Journal of Alloys and Compounds 689 (2016) 394–400

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

CdS surface encapsulated ZnO nanorods: Synthesis to solar cell application

Pratibha R. Nikam [a], Prashant K. Baviskar [a], Jaydeep V. Sali [a], Kishor V. Gurav [b], Jin H. Kim [b], Babasaheb R. Sankapal [c, *]

[a] Department of Physics, School of Physical Sciences, North Maharashtra University, Jalgaon 425001, M.S., India
[b] Photonic and Electronic Thin Film Laboratory, Department of Material Science and Engineering, Chonnam National University, Gwangju 500-757, Republic of Korea
[c] Nano Materials and Device Laboratory, Department of Applied Physics, Visvesvaraya National Institute of Technology, South Ambazari Road, Nagpur 440010, M.S., India

ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form
11 July 2016
Accepted 26 July 2016
Available online 29 July 2016

Keywords:
Wet chemistry
ZnO nanorods
CdS nanoparticles
Nano heterostructure solar cell

ABSTRACT

Surface coating of CdS nanoparticles over the ZnO nanorods have been performed by using simple successive ionic layer adsorption and reaction at room temperature. Initially, the seed/compact ZnO layer have been deposited via SILAR (successive ionic layer adsorption and reaction) on to fluorine doped tin oxide coated glass (FTO) substrate followed by synthesis of ZnO nanorods by chemical bath deposition method. The synthesized nano heterostructure was characterized by X-ray diffraction (XRD), UV–Vis spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), field emission-scanning electron microscopy (FE-SEM), energy dispersive X-ray analysis (EDX) and high resolution-transmission electron microscopy (HR-TEM) techniques. The photovoltaic performance of the cell was recorded with a conversion efficiency of 0.123% under 100 mW/cm^2 simulated sunlight at AM 1.5G conditions.

1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor having a direct band gap of 3.3 eV with a free exciton binding energy [1]. It is also being actively investigated as a substitute material in solar cell application due to its higher electronic mobility, similar electron affinity and optical band gap with that of TiO_2 [2] along with a similar electron injection process from excited dyes [3]. One-dimensional (1-D) nanostructures exhibit unique optoelectronic properties and provide larger surface areas than films prepared from randomly oriented nanoparticles with efficient photon absorption, fast and effective electron transport and collection.

In a last two decades, the vertically aligned ZnO nanostructures have gained enormous interest towards dye sensitized and quantum dot solar cells [4–6]. Quantum dot sensitized solar cells (QDSC) have been received a lot of interest in recent years as a cost effective alternative to silicon-based photovoltaic technology [7]. As an alternative to routine organic dyes, metal chalcogenide semiconductor materials have been used as the photo sensitizers in combination with ZnO such as PbS, CdS, PbSe, CdSe and CdTe [8–13] due to their flexible optical and electrical properties. These materials provide additional opportunities which are not available in DSSC; i.e. the shape and size of semiconductor can be tuned to cover the complete region of the solar spectrum, and are effortlessly processes. CdS and CdSe quantum dots (QDs) and nanoparticles (NPs) are frequently used as the inorganic semiconductor co-sensitizers because of their advantages in light harvesting and electron injection, and much progress has been achieved based on TiO_2 photo anodes [14]. The highest efficiency of 5.4% has been reported for TiO_2 sensitized with Mn-doped CdS/CdSe for QDSC [15]. A maximum power conversion efficiency of 4.46% has been achieved for mesoporous ZnO photoanode prepared by the simple doctor blade method in combination with CdS/CdSe towards QDSC [16]. QDSCs have been pushed to take benefit of the quantum dots, including high absorption coefficient, tunable band gap by size, which open a new avenue for clean and cost-efficient photovoltaics. Despite their huge potentiality, the performance of QDSCs has still remained low after many years of effort. It is tricky to control and grow vertically aligned ZnO nanorods (NRs) longer than 10 μm in

* Corresponding author.
E-mail address: brsankapal@gmail.com (B.R. Sankapal).

http://dx.doi.org/10.1016/j.jallcom.2016.07.295
0925-8388/

length and less than 100 nm in diameter for solar cells using cost effective methods at low temperature. However, the low temperature synthesis of ZnO NRs array is still a crucial challenge along with reduction in post annealing temperature. This task can open the window for possible use of flexible plastic substrate in future to develop flexible solar cells and further lower down the production cost.

Current article mainly focuses the low temperature synthesis of ZnO NRs array onto fluorine doped tin oxide (FTO) coated glass substrate by using chemical bath deposition method. CdS nanoparticles assembly grown over ZnO NRs array by using simple and inexpensive method viz. successive ionic layer adsorption and reaction (SILAR) with an effortlessness linker free approach which will compile to the formation of heterostructure. This structure has been characterized for structural, optical, morphological and compositional studies with the help of different types of characterization techniques. At last, the current density-voltage (J-V) characteristics were measured for sandwich type solar cell having the structure FTO/ZnO compact layer/ZnO NR/polysulphide electrolyte/Platinum under illumination of 100 mW/cm^2 simulated sunlight at AM 1.5G conditions. Seed/compact ZnO layer plays an important role in dropping the electron back transfer from the FTO to the polysulphide electrolyte and avoid short-circuit in device.

2. Experimental details

2.1. Synthesis of ZnO nanorods by chemical bath deposition method

In this report, we account the two disparate sets of experiments viz. SILAR (successive ionic layer adsorption and reaction) and CBD (chemical bath deposition) method. First seed/compact ZnO layer on the pre cleaned FTO substrate was deposited using a SILAR method [17]. The deposition was performed at low temperature. For seed layer deposition, solution was prepared in double-distilled-water (DDW) with 20 mM concentration of zinc source. The Zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$, Sigma-Aldrich, 98%] dissolved in DDW was used as cationic solution complexed with ammonia (25%) having resulting pH~11. The DDW maintained at 90 ± 2 °C was used as an anionic solution. The dipping time in a cationic and anionic solution was 5 s and 10 s, respectively. Subsequently on the completion of 10 immersion cycles, the appropriate seeded ZnO layer was formed. This was rinsed in DDW, dried in air and finally annealed in air at 200 °C for 1 h to remove the hydroxide phase and to improve the crystalline nature.

The array of ZnO nanorods were synthesized on pre-seeded ZnO substrate by using CBD method. An equimolar solution (25 mM) of zinc nitrate hexahydrate and hexamethylene tetramine [HMTA ($C_6H_{12}N_4$), Sigma-Aldrich, 98%] was used as a reacting source with resultant pH~6. With a constant stirring of reacting bath, 25% ammonia (NH_3) solution was added drop wise to have pH~10 which was resulted into the formation of white precipitate. The precipitate was re-dissolved by supplementary addition of ammonia with the formation of clear zincate ($[Zn(NH_3)_4]^{2+}$) ionic solution. The pre-seeded ZnO substrate was introduced in the above solution which was maintained at 90 ± 2 °C for 1 h. Finally, the substrate with the deposited film was rinsed with DDW, dried in air followed by annealing in air at 200 °C for 1 h to improve the crystallinity of the ZnO nanorods and the interfacial structures. The detail reaction mechanism for the ZnO film formation of vertically aligned 1-D ZnO nanorods was well explained in our recent review [18].

$$\left.\begin{array}{l} Zn(NO_3)_2 + 2(NH_4OH) \rightarrow Zn(OH)_2 + 2NH_4NO_3 \\ (CH_2)_6N_4 + 6H_2O \rightarrow 6HCHO + 4NH_3 \end{array}\right\} \rightarrow Zn(NH_3)_4^{+2} + 2OH^- \quad (1)$$

$$ZnO + H_2O \xleftarrow{\Delta} Zn(OH)_2 + H_2O + 4NH_3\uparrow \quad (2)$$

2.2. Sensitization of CdS nanoparticles using SILAR method

The CdS nanoparticles over ZnO nanorods were achieved by SILAR approach. Direct chemisorption involved in the reaction kinetics of the SILAR approach which facilitates chemical reaction resulting in the growth of particle and hence, the growth can be controlled at ionic level [19]. Van-der-Waals and electrostatic forces were acting in heterogeneous nucleation and resulted into growth of nano size CdS particles on ZnO surface. By varying the number of SILAR cycles, the growth of CdS can be controlled. This method enables the systematic monitoring of nucleation and growth of accumulation CdS nanoparticles on ZnO electrode by ion by ion reaction mechanism. Pre-deposited ZnO nanorod thin film exposed to Cd^{2+} and S^{2-} ions by their successive immersion in the Cd^{2+} ionic solution and S^{2-} ionic solution. CdS nanoparticles were prepared by a simple chemical route. Cadmium acetate dihydrate GR grade [$(Cd(CHCOO)_2 \cdot 2H_2O)$, Loba Chmie, 99%] and sodium sulphide flakes [(Na_2S), Loba Chmie, 99%] were used as the source precursors. The cadmium acetate (1 mM, pH~6) was used as cationic precursor whereas sodium sulphide flakes (1 mM, pH~9) was used as an anionic precursor. Fig. 1 shows the schematic experimental set up of SILAR method used for the deposition of CdS nanoparticles on ZnO nanorods. CdS deposition involves the immersion of ZnO NR film into the separately placed cationic and anionic precursors followed by rinsing in between with DDW to remove un-adsorbed or loosely bonded ions. Cadmium ions (Cd^{2+}) are adsorbed over ZnO NR's when it is immersed into the cationic precursor for 60 s (step A). The un-adsorbed ions (Cd^{2+}) were removed by rinsing the

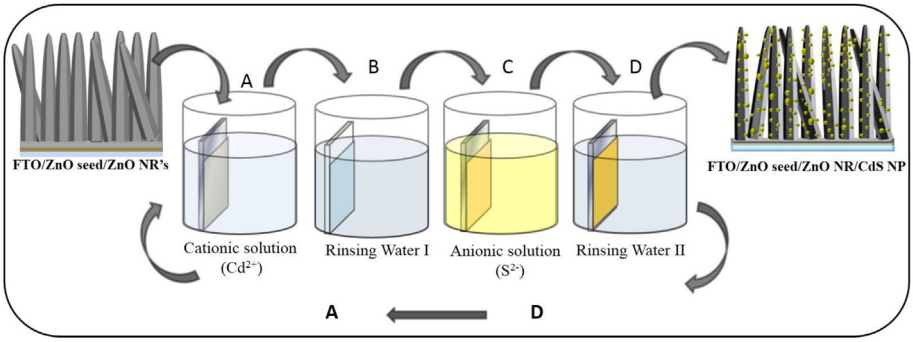

Fig. 1. Schematic experimental set up of SILAR technique used for the deposition of CdS nanoparticles on ZnO nanorods.