflakes [8], nano petals [9] and nano-cube [10]. As-deposited ZnO tends to exhibit n-type conduction behaviour [11–13]. The inherent n-type characteristics are believed to have originated from oxygen related vacancies and can be further adjusted by the addition of dopants such as Al [14], Ga [15], In [16] or F [17]. Although n-type ZnO can be readily obtained via the doping process, it is difficult to achieve stable p-type doping in ZnO materials [18], which presents a serious obstacle towards formation of an all ZnO-based homojunction. Consequently, many researchers have turned their focus to pairing ZnO with p-type materials such as Si [19], Cu_2O [20], NiO [21] to form stable heterojunction devices.

Copper sulphide (CuS) is a natural p-type semiconductor [22] that has been widely investigated for its application in ammonia gas sensors [23], photo-catalysts [24] and solar cells [25]. However, to our best knowledge, there has only been limited study on CuS coated ZnO nanowire [26,27].

In the past, ZnO nanowires have been prepared by thermal chemical vapor deposition (CVD) [28], electrodeposition [29], sputter coater [30] and a hydrothermal technique [31]. The hydrothermal method is particularly attractive due to its simple set-up, low process temperature (<90 °C) and possibility of industrial scaling [31]. Such a low deposition temperature have

* Tel.: +886 972506900; fax: +886 73645589.
E-mail address: ianbu@hotmail.com

http://dx.doi.org/10.1016/j.photonics.2014.06.004
1569-4410/

enabled the successful integration of ZnO nanowires onto flexible plastic [32] and paper substrates [33], whilst, CuS thin films have been synthesized by chemical techniques such as microemulsion [34] and a solvothermal methods [35].

In this study, p-type CuS thin films were deposited onto hydrothermally grown ZnO nanowires by chemical bath deposition to form a hybrid heterojunction. The structural and optoelectronic properties of the CuS and ZnO nanowires were investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), UV–vis spectroscopy and electrical measurements.

2. Experimental

All chemicals used in this study were of reagent grade and used without further purification. Indium tin oxide (ITO) coated Corning glass was used as the deposition substrates. The Corning glass substrates were cleaned by sequential ultrasonic agitation in baths of acetone, isopropanoal and deionized (D.I.) water in order to remove organic contaminants. ZnO nanowires were grown under the conditions described in our previous studies [36].

Prior to the growth of ZnO nanowires, a 10 nm thickness zinc oxide seed layer was spun onto the ITO coated glass substrate using 0.1 M ethanoic zinc acetate solution. Subsequently, the seed coated substrate was transferred into the growth solution, which consisted of equimolar (30 mM) of zinc nitrate hexahydrate and hexamethylenetetramine in D.I. water. The total growth process lasted for 2 h at 90 °C. The growth of the ZnO nanowires was terminated by a dip in D.I water and these were then dried under a N_2 flow in order to remove residual reactants on the surfaces.

CuS precursor was prepared by mixing copper acetate and thioacetamide in D.I. water. A homogeneous solution was yielded under magnetic stirring. This solution was transferred into a glass beaker with a capacity of 60 ml along with glass/ITO/ZnO nanowire coated glass substrates and maintained at 80 °C on a hotplate for 2 h. After the reaction was completed, the sample was then cooled to room temperature and washed in ethanol.

The morphology, size and chemical composition of the investigated samples were evaluated by using an FEI Quanta 400 F Environmental Scanning Electron Microscope (SEM) equipped with an energy dispersive spectroscopy EDS. A Siemens D5000 X-ray diffractometer (XRD) using Cu Kα radiation was used to determine crystal orientation. Room temperature photoluminescence measurements of the samples were conducted using a Dongwoo Macro Raman spectrometer/PL system. Heterojunction ITO/ZnO NW/CuS were contacted by sputtering Al through prefabricated metal masks, with a defined diameter of 60 μm diameter. Electrical *I–V* measurements of the fabricated heterojunction were taken with a source metre (Keithley 2400). Optical transparency measurements were obtained through UV–vis spectroscopy (Jasco) sweeping in the range of 200–1800 nm. Current density–voltage (*J–V*) characteristics were measured using a Keithley 2400 source-measure unit, under illumination (100 mW/cm^2), using a solar simulator (Science-tech).

3. Results and discussions

Fig. 1a shows a schematic diagram of the fabricated device that consists of stack layers of ITO/ZnO nanowires/CuS. Fig. 1b is an SEM image of the as-deposited CuS nanoparticles. The average diameter of the CuS nanoparticles is around 50 nm. Fig. 1c shows the top view of the CuS-coated ZnO nanowire. The SEM image shows good coverage of the CuS nanoparticles onto the ZnO nanowires. Furthermore, some ZnO nanowires have appeared on the surface due to their detachment during the hydrothermal synthesis process. Fig. 1d shows a tilted view of the same sample, in which it can be seen that the CuS coating bundles the ZnO nanowires together, due to capillary force during the drying process. This phenomenon has also been observed during drying of carbon nanotubes and silicon nanowires. The bunching process tends to form pyramid-like clusters of nanostructures. In order to determine the elemental composition of the deposited composite, an EDS was used to confirm the presence of Zn, O, Cu and S. Fig. 1e shows the result of the representative EDS analysis of the CuS/ZnO nanowire composite sample, and it can be seen that is the sample is sulphur-rich with stoichiometric ratio of Zn:O.

Fig. 2 shows the XRD patterns of the deposited ZnO nanowire/CuS nanocomposite sample. The diffraction peaks are well-defined and can be assigned to the hexagonal phase of CuS (JCPDS06-0464) and ZnO (wurtzite structure), respectively. No other impurities, such as $Cu_{1.8}S$, Cu_2S or oxides related to the precursor solution were detected. XRD peaks related to CuS can be observed at the (1 0 1), (1 1 0), (1 0 8) and (1 1 6) orientations. As for ZnO nanowires a single diffraction peak can be observed at the (0 0 2) orientation, consistent with results from other studies. Crystals tend to grow with the plane with the lowest surface energy. For ZnO, it has been shown that the surface energy is at the lowest in the (0 0 2) orientation, and this results in preferential growth. During ZnO synthesis, hexamine is often added to the growth solution. Hexamine is