



Fabrication and optoelectronic properties of novel p-Si/PPy/n-Cu_xIn_{1-x}O hybrid heterojunction



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ARTICLE INFO

Article history:

Received 3 March 2016

Received in revised form

31 July 2016

Accepted 3 August 2016

Available online 4 August 2016

Keywords:

Hybrid heterojunction

Cu_xIn_{1-x}O

Polypyrrole

Sol-gel

Chemical polymerization

Photoresponse

ABSTRACT

In the present work, we report the photoresponse characteristics of the hybrid heterojunction consisting of polypyrrole (PPy) sandwiched between p-Si substrate and n-Cu_xIn_{1-x}O film. Experimental results revealed that the PPy interlayer influence the electronic conduction through the hybrid heterojunction. Structural analysis by X-ray diffraction showed the diffraction peaks corresponding to CuO and In₂O₃, while the optical absorption spectra exhibited strong absorption in both the UV as well as visible regions. Morphological analysis by scanning electron microscopy showed the uniform coverage on the Si substrate, and the effective binding of Cu_xIn_{1-x}O and PPy. Raman spectroscopy showed the vibration modes corresponding to CuO, In₂O₃ and PPy. The p-Si/PPy/n-Cu_xIn_{1-x}O hybrid heterojunction demonstrated excellent rectifying behavior and improved electrical characteristics such as high rectification ratio (~220), lower threshold voltage (~1.8 V) and ideality factor (~2.06) due to the PPy insertion and photon illumination. The enhanced electrical characteristics of the hybrid p-Si/PPy/n-Cu_xIn_{1-x}O heterojunction was discussed with respect to the energy band structure, and found that the intermediate PPy layer acting as a hole transporting layer improves the charge selectivity and facilitates the effective transport of charge carriers towards the respective electrodes.

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1. Introduction

Recent advancements in solution-processable organic-inorganic hybrid heterostructures have garnered significant momentum for the development of cost effective electronic and optoelectronic devices. Hence, the hybrid heterojunctions composed of conjugated polymer-inorganic materials attracted renewed attention due to their improved functionalities resulting from the combination of two materials system, and are currently viewed as the potential alternates for the conventional inorganic and organic heterojunctions [1]. The growing interest in this sector is believed to be fueled by the rich advantages attributed to the conjugated polymers, such as tunable absorption properties, exceptional mechanical flexibility, light weight, low cost, large area deposition and roll-to-roll production, in conjunction with the morphological stability, controllable conductivity, high carrier mobility and wide absorption spectrum of the inorganic materials [1–3]. Driven by these merits, a variety of hybrid heterojunctions like GaN/P3HT [4],

PbS/PPy [5], CZTS/PANI [6], Si/TiOPc [3], TiO₂/PFH [7], ZnO/P3HT/TiO₂ [2], Al–ZnO/PPy [8] with different micro/nano architecture has been fabricated and reported with improved device performances. Although considerable research efforts have been devoted to the fabrication and device application of hybrid heterojunctions, their research perspective are still at a nascent stage. Hence, the exploration and rational designing of novel and complex materials with improved or unusual features are highly desired. Semiconducting metal oxides are widely regarded as the most promising class of functional materials for various technological applications, such as optics, optoelectronics, photovoltaic, electrochemical, photocatalysis and so on, due to their remarkable physicochemical properties, environmental stability and low-cost manufacturing techniques [9]. Among the various metal oxides, both ZnO and TiO₂ are the work-horse oxide materials that have been used in diverse applications including hybrid heterojunctions. On the other hand, Cu–In–O materials system has recently engendered extensive attention and has emerged in the frameworks of photocatalysis, thermoelectrics and gas sensor applications [10–12]. The unique advantage of this materials system is that by combining copper oxide (CuO) and indium oxide (In₂O₃) either p-type or n-type character Cu–In–O alloy could be obtained by simply varying the

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film composition [11]. Unfortunately, despite this potential benefit fabrication of (hybrid) heterojunctions using Cu–In–O materials system has not yet been reported. In order to realize the full potential of Cu–In–O system, a better understanding of the band gap alignment and the nature of charge transport is of great significance from the modest application point of view. CuO is a p-type semiconductor having a narrow energy band gap of 1.2–1.5 eV, high optical absorption in the visible region and environmentally friendly properties like non-toxicity and low cost; while In_2O_3 is a wide band gap material (~3.7 eV) possessing n-type conductivity, high visible transparency and free carrier mobility [13–16]. Hence, the combination of CuO and In_2O_3 could open up a multitude of applications in next generation electronic and optoelectronic devices.

In light of this above background, in the present work, we have fabricated a novel hybrid p–n junction based on p-Si/n- $\text{Cu}_x\text{In}_{1-x}\text{O}$ with polypyrrole (PPy) as a promising interfacial layer. The interfacial PPy layer improves the charge transfer kinetics across the device by reducing the charge carrier recombination and providing an efficient pathway for the charge transport, which is a prerequisite to enhance the device characteristics. As a p-type conducting polymer, PPy has been widely used as an active layer in various optoelectronic devices in recent years due to its rich attributes like high electrical conductivity, optimum band gap ($E_g \sim 3.2$ eV), good chemical and environmental stability, ease of its preparation, good solubility and oxidizability of their monomers in water [17–20]. The hybrid heterostructures was realized through a sequential deposition route by chemical polymerization and drop casting of PPy film and $\text{Cu}_x\text{In}_{1-x}\text{O}$ nanoparticles (NPs), respectively, on Si substrate. The structural, morphological, optical and photoelectric properties of the hybrid heterojunction (made up of $\text{Cu}_x\text{In}_{1-x}\text{O}$ and PPy) were collectively studied by contemporary techniques, and the possible mechanism of charge separation and carrier transport occurring at the interface was discussed in detail.

2. Experimental details

2.1. Synthesis of $\text{Cu}_x\text{In}_{1-x}\text{O}$ NPs

Copper (II) acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), indium (III) acetate ($\text{In}(\text{CH}_3\text{COO})_3$), ammonium hydroxide (NH_4OH) and pyrrole monomers were purchased from Sigma-Aldrich. All the chemicals used in the experiments were of analytical grade and used as received without further purification. In a typical synthesis, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{In}(\text{CH}_3\text{COO})_3$ (weight percentage of 20:80) were mixed in 100 ml of deionized (DI) water. Appropriate amount of aqueous NH_4OH solution was added to the above mixture, and the resulting suspension was refluxed at 100 °C for 9 h. After the reaction complete, the resulting black-gray colored precipitates was washed in DI water and methanol for several times to remove the byproducts. Finally, the NPs were subjected to calcination at 500 °C for 2 h.

2.2. PPy deposition by in situ chemical polymerization

For the PPy deposition, an oxidizing and polymerization media were separately prepared by dissolving 4.2 mmol FeCl_3 and 2 mmol pyrrole in 50 ml of DI water, respectively. FeCl_3 aqueous solution was then added to pyrrole solution under constant stirring for 5–10 min, and then the target substrates were immersed into the solution. The polymerization reaction gets initiated through the aid of the oxidizing agent and the deposition of PPy onto the substrate occurs. The polymerization reactions were carried out under dark conditions for a period of 24 h at room temperature to obtain a

uniform blackish-gray colored thin film. The PPy deposits were then heat treated at 90 °C prior to their characterization.

2.3. Fabrication of working electrode

A highly transparent dark black-gray colored colloidal solution was prepared by dispersing $\text{Cu}_x\text{In}_{1-x}\text{O}$ NPs in ethanol and subjecting to sonication for about 30 min. After sonication, the solution was aged for 6–12 h to separate the larger particulates (through decantation) from the colloidal media. The dispersed sol was then drop cast at room temperature onto Si substrate with and without PPy deposit. The depositions were repeated seven times, and between each deposition the substrate was heated at 90 °C for 10 min. The prepared structures were finally heat treated at 90 °C for 30 min to remove the residual solvents before the device studies. 50 nm thick platinum (Pt) metal contacts were sputtered through a shadow mask onto n- $\text{Cu}_x\text{In}_{1-x}\text{O}$ and p-Si to form top and bottom electrodes, respectively. The heterojunction device area is 1.5×1.5 cm².

2.4. Characterization

The structural properties were investigated by X-ray diffraction (XRD, Rigaku D/MAX/2500/PC X-ray diffractometer) and Raman spectroscopy (750i/ELT1000 micro confocal Raman spectrophotometer). The morphological analysis was carried out using field emission scanning electron microscope (FESEM, Hitachi S-4800) attached with energy-dispersive X-ray spectroscopy (EDS). The optical absorption characteristics were analyzed by UV–vis absorption spectrum (Cary UV/vis/NIR spectrophotometer, $\lambda = 300$ –800 nm). The current–voltage (I–V) measurements were recorded using a probe station equipped with Keithley series 2400 digital source meter in the dark and under illuminated conditions (using a 140 W Xenon lamp). For each heterojunction configuration we have tested about 5 devices checking each device at least 3 times, and the photoresponse of these devices was within $\pm 10\%$ error limit.

3. Results and discussion

The crystallinity and the phase information of the as-synthesized product were characterized by XRD and are shown in Fig. 1(a). The diffraction peak in the XRD pattern matches with the cubic crystal structure of In_2O_3 (JCPDS card no. 06-416) and monoclinic crystal structure of CuO (JCPDS card no. 45-0937), demonstrating the coexistence of CuO and In_2O_3 characteristics in the CuInO system. The intensity variation between CuO and In_2O_3 clearly demonstrates the predominance in the formation of In_2O_3 phase. The diffraction peaks and the intensities of CuO are much weaker than those of In_2O_3 , indicating that the CuO content in the prepared product is relatively low. The diffraction peaks are relatively broadened, which suggests that the NPs have very small crystal sizes. The mean crystallite size of CuO and In_2O_3 NPs was estimated for the predominant (002) and (222) planes, respectively, using the well-known Scherrer's formula [21], and found to be 17 nm and 9 nm, respectively. FESEM was employed to get more insight into the morphology of the as-synthesized $\text{Cu}_x\text{In}_{1-x}\text{O}$ NPs. FESEM image in Fig. 1(b) shows the clusters of NPs randomly aggregated to form cauliflower-like structure. The elemental composition of $\text{Cu}_x\text{In}_{1-x}\text{O}$ NPs analyzed by EDS was given in Fig. 1(c), displaying the presence of indium, copper and oxygen elements in these NPs. Further the quantitative analysis of the EDS reveals that the atomic (weight) percentage of In, Cu and O are ~16.51 (49.41), 12.73 (21.08) and 70.76 (29.51), respectively.

The Raman spectrum of $\text{Cu}_x\text{In}_{1-x}\text{O}$ NPs is shown in Fig. 2. The

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